# Volatile Organic Compounds at the Air-Sea Interface: Gas Exchange Rates, Oceanic Emissions and the Effect of Ocean Acidification

Dissertation zur Erlangung des Grades "Doktor der Naturwissenschaften" im Promotionsfach: Chemie im Fachbereich Chemie, Pharmazie und Geowissenschaften der Johannes Gutenberg-Universität in Mainz

Evridiki Mesarchaki

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Zusammenfassung Ozeane sind bedeutende Quellen und Senken in globalen Budgets wichtiger atmosphärischer Spurengase, den flüchtigen Kohlenwasserstoffen (engl. Abk.: VOCs). Trotz ihrer geringen Konzentrationen nehmen diese Spezies eine wichtige Rolle in der Atmosphäre ein, und beeinflussen beispielsweise die Ozon-Photochemie und Aerosolphysik. Überraschend wenig wurde bisher zur Abschätzung der Emissions- und Transportmechanismen dieser Gase, sowie ihrer Austauschraten zwischen Ozean und Atmosphäre investiert, wobei die Gesamtheit dieser Parameter wichtig für die akkurate atmosphärische Modellierung sind. Für eine effektive Beprobung und Analyse von in Seewasser gelösten VOCs wurde die Needle Trap Device (NTD) GC-MS Methode neu entwickelt. Gute Reproduzierbarkeiten (RSDs <16%), Linearitäten ( $\mathbb{R}^2 = 0.96 - 0.99$ ) und Nachweisgrenzen im Bereich von pM wurden für DMS, Isopren, Benzol, Methylbenzol, Dimethylbenzol, (+)- $\alpha$ -Pinen und (-)- $\alpha$ -Pinen erzielt. Die Evaluierung im Labor und im nachfolgenden Feldeinsatz zeigte, dass die vorgeschlagene Methode erfolgreich anstelle der gewöhnlich angewandten Extraktionstechnik (P&T, SPME) treten kann, um die Anzahl von Spurengasspezies, die typischerweise im Ozean gemessen werden, zu erweitern und die Nachweisgrenzen zu verbessern.

Während einer  $CO_2$ -Anreicherungsstudie, die in Mesokosmmen durchgeführt wurde, wurden DMS, Isopren und  $\alpha$ -Pinen unter Verwendung der oben genannten Methode in Seewasserproben nachgewiesen und quantifiziert. Auf der Basis von Korrelationsanalysen mit verfügbaren biologischen Datensätzen wurde der Effekt einer Versauerung der Ozeane sowie potentielle biologische Meeresquellen für alle untersuchten Verbindungen erforscht. Es konnte gezeigt werden, dass die zukünftige Meeresversauerung die maritime DMS-Produktion verringern, möglicherweise Isoprenemissionen beeinflussen und geringe Bedeutung für die  $\alpha$ -Pinen Produktion haben wird.

Bei einer separaten Messkampagne wurden die Interaktionen zwischen Ozean und Atmosphäre in einem grossformatigem Windwellenkanal simuliert, um den Gasaustauschprozess und die ihn kontrollierenden Wirkungsmechanismen zu erforschen. Für 14 chemische Verbindungen (darunter 11 VOCs) wurden Austauschraten zwischen Luft und Wasser bestimmt. Die VOCs umfassten einen weiten Löslichkeits- (dimensionslose Löslichkeit,  $\alpha = 0.4$  to 5470) und Diffusivitätsbereich (Schmidtnummer in Wasser,  $Sc_w = 594$  - 1194). Au $\widetilde{A}$ erdem wurden, durch die Regulierung von Turbulenz (Windgeschwindigkeit in 10 m Höhe,  $u_{10} = 0.8$ to  $15 \, m \, s^{-1}$ ) und die Benetzung der Wasser-Luft Grenzschicht mit einem oberflächenaktivem Stoff (zwei unterschiedlich dicke Triton-X100 Schichten), verschiedene Oberflächenbedingungen erforscht. Es wurden verlässliche und reproduzierbare Transfergeschwindigkeiten für den totalen Gasaustausch hergeleitet und die Werte und der Trend waren vergleichbar zu früheren Studien. Durch diese Untersuchung wurde ein wesentlich besseres und umfassenderes Verständnis des Luft-Meer Gasaustausches erreicht. Als sehr wichtig wurde die Funktion der Schubspannungsgeschwindigkeit  $(u_*)$  und der mittleren quadratischen Neigung  $(\sigma_*^2)$  für die Bildung von Phänomenen wie Wellen, Wellenbrechen, oberflächennaher Turbulenz, Blasen und Oberflächenfilmen erkannt.  $u_*$  wurde als der ideale âTurbulenzparameterâ ermittelt, und  $\sigma_s^2$  beschreibt am besten die zugehörigen Oberflächenbedingungen. Mit einer Kombination von  $u_*$  und  $\sigma_s^2$  kann der Luft-Meer Gasaustausch wirklichkeitsgetreu reproduziert werden. Zum ersten Mal wurde ein Modell zur Ermittlung der totalen Transfergeschwindigkeit (engl.: Total Transfer Velocity (TTV)) auf der Basis von 14 Spurengasen und einer Kombination von beiden  $u_*$  und  $\sigma_s^2$  Parametern aufgestellt. Durch die vorgeschlagene TTV-Parametrisierung wird eine neue physikalische Perspektive eröffnet, die eine exakte TTV für jeden Tracer im untersuchten Löslichkeitsbereich bereitstellt. Die Entwicklung einer solch umfassenden Parametrisierung des Luft-Meer Gasaustausches repräsentiert ein höchst bedeutsames Werkzeug für regionale und globale Modelle. Die Parametrisierung bietet akkurate Abschätzungen der totalen Transfergeschwindigkeit für jeden Tracer unter allen Oberflächenbedingungen des Meeres, was den Rechenprozess vereinfacht. Zudem werden Unsicherheiten, die bei früheren TTV-Berechnungen im Zusammenhang mit der Auswahl und Kombination diverser Parametrisierungen entstanden, unweigerlich verringert.

**Summary.** Oceans are key sources and sinks in the global budgets of significant atmospheric trace gases, termed Volatile Organic Compounds (VOCs). Despite their low concentrations, these species have an important role in the atmosphere, influencing ozone photochemistry and aerosol physics. Surprisingly, little work has been done on assessing their emissions or transport mechanisms and rates between ocean and atmosphere, all of which are important when modelling the atmosphere accurately.

A new Needle Trap Device (NTD) - GC-MS method was developed for the effective sampling and analysis of VOCs in seawater. Good repeatability (RSDs <16%), linearity ( $\mathbb{R}^2 = 0.96 - 0.99$ ) and limits of detection in the range of pM were obtained for DMS, isoprene, benzene, toluene, p-xylene, (+)- $\alpha$ -pinene and (-)- $\alpha$ -pinene. Laboratory evaluation and subsequent field application indicated that the proposed method can be used successfully in place of the more usually applied extraction techniques (P&T, SPME) to extend the suite of species typically measured in the ocean and improve detection limits.

During a mesocosm  $CO_2$  enrichment study, DMS, isoprene and  $\alpha$ -pinene were identified and quantified in seawater samples, using the above mentioned method. Based on correlations with available biological datasets, the effects of ocean acidification as well as possible ocean biological sources were investigated for all examined compounds. Future ocean's acidity was shown to decrease oceanic DMS production, possibly impact isoprene emissions but not affect the production of  $\alpha$ -pinene.

In a separate activity, ocean - atmosphere interactions were simulated in a large scale windwave canal facility, in order to investigate the gas exchange process and its controlling mechanisms. Air-water exchange rates of 14 chemical species (of which 11 VOCs) spanning a wide range of solubility (dimensionless solubility,  $\alpha = 0.4$  to 5470) and diffusivity (Schmidt number in water,  $Sc_w = 594$  to 1194) were obtained under various turbulent (wind speed at ten meters height,  $u_{10} = 0.8$  to  $15 \, m \, s^{-1}$ ) and surfactant modulated (two different sized Triton-X100 layers) surface conditions. Reliable and reproducible total gas transfer velocities were obtained and the derived values and trends were comparable to previous investigations. Through this study, a much better and more comprehensive understanding of the gas exchange process was accomplished. The role of friction velocity,  $u_*$  and mean square slope,  $\sigma_s^2$  in defining phenomena such as waves and wave breaking, near surface turbulence, bubbles and surface films was recognised as very significant.  $u_*$  was determined as the ideal "turbulent" parameter while  $\sigma_s^2$  described best the related surface conditions. A combination of both  $u_*$ and  $\sigma_s^2$  variables, was found to reproduce faithfully the air-water gas exchange process.

A Total Transfer Velocity (TTV) model provided by a compilation of 14 tracers and a combination of both  $u_*$  and  $\sigma_s^2$  parameters, is proposed for the first time. Through the proposed TTV parameterization, a new physical perspective is presented which provides an accurate TTV for any tracer within the examined solubility range.

The development of such a comprehensive air-sea gas exchange parameterization represents a highly useful tool for regional and global models, providing accurate total transfer velocity estimations for any tracer and any sea-surface status, simplifying the calculation process and eliminating inevitable calculation uncertainty connected with the selection or combination of different parameterizations.

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## 0.1 Overview

Air quality and climate change are two of the most important challenges that our societies face as we enter "the Anthropocene". Despite decades of research, large uncertainties remain in the quantification of the Earth system response to natural and anthropogenic emissions, in particular in the oceanic domain. For such a prediction, accurate global budgets of trace gases are of critical importance. The present study focuses on key atmospheric trace gases which belong to the Volatile Organic Compound (VOCs) family. The investigation of VOCs in terms of their marine concentrations, possible ocean sources, response to ocean acidification and their ocean-atmosphere exchange rates, is documented here. The above mentioned aspects are divided into two sections, one involving ocean VOC measurements under present and future  $CO_2$  levels (Chapters 1, 2 and 3) and the other measurements of gas exchange rates under various physical and chemical controls (Chapters 4, 5 and 6).

Included in this Thesis are:

## 1) Method Developments

- A novel analytical method using newly developed Needle Trap Devices (NTD) and a gas chromatograph mass spectrometer (GC-MS) has been developed for the analysis of VOCs out of water samples.
- A mass balance approach has been developed for the estimation of total gas transfer velocities in a wind-wave canal, whereby parallel air and water side concentration measurements were monitored on-line. An external membrane equilibrator set-up in conjunction with a Proton Transfer Reaction Mass Spectrometry (PTR-MS) system was settled for the measurement of VOC concentrations out of the water.

### 2) Large-scale Field Campaign

• VOC concentration measurements during a community mesocosm CO<sub>2</sub> enrichment study in a Norwegian Fjord.

### 3) Large-scale Laboratory Study

• Transfer Rate measurements of 14 trace gases across the air-water interface, conducted in the world's largest Wind-Wave Canal in Heidelberg Germany

## 4) Intensive Model Study

• Development of a new universal gas exchange parameterization based on experimentally derived transfer velocities and relevant surface parameters.

## 1

## Introduction: Marine VOCs & Ocean Acidification

## 1.1 Marine VOCs

Oceans, cover circa 70 % of the Earth's surface and have an enormous effect on the budgets of atmospherically relevant trace gases (e.g Carpenter et al. (2012)). The natural cycles of VOC gases in the surface ocean and the troposphere provide main inputs to the global trace gas budgets. Marine biological, physical and photochemical processes lead to an uptake from, or an emission to, the overlying atmosphere for a suite of organic gases (e.g. DMS, isoprene, terpenes, acetone, methanol, acetaldehyde) (Sinha et al. (2007), Millet et al. (2008), Millet et al. (2010), Shaw et al. (2010)). These gases are known to significantly impact the atmosphere, influencing ozone photochemistry and aerosol physics even at trace concentrations (Williams (2004) and references therein). A simplified diagram of the major interactions between oceanic emissions and the lower atmosphere is presented in Figure 1.1.

Key atmospheric VOCs have been extensively studied in various regions, though comparatively little work has been done on assessing their emission from the ocean. Marine VOC emissions need to be identified and quantified in order to evaluate the ocean's impact on Earth system in local to global scales, both presently and in future.

Dimethyl Sulphide (DMS) is the most studied marine trace gas emission. DMS is largely produced in the ocean by phytoplankton species and when released in the atmosphere, it can contribute to sulphate aerosol formation. Isoprene is also known to be emitted by the ocean. Its production has been related to many phytoplankton species although so far no clear major source is apparent. In addition to it's photochemical role, isoprene has been suggested as significant source of secondary organic aerosols (SOA) to the remote atmosphere (Claeys et al. (2004), Kroll and Seinfeld (2008)). Other marine BVOCs, such as terpenes have been also suggested as SOA sources (e.g Luo and Yu (2010)). Monoterpenes have been recently observed in the marine environment and in laboratory phytoplankton experiments (Yassaa et al. (2008)). Monoterpene ocean concentration levels as well as possible sources are very uncertain at the moment.

A firm understanding and quantification of ocean VOC sources and sinks is key to pre-



Fig. 1.1: Major interactions of oceanic emissions with the lower atmosphere, schematic from Carpenter et al. (2012).

dict climate and environmental change appropriately within the on-going Anthropocene (Williams and Crutzen (2013)). Improved measurement technology developments support such efforts and are therefore worth research investment.

## 1.2 Ocean Acidification

The ocean and biosphere take up about 50 % of the emitted CO<sub>2</sub>. The recent rise in CO<sub>2</sub> levels in the atmosphere is known to be mainly due to human activity. Burning of fossil fuels such as coal and petroleum is the major anthropogenic source of atmospheric CO<sub>2</sub> followed by deforestation (Intergovernmental Panel on Climate Change (IPCC), 1995). Over the part 800.000 years, CO<sub>2</sub> concentrations varied between 180 and 280 ppmv, as the planet went in and out of the glacial periods. Since the middle of the 18th century, the atmospheric CO<sub>2</sub> has increased rapidly from 280 to todays level of 394 ppmv (Figure 1.2, www.esrl.noaa.gov). Future scenarios predict a further increase between 550 and 1000 ppmv by the year 2100 (IPCC 2007)). As stated by Revelle and Suess (1957) "Human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future" Oceans provide a major sink for CO<sub>2</sub> and, since 1980s, have absorbed around 30% of all anthropogenic CO<sub>2</sub> (Caldeira and Wickett (2003), Siegenthaler et al. (2005)).



Fig. 1.2: The Keeling Curve of atmospheric  $CO_2$  concentrations measured at the Mauna Loa Observatory.

The uptake of this additional  $CO_2$  is resulting in a decrease in the pH of surface waters, manifested as increasing H<sup>+</sup> ion concentrations and decreasing calcium carbonate (CaCO<sub>3</sub>) saturation states. This effect is widely termed "Ocean Acidification" (e.g Caldeira and Wickett (2003)).

 $\rm CO_2~(aq) + H_2O \leftrightarrow HCO_3^- + H^+$ 

 $\mathrm{CO}_3^{2-} + \mathrm{H}^+ \leftrightarrow HCO_3^{--}$ 

Between 1751 and 1994 surface ocean pH is estimated to have decreased by approximately 0.1 units, an increase of almost 30 % in H<sup>+</sup> ion concentration in the world's oceans (Jacobson, M. Z. (2005)). The projected CO<sub>2</sub> increase (IPCC 2007), will result in a decrease of ocean's pH by 0.4 units, an increase in H<sup>+</sup> ion by a factor of three and a ~ 50% fall of CO<sub>3</sub><sup>2-</sup> since 1750 (Raven et al. (2005)). Such a sudden and dramatic change, is thought to have a negative impact in ocean life, affecting directly and indirectly marine organisms (species composition and competition), their ecosystems as well as the budgets of biogeochemical key elements, such as C, N, P and Fe (Engel et al. (2005), Gattuso and Hansson (2011)).

One of the most important consequences of ocean acidification relates to the production of shells and plates out of calcium carbonate (CaCO<sub>3</sub>) (Raven et al. (2005)). This process is called calcification and is important to the biology and survival of a wide



Fig. 1.3: Simplified schematic depiction of Ocean Acidification.

range of marine organisms (Figure 1.3). Previous studies have already found that corals (e.g Gattuso et al. (1998)), coccolithophore algae (e.g Delille et al. (2005)) coralline algae (e.g Kuffner et al. (2007)), shellfish (e.g Gazeau et al. (2007)) and pteropods (e.g Comeau et al. (2009)) express reduced calcification or enhanced dissolution when exposed to elevated  $CO_2$ .

Increased  $CO_2$  and temperature levels will cause a distribution of the biological communities and affect the biological processes. More  $CO_2$  dissolving in the polar regions will force marine organisms to the tropics but the warming of the tropic regions will pull them north (Williams and Crutzen (2013)).

Changes in ocean biology will consequently affect the ocean's effect on atmosphericrelevant trace gases. Apart from marine DMS, for which further investigation is required due to conflicting results of previous studies (more in Mesarchaki et al. (2014), Gattuso and Hansson (2011) and therein references), only few other trace gases have been investigated under elevated  $CO_2$  conditions, i.e halogenated compounds (iodo and bromo compounds, e.g Wingenter et al. (2007), Hopkins et al. (2010)). With the pace of ocean acidification accelerating, sustained efforts are required in order to elucidate the response of various marine species to a higher  $CO_2$  world and its consequent effect on the production rates of significant trace gases.

## 1.3 Open Research Questions and Thesis Goals

Key volatile organic compounds, in terms of marine concentration levels, ocean sources and ocean acidification vulnerability, have received very little attention. In particular, five aspects requiring further elucidation, motivated this study:

## 1) The research world needs a description of the present state of key VOC budgets in order to have a well defined reference point for calibrating predictive models better.

- Additional measurements of potentially important VOCs in various ocean environments should be supplied to regional and global databases.
- Ocean measurements of VOCs should include a large number of tracers in order to provide more comprehensive datasets which could be used to account for all possible climate and environmental impacts and to decipher possible process linckages between species.

2) Marine VOCs, once thought to have a minor role in atmospheric chemistry, have been recognized as significant. Recent studies have reported the ocean as an important source of various VOCs (i.e methanol, acetaldehyde, monoterpenes) which were until now considered of primary terrestrial origin.

• Appropriate measuring technologies can provide concentration levels of such tracers and help evaluate their impact in the atmosphere.

3) The quantification of marine VOC requires technology with high sensitivity and tractability. Relative to the type of investigation, the analytical criteria may be different. For example, for shipboard studies where large volume samples are available, recent innovations using API-MS and PTR-MS systems coupled to membrane or bubble equilibrators, have achieved very low detection limits (Saltzman (2009), Kameyama et al. (2010)). Laboratory or mesocosm studies provide limited samples volumes. For such studies, the SPME and P&T techniques provide efficient seawater measurements of VOCs, though improvements are still required considering the sensitivity, ease of use and number of tracers analyzed. • The development of new improved methodologies for the investigation of VOCs in seawater can provide the potential to identify an extended number of tracers, easily accurately and at very low limits of detection.

4) DMS, an important oceanic trace gas, has been widely studied in the marine environment. Various studies have assessed its production under elevated  $CO_2$  levels. The majority of  $CO_2$  perturbation studies have shown a decrease in DMS emissions with increasing  $CO_2$  (Gattuso and Hansson (2011)). Though, in Vogt et al. (2008a) and Wingenter et al. (2007), no effect or even a slight increase in DMS levels was observed. Further investigation is therefore needed, in order to evaluate the impact of ocean acidification on the DMS production. Future levels of marine DMS represent a key factor to projected global scenarios.

• A further mesocosm CO<sub>2</sub> enrichment experiment where a number of physical and biological parameters are controlled, can provide an optimum environment for such an investigation.

5) Isoprene is known to be emitted by the ocean. The effect of ocean acidification has so far not been assessed by any of the previous  $CO_2$  perturbation studies.

• Here, a mesocosm CO<sub>2</sub> enrichment experiment can be used to provide the optimum environment for such an investigation.

In this thesis, a new methodology using Needle Trap Devices (NTD) and a gas chromatograph mass spectrometer (GC-MS) was developed and evaluated for various VOCs, in order to examine the above discussed aspects. After devolopment, the suitability of the NTD method was tested in seawater samples during a community mesocosm CO<sub>2</sub> perturbation experiment. In the field, additional method validation was achieved for DMS through an inter laboratory comparison between the NTD - GC-MS method and a purge and trap technique using gas chromatograph flame photometric analysis (P&T GC-FPD). Concentration levels of DMS, isoprene, (+)- $\alpha$ -pinene and (-)- $\alpha$ -pinene were obtained at present and future acidity mesocosm enclosures. Based on correlations with the available biological datasets, the effect of ocean acidification as well as possible ocean sources was thereafter investigated for all examined compounds.

## A novel method for the measurement of VOCs in seawater using needle trap devices and GC-MS

Evridiki Mesarchaki<sup>a,\*</sup>, Noureddine Yassaa<sup>b,c</sup>, Dietmar Hein<sup>d</sup>, Hannah E. Lutterbeck<sup>e</sup>, Cathleen Zindler<sup>e</sup> and Jonathan Williams<sup>a,\*</sup>

<sup>a</sup>Max Plank Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
<sup>b</sup>USTHB, University of Sciences and Technology Houari Boumediene, Faculty of Chemistry, Algiers, Algeria.
<sup>c</sup>Centre de Developpement Des Energies Renouvelables, CDER, Algiers, Algeria
<sup>d</sup>Pas Technology, Gernamy GmbH
<sup>e</sup>GEOMAR Hemholtz Centre for Ocean Research Kiel, Germany

\*Corresponding author. Tel: +49(6131)-305 4541; e-mail: evridiki.mesarchaki@mpic.de Max-Planck Institute for Chemistry, Hahn-Meitner Weg 1, 55128 Mainz, Germany

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Summary. A novel analytical method using newly developed Needle Trap Devices (NTDs) and a gas chromatograph mass spectrometer (GC-MS) system was developed. It has been applied for the first time on seawater samples to quantify marine volatile organic compounds (VOC) relevant to atmospheric chemistry and climate. By purging gases from small water volumes (10 ml) onto sealable NTDs and then desorbing them thermally within the GC injection port, an effective analysis of a wide range of VOCs (isoprene to  $\alpha$ -pinene) was achieved within 23 minutes. Good repeatability (RSD<sub>s</sub> < 16%), linearity ( $R^2 = 0.96 - 0.99$ ) and limits of detection in the range of pM were obtained for all examined compounds. Following laboratory validation, the NTD method was applied in a mesocosm field study in a Norwegian Fjord. Nine individual mesocosm ecosystems under different CO<sub>2</sub> regimes were examined. Dimethylsulphide (DMS), isoprene and monoterpenes were identified and quantified in mesocosm seawater. The DMS measurements are compared with parallel measurements provided by an independent P&T GC-FPD system showing good correlation,  $R^2 = 0.8$ . Our study indicates that the NTD method can be used successfully in place of the traditionally used extraction techniques (P&T, SPME) in marine environments to extend the suite of species typically measured and improve detection limits.

## 2.1 Introduction

The oceans contribute significantly to the global budget of a number of atmospherically important volatile organic compounds (VOCs) (Carpenter et al. (2012), Field et al. (1998), Millet et al. (2010), Millet et al. (2008)). Marine biological, physical and photochemical processes lead to an uptake from, or an emission to, the overlying atmosphere for a suite of organic gases (e.g. DMS, isoprene, acetone, terpenes) (Lana (2011), Shaw et al. (2010), Sinha et al. (2007)). These gases are known to significantly impact the atmosphere, influencing ozone photochemistry and aerosol physics even at trace concentrations (Williams (2004)). For many VOCs very little work has been done on assessing their emission from the ocean.

Anthropogenic emissions of  $CO_2$  to the atmosphere have already increased ocean acidity and this is projected to continue through this century. The uptake or emission of trace gases from the ocean is likely to change in a future higher  $CO_2$  world, since the distribution of biological communities and biological processes will be affected (Gattuso and Hansson (2011)). In order to monitor the concomitant changes in VOC concentrations for such studies, the marine chemist will be required to frequently analyze large numbers of organic compounds in seawater, accurately and precisely even at very low concentration levels. A suitable analytical method must be sensitive, reliable, simple, robust, fast, reproducible, accurate, constructed to minimize biological influence and capable of measuring diverse VOCs.

The most common extraction techniques currently used for the analysis of dissolved VOCs in small volumes of marine samples are the purge-and-trap (P&T) and the solid phase microextraction (SPME) techniques. Adequate limits of detection have been reported for the first (e.g Huybrechts et al. (2000), Kiene and Service (1991), Li et al. (2007), Orlikowska and Schulz-Bull (2009), Vogt et al. (2008a)) and the second method (e.g Li et al. (2010), Niki et al. (2004), Niri et al. (2008), Sakamoto et al. (2006), Yassaa et al. (2006)) in previous aqueous studies. However, further improvement in sensitivity is required due to the low marine derived VOC concentrations usually present in seawater samples. The PT method requires that the sample stream is dried (by Nafion or chemical agents) prior to entering the concentration trap, a process that can compromise the measurement of some VOCs (e.g oxygenated species). The SPME method has a relatively easy sampling procedure and does not require additional sample preparation. However, the SPME has a relatively limited coating capacity and robustness (Bigham et al. (2002), Yassaa et al. (2006)), the extraction efficiency depends on the fibre coating type and analytes used (Niri et al. (2008)), and the overall analytical

sensitivity cannot be further enhanced by increasing sample volumes (Bigham et al., 2002). Furthermore, the problem of competitive displacement limits the scope of VOCs that can be simultaneously sampled, meaning that a SPME method must be developed for a specific compound or family (Hudson et al. (2007), Yassaa et al. (2006)).

Recently developed methods using NTDs (found in the review article (Lord et al. (2010)) and more resently (Alonso et al. (2011a), Alonso et al. (2011b), Bagheri et al. (2011), Trefz et al. (2012)) overcome these problems. In this study, appropriate sorbent packed syringes are used during extraction and concentration followed by a thermal desorption into GC systems. Directing moist gaseous samples through the NTD leads to VOCs and some water being trapped within the needle. Once sample has been acquired, then the end of the needle is sealed and the needle body is inserted into the hot injector of the gas chromatograph. Water collected with the sample is in this case an advantage as the pressure change associated with its vaporization is used to drive the VOC into the column. Sensitivity can be increased simply by increasing the sample volume, until breakthrough occurs (Trefz et al. (2012)). Needle trap methods provide a simple, robust, high sensitivity and low cost alternative to presently used seawater sampling methods (Alonso et al. (2011a), Bagheri et al. (2011), Risticevic et al. (2009)).

Here, we exploit the suitability of needle trap devices for the study of VOCs in seawater samples. A sampling method based on purging volatile tracers out of water samples directly onto the needle traps has been developed and evaluated for DMS, isoprene, benzene, toluene, p-xylene, (+)- $\alpha$ -pinene and (-)- $\alpha$ -pinene. Subsequently the method was applied in a CO<sub>2</sub> enrichment field study. Seawater concentrations of dimethylsulphide (DMS), isoprene and monoterpenes were monitored from May 8 to June 6 2011. Datasets of DMS and isoprene during this period are presented here. These examples show contrasting responses upon ocean acidification. In the field, additional method validation was achieved for DMS through an inter-laboratory comparison between our NTD - GC-MS method and an independent purge and trap technique using gas chromatograph flame photometric analysis (P&T GC-FPD).

## 2.2 Experimental Section

### 2.2.1 Chemicals and Materials

Commercial side-hole NTDs consisting of a 23-gauge, 60 mm long stainless steel needle, packed with 1mg polydimethyl siloxane (PDMS), 0.4 mg Carbopack X and 0.5 mg Carboxen 1000 (1 cm each), were purchased from PAS Technology, Magdala, Germany (Figure 2.1). Gas entering the trap was directed over the weaker adsorber first (PDMS). Prior to first use, the NTDs were conditioned in the Gas Chromatograph injection port at 300°C for 30 min under a permanent helium flow (1 ml/min) to remove impurities. Gas tight syringes, glass fiber filters (25 mm, Whatman GF/F) and water sampling syringes (10 ml) were purchased from Sigma Aldrich. A commercial multi-component gas standard mix (Apel-Reimer Environmental Inc.) was used for calibrations (stated accuracy 5%). Helium 6.0 and synthetic air (20.5%  $O_2$ , rest  $N_2$ , Hydrocarbon free) were from Westfalen AG, Germany.



Fig. 2.1: Needle trap device with side hole and packing materials A: PDMS, B: Carbopack X and C: Carboxen 1000, 1 cm each.

#### 2.2.2 Instrumentation

Needle Trap Sampling system. A sampling set up (supplied by PAS Technology) comprising of a mass flow controller (5 - 250 ml/min, calibrated on He), vacuum pump, voltage regulator, temperature regulator, purge tube heating body and a manual water inlet kit was used to extract VOCs from water samples. The set-up is shown schematically in Figure 2.2. Glass purging tubes (10 ml sampling volume) including a bottom frit were prepared in the glass workshop of the Max Plank Institute in Mainz. An in-line T-piece including a through-hole septa, was used for the introduction of the gas calibration mixture (see Figure 2.2).

GC-MS system. Analyses ware conducted using a gas chromatograph (Agilent Technologies, GC 6890A) coupled to a Mass Selective Detector (MSD 5973 inert) from the same company. VOCs were resolved using a  $\beta$ -cyclodextrin capillary column (CYCLODEX-B, 30 m long, 0.256 mm ID, 0.25  $\mu$ m film thickness) supplied by Sigma Aldrich (Taufkirchen, Germany). The internal coating was composed of a permethylated  $\beta$ -cyclodextrin dissolved into a cyanopropyl-dimethyl polysiloxane liquid. Glass inlet liners with a narrow internal diameter (0.75 mm I.D) were supplied by Sigma Aldrich (Taufkirchen, Germany). A Merlin microseal septum and a microseal nut (Sigma Aldrich, Taufkirchen, Germany) were used to ensure gas integrity against leaks during the time of injection.

#### 2.2.3 Seawater Samples (Nature of Dataset)

Seawater samples of marine VOCs were taken during a mesocosm  $CO_2$  enrichment study conducted in a Norwegian Fjord, close to the city of Bergen. Nine flexible,

polyethylene enclosures (2 m diameter, 25 m length, details in (Riebesell et al. (2012)))containing unfiltered fjord water were moored off-shore of the Raunefjord ( $60^{\circ}$  15' 40" N, 5° 12' 0" E, water depth: 80 m). The partial pressure of  $CO_2$  ( $pCO_2$ ) in the seawater of each enclosure was modified by injecting  $CO_2$  saturated seawater. VOC concentrations of low (280, 280, 360  $\mu$ atm), middle (560, 840, 1120  $\mu$ atm) and high  $pCO_2$  (1400, 2000, 3000  $\mu$ atm) treated mesocosm enclosures were monitored for a period of 29 days. Fertilization with nitrate and phosphate was used (day 14) to instigate a phytoplankton bloom growth. Depth integrated water samples (0 - 12m) were collected daily using 5 L polyethylene aspirators (Hydro-Bios). Gentle rotation of the aspirators (post collection) ensured sample homogeneity. Directly after collection, sub-samples were decanted into air-tight, UV protected glass bottles, using Teflon tubing. Bottle and tubing were initially rinsed with sample water. Then, the tubing was placed at the bottom of the bottle which was allowed to overflow briefly and thereafter capped. In this way, the effect of water-air contact was minimized to almost zero (bubble-free collection). The analysis of samples was completed on the same day as collection. The samples waiting analysis (maximum 8 hours) were kept in the dark and under cool (circa 4°C) conditions, approximately same as present in the fjord. In this way, sample instabilities due to biological activity were minimized.

#### 2.2.4 Sampling Method

The needle trap sampling system is based on purging gases from water samples onto a needle trap device, as shown in Figure 2.2. A fixed 10 ml volume was used for all water samples. Seawater samples were introduced into the purging glass tube, through the water inlet port (part 8, Figure 2.2), using a 10 ml water sampling syringe. The tip of the syringe was placed at the bottom of the bottle straight after the sample was opened and then immediately into the inlet port of the sampling system. In order to prevent phytoplankton and zooplankton organisms from entering the purging tube, an in-line holder containing a glass-fibre filter (0.7 mesh, 25 mm, Whatman GF/F) was attached between the syringe and the water inlet port. Water samples were purged with Helium 6.0 at a flow rate of 40 ml/min for 10 minutes (see more in: Selection of purging *volume*). Regular cleaning of the purging tube with deionized water, prevented salt crystal formation in the frit and purge efficiency reduction. During purging, the water samples were heated to a few degrees above room temperature using a tube heating mantle connected to a temperature regulator (parts 5 - 6, Figure 2.2). Gaseous VOCs extracted from the water sample were then trapped onto the sorbent material of the needle. Because of the temperature difference between the sampling air stream  $(30 \,^{\circ}\text{C})$ and the needle (room temperature  $25 \,^{\circ}$ C), some water vapor contained in the sampling air condensed in the NTD during sampling. Condensed water is a prerequisite of the NTD method. When the needle was inserted into the hot injector  $(310 \,^{\circ}\text{C})$ , the



Fig. 2.2: Schematic of needle trap sampling system: 1. calibration gas injection port (T-piece with fitted septum), 2. purging glass tube, 3. holder, 4. glass frit, 5. tube heating mantle, 6. temperature regulator, 7. needle trap device, 8. manual water inlet port.

instantaneous transformation of trapped condensed water vapor into gas created high pressure within the needle (estimated > 50 bar) which served to drive the collected VOCs from the absorbent into the GC column. The 3-step procedure of the needle trap sampling is shown in Figure 2.3. After sampling, both ends of the needle were sealed with Teflon caps until subsequent analysis. The same NTD was used for up to 80 sample injections.

#### Calibration

To calibrate the system, deionized water was introduced into the glass tube without filtering. Using a gas-tight syringe, the VOC calibration gas mixture was introduced into the He stream (part 1, Figure 2.2) which then passed through the deionized water and afterwards through the needle trap device. Thereafter, the same procedure as with the seawater samples was followed. The desired concentration levels were obtained by appropriate dilution of the multi-component mix gas standard with synthetic air.



Fig. 2.3: 3-Step needle trap sampling, A. Sampling, B. Sealed after sampling, C. Thermal desorption.

#### Selection of purging volume

For a given volatile organic compound, the ideal purging time, and hence volume, will depend both on how easily it can be purged out of the water-phase and on how effectively it can be retained on the needle trap adsorbent. High volatile tracers need to be purged for a shorter time than the low volatile. If purging times are too long the amount of a selected compound will reduce as it is flushed from the needle trap. Purging volumes ranging from 50 to 700 ml were examined for all species. The contrasting behavior of isoprene and  $\alpha$ -pinene is shown in Figure 2.4, where the recorded peak areas (normalized to the higher value) are plotted against different purging volumes. Isoprene gave highest peak areas after 5 min of purging (200 ml) while  $\alpha$ -pinene after 15 min (600 ml). Individual plots for all tracers are available in the supplementary data section. Calibrations (0.07 - 5 nM) performed at both short (100 ml) and long purging times (400 ml) exhibited linear relationships in both cases ( $R^2 \simeq 0.96$  for all tracers, see Table 2.1 in supplementary data). The linearity results confirm a stable sampling process. The selection of a suitable purging time was based on the desired sensitivity for the analyzed tracers (nature of sample). Short purging time increased the analytical sensitivity to isoprene, DMS and benzene while longer purging time increased the sensitivity to toluene, xylenes and  $\alpha$ -pinenes. In our case, ocean samples were analyzed. DMS and isoprene are known ocean emissions (17-34 Tg S/yr (Carpenter et al. (2012), Spielmeyer and Pohnert (2012)) and 1 - 11.6 Tg C/yr (Arnold et al. (2009), Carpenter et al. (2012), Shaw et al. (2010)) accordingly) while tracers like  $\alpha$ -pinenes have been reported only rarely in the marine environment (first reference (Yassaa et al., 2008)) and therefore concentrations were expected to be low. Taking this into consideration, a purging time of  $10 \min (400 \text{ mL})$  was chosen here as a good compromise for all investigated tracers. The method was evaluated using the selected purging volume providing good sensitivity and reproducibility for all examined tracers

(see Section 2.3.1 Method Evaluation).



Fig. 2.4: Peak area responses at different purging volumes for isoprene (blue) and  $\alpha$ -pinene (orange).

#### 2.2.5 Analytical Method

Seawater and calibration standard samples were analyzed immediately after sampling. The NTDs were thermally desorbed in the injection port of the GC. The injector temperature was set to 310°C to ensure complete and fast desorption. As shown, in a previous study (Trefz et al. (2012)), a temperature of 290°C or higher is recommended in order to achieve complete desorption and negligible carry over for needle traps containing PDMS as a sorbent material. The whole length of the needle was inserted into the GC injector through a Merlin microseal septum while the Luer lock end of the needle remained sealed with a Teflon cap. Desorption was achieved in split-less mode of the GC injector for 30 seconds. Rapid introduction of analytes into the column was accomplished through the narrow glass liner. The temperature of the GC-column was maintained at 40°C for 5 min, then increased to 95°C at 1.5°C per minute and held at this temperature for the rest of the analysis. Helium 6.0 was used as carrier gas at a flow rate of  $0.8 \,\mathrm{mL/min}$ . The mass spectrometer (MS), with an electron impact source running in SIM mode, was operated with the following conditions: ionization potential 70 eV and source temperature  $230^{\circ}$ C. The examined compounds were separated into five groups where for each compound a dwell time of 100 ms was applied. In this way, clean (artifact peak free) chromatograms were obtained with high sensitivity for each compound. The SIM parameters used are presented in Table 2.1. After analysis, the column temperature and flow rate were slightly increased for a few minutes (above 100°C) so that any water remaining in the column would be purged from the system and not affect the subsequent analysis.



Fig. 2.5: Example total ion current chromatogram of a gas standard calibration sample.

The above settings provided sharp, reproducible peaks and good separation for all examined compounds within 23 minutes. The separation of the chiral molecule  $\alpha$ -pinene into its (-) and (+) enantiomers was also achieved. An example of a total ion current chromatogram of a gas standard calibration is displayed in Figure 2.5.

The molecule acetone, despite being present in all samples, was not accurately quantifiable by the selected absorbent material (i.e PDMS, Carbopack X and Carboxen 1000). Acetone was therefore considered as an NTD artifact. Other significant artifact peaks originating from the NTD polymers were ions with masses such as: 130, 45, 207, 118, 56, and 281. As shown in Figure 2.5, using the SIM parameters of Table 2.1, artifact peaks or fraction peaks of artifact molecules landing on the examined ion masses, were avoided.

The chromatogram peak integration was accomplished using an automated Gaussian curve fitting program (iau\_chrom version 7.0 (Bönisch et al. (2010)) and the Agilent Chemstation software.

### 2.3 Results and Discussion

#### 2.3.1 Method Evaluation

Initial analyses of seawater and deionized water blank and calibration samples showed equivalent background peak areas. This was taken to indicate that salt does not affect the behavior of the examined compounds under analysis. The same was observed by

| Group   | Time range        | Compound                       | Mass |
|---------|-------------------|--------------------------------|------|
|         |                   | isoprene                       | 67   |
| Group 1 | (0 – 3.5 min)     | DMS                            | 62   |
|         |                   | acetone                        | 58   |
| Group 2 | (3.5 – 6.0 min)   | benzene                        | 78   |
| Group 3 | (6.0 – 10.0 min)  | toluene                        | 91   |
| Group 4 | (10.0 – 18.0 min) | <i>p</i> -xylene               | 91   |
| Group 5 | (18.0 – 24.0 min) | (-) α -pinene<br>(+) α -pinene | 93   |

Table 2.1: SIM parameters - Separation of the analyzed tracers into five groups.

Sakamoto et al. (2006) for DMS, wherein the reported % salinity effect lies within our stated precision (details in Section: *Desorption Efficiency, Recovery and Repeatability*). For reasons of simplicity and practicality, the method was evaluated using pure water instead of sea-water.

#### LOD/LOQ and Linearity

In order to examine the sensitivity of the system, ten blank samples (deionized water) were analyzed. Table 2.2 shows the Limits of Detection (LOD) and Quantification (LOQ) calculated as three and ten times the standard deviation of the blank, respectively. The method shows high sensitivity towards the examined VOCs and low LODs. The water driven injection of the sample is clearly effective at producing sharp defined peaks and therefore low LODs (0.001 - 0.4 nM in 10 ml sample). Best LOD results were found for the enantiomers of  $\alpha$ -pinene while the highest values were obtained for toluene. The results reported here are in good agreement with previously reported applications for the same needle type (Trefz et al. (2012)). LODs provided by previous characteristic SPME and P&T applications in aqueous studies, are presented in Table 2.3. Overall, the NTD method showed comparable or even better LODs providing a promising alternative for future water-sample applications.

The linearity of the method for a wide range of concentrations (from 0.07 to 10 nM) was sufficient to conduct quantitative evaluation. As reported in Table 2.2, all studied chemicals responded linearly with correlation coefficients ( $R^2$ ) greater than 0.96.

Desorption Efficiency, Recovery and Repeatability

| Compound         | LO    | )D    | LO    | DQ     | Linearity      |
|------------------|-------|-------|-------|--------|----------------|
| Compound         | nM    | ng /l | nM    | ng /l  | $\mathbf{r}^2$ |
| isoprene         | 0.02  | 1.57  | 0.08  | 5.23   | 0.989          |
| DMS              | 0.04  | 2.63  | 0.14  | 8.76   | 0.991          |
| benzene          | 0.05  | 3.86  | 0.16  | 12.86  | 0.982          |
| toluene          | 0.42  | 39.00 | 1.41  | 129.99 | 0.966          |
| <i>p</i> -xylene | 0.29  | 31.02 | 0.97  | 103.39 | 0.962          |
| (-) α -pinene    | 0.001 | 0.15  | 0.004 | 0.48   | 0.971          |
| (+)α -pinene     | 0.002 | 0.26  | 0.006 | 0.87   | 0.967          |

Table 2.2: LODs, LOQs in nM and ng/l (n=10) and correlation coefficients  $(R^2)$  in the range of 0.07 - 10 nM (n=7).

Desorption efficiency was tested using two subsequent samples of the same needle. For the first desorption the needle was loaded with a typical sample concentration of 2 nM and for the second just with humid air. As shown in Table 2.4, the desorption temperature ( $310^{\circ}$ C) and desorption time (30 s) proved sufficient to remove the examined VOCs from the NTD without carry over (desorption efficiency close to 100% and the second injection was equal to the blank). Sample recoveries were tested at two concentration levels (2 and 3 nM) mimicking the average field sample concentrations. Two subsequent analyses of the same water volume were performed. For the first, a known concentration was resampled. Recoveries (R%) shown in Table 2.4, varied from 90.3% to 100% and were deemed very satisfactory. Repeatability was investigated also at concentration levels of 2 and 3 nM. Four concentration replicates for each concentration level were analyzed and their relative standard deviations, shown in Table 2.4, ranged from 3.1 to 16%. A trend of increasing RSD% with decreasing concentration was observed.

#### Overall method accuracy

The overall accuracy for the NTD method was estimated always better than 7.4%. The estimation took into account a 5% uncertainty for the concentration measurement of each tracer as provided by the calibration gas bottle, a 2% uncertainty for the measurement of the dilutions volumes used for the preparation of the desired calibration concentration ranges, a 5% uncertainty for the volume measurement of the 10 ml seawater sampling and a 1% uncertainty for the measurement of the purging volume.

|          | LOD in previous aqueous studies (ng/l)                 |   |  |  |  |
|----------|--|---|--|--|--|
| Compound | SPME   | Р&Т   |  |  |  |
| DMS      | 3.1 <sup>1</sup> , 12.5 <sup>6</sup> , 31 <sup>7</sup> | $0.62^2$ , $3.1 - 31^3$ , $18.64^7$ , $6.2^8$ |  |  |  |
| isoprene |  | 0.102 <sup>2</sup>                            |  |  |  |
| benzene  | 26 <sup>4</sup> , 66 <sup>5</sup> , 382 <sup>11</sup>  | 22.05 <sup>9</sup> , 7.3 <sup>10</sup>        |  |  |  |
| toluene  | 13 <sup>4</sup> , 38 <sup>5</sup> , 144 <sup>11</sup>  | 4.99 <sup>9</sup> , 8.1 <sup>10</sup>         |  |  |  |

 Table 2.3: LODs for the examined compounds, in previous SPME and P&T aqueous applications.

<sup>1</sup> (Niki et al., 2004), <sup>2</sup> (Orlikowska and Schulz-Bull, 2009), <sup>3</sup> (Kiene and Service, 1991), <sup>4</sup> (Li et al., 2010),
<sup>5</sup> (Niri et al., 2008), <sup>6</sup> (Sakamoto et al., 2006), <sup>7</sup> (Vogt et al., 2008b), <sup>8</sup> (Li et al., 2007), <sup>9</sup> (Huybrechts et al., 2000), <sup>10</sup> (Han et al., 2006), <sup>11</sup> (Prikryl et al., 2006).

#### 2.3.2 Seawater Samples from Mesocosm Enclosures

As mentioned in the experimental section, nine mesocosm enclosures with modified  $pCO_2$  concentrations were studied. Based on their  $CO_2$  concentration differences, the mesocosms were divided into three  $pCO_2$  groups. Mesocosms M2, M4, M6 (280, 280,  $360 \,\mu \text{atm} \, p \text{CO2}$ , respectively) represent the low  $p \text{CO}_2$  group, mesocosms M1, M3, M8  $(560, 840, 1120 \,\mu \text{atm})$  the middle  $p \text{CO}_2$  group and mesocosms M5, M7, M9 (1400, 2000,  $3000 \,\mu \text{atm}$ ) the high pCO<sub>2</sub> group. The applied low pCO<sub>2</sub> values are characteristic of our present day environment, the middle ones represent the predicted atmospheric  $CO_2$ levels for 2100 and the third ones provide a more extreme future scenario (Gattuso and Hansson (2011)). Seawater samples from all mesocosms were collected, purged and analyzed as described in the experimental section. Throughout the experiment, calibrations of one concentration level were performed against a working gas - mixture standard, routinely, every five sample measurements. The response factor of these standard analyses was used to calibrate the samples measured in between. On days where the ambient temperature remained stable within the day, the GC responded similarly to all calibration samples. On days with stronger ambient temperature differences the GC responses between the various calibrations were more diverse. Representative averages of the % variation of the calibration factor (% RSD) within one day were in

| Compound             | Desorption efficiency | 2    | nM    | 3 nM  |      |
|----------------------|-----------------------|------|-------|-------|------|
| Compound             | %                     | R%   | RSD % | R%    | RSD% |
| Isoprene             | 99.4                  | 99.6 | 7.8   | 98.7  | 5.5  |
| DMS                  | 99.3                  | 99.1 | 12.4  | 93.1  | 7.0  |
| Benzene              | 100.0                 | 98.4 | 4.9   | 98.7  | 3.9  |
| Toluene              | 98.5                  | 90.3 | 4.4   | 100.0 | 4.6  |
| <i>p</i> -xylene     | 100.0                 | 94.2 | 11.3  | 100.0 | 16.0 |
| (-) α -pinene        | 100.0                 | 99.8 | 9.2   | 100.0 | 11.6 |
| (+) $\alpha$ -pinene | 100.0                 | 99.9 | 12.1  | 100.0 | 3.1  |

Table 2.4: Desorption efficiencies (%), Recoveries (R%) and Repeatabilities (RSD%) (n=4) for concentrations of 2 and 3 nM.

the order of 21.5, 18.54 and 30 % for dms, isoprene and the  $\alpha$ -pinenes, respectively. At least one blank analysis was performed in each measurement sequence (day of analysis). Linearity of the system was confirmed regularly (five times) during the course of the experiment, over wide ranges of concentrations (1.3 - 9.3 nM for DMS, 1.5 - 10.4 nM for isoprene and 1.7 - 12.4 nM for  $\alpha$ -pinene). The working standard was calibrated after the end of the experiment, in the laboratory, relative to a commercial multi-component gas standard supplied by Apel-Reimer Environmental Inc.

#### Identification of VOC in Seawater Samples

The most abundant marine organic compound identified in the mesocosm enclosures was DMS at concentrations ranging from 0.3 to 6 nM. Isoprene was the second most abundant tracer (0.02 to 0.42 nM), followed by (-)  $\alpha$ -pinene (0.0041 to 0.063 nM) and (+)  $\alpha$ -pinene (0.002 to 0.055 nM).

In Figure 2.6, we present our findings for DMS and isoprene over a period of 29 days. Each line shows the mean value of a  $pCO_2$  group (low, middle and high  $pCO_2$ ) and the error bars display the standard deviation of each group. For DMS (Figure 2.6(a)), generally the same trend was observed for all three  $pCO_2$  groups over the course of the experiment. One small concentration increase appeared on day 3 followed by a bigger increase which started around day 15 and continued until the end of the experiment. From day 8 onward, a clear consistent concentration difference was observed between the three  $CO_2$  treatments. Significantly higher DMS concentrations were observed in the low  $pCO_2$  mesocosms, while higher  $pCO_2$  concentrations led to smaller DMS production.

This study suggests that a higher  $CO_2$  world would result in lower DMS emissions. Previous mesocosms studies in 2004 and 2006 (Avgoustidi et al. (2012), Hopkins et



Fig. 2.6: Mean DMS (a) and isoprene (b) concentration for three  $pCO_2$  groups (low, middle and high  $pCO_2$ ) and their standard deviations during the course of the experiment.

al. (2010)) have shown the same  $CO_2$  effect on DMS emissions. One exception to this apparent consensus was a mesocosm study in 2005 which reported no significant differences between treatments (Vogt et al. (2008a)) or even small increase of DMS production (Wingenter et al. (2007)). The different responses of DMS to elevated  $CO_2$ could have been a function of different phytoplankton compositions and abundances as well as different physical and biological processes (Avgoustidi et al. (2012), Hopkins et al. (2010), Vogt et al. (2008a), Wingenter et al. (2007)).

For isoprene (Figure 2.6(b)), the situation was different. Differences in the concentration levels were apparent between the three  $CO_2$  treatments although low  $CO_2$  levels and high isoprene emissions did not correspond as clearly as in the case of DMS. At the beginning and end of the experiment, all  $CO_2$  treatments provided similar isoprene concentrations. Between days 1-4 but also 8-15, the middle  $CO_2$  treatment showed higher isoprene emissions. A possible explanation could be the uneven distribution of phytoplankton families mainly responsible for isoprene production in these mesocosms. A more detailed investigation on the effect of elevated  $CO_2$  on DMS, isoprene,  $(+) \alpha$ pinene and  $(-) \alpha$ -pinene based on correlations with the available biological datasets will



Fig. 2.7: DMS concentrations over the course of the experiment measured with NTD GC-MS (filled cycles) and P&T GC-FPD (star symbols) methods. Mean values and their standard deviations for both methods at (a) low  $pCO_2$ , (b) middle  $pCO_2$  and (c) high  $pCO_2$  treatments. (d) Linear regression of the two methods (P&T GC-FPD / NTD GC-MS) for all treatments.

be reported in a following publication.

DMS measurement Comparison between NTD GC-MS and P&T GC-FPD methods

In the course of the mesocosm field experiment, a comparison between the Max Plank Institute for Chemistry (MPIC) using the NTD GC-MS and the co-participant Helmholtz - Centre for Ocean Research (GEOMAR) using the established P&T GC-FPD method was performed. The target compound for the comparison of the two methods was the dimethyl sulphide (DMS) sampled out of nine independent meso-cosm enclosures.

Both techniques used sub-samples taken from the same original aspirators. However, each method was performed by a different person, using a different sample preparation process, type of calibration, calibration standard and analytical instrumentation. The NTD GC-MS sampling and analysis processes are described in detail in the experimental section while detailed information about the P&T GC-FPD method can be found in

earlier studies (Kiene and Service (1991), Zindler et al. (2012a), Zindler et al. (2012b)). In short, there are three main differences between the NTD GC-MS (method A) and P&T GC-FPD (method B) techniques: 1) method B used liquid nitrogen (LN<sub>2</sub>) for pre-concentration while in method A sample tracers were trapped directly using threebed NTDs, 2) method B used a potassium carbonate ( $K_2CO_3$ ) column to trap the moisture while for method A the condensed water was used as an extracting medium in the desorption process and 3) immersion in hot water was used in method B for the injection of DMS into the GC where in method A desorption of the NTDs occurred directly into the injection port of the GC.

The two techniques were calibrated independently. The NTD GC-MS method used a multi-component gas standard (5% stated accuracy) while the P&T GC-FPD method used a liquid DMS standard for calibration (Kiene and Service (1991), Zindler et al. (2012b)). The liquid standard from the GEOMAR team was analyzed also using the NTD method. The difference between the two standards was found to be 7% which was not considered significant as it is within the range of the NTD method precision (RSD % 7 - 12.4) at the examined concentration levels (see Table 2.2). The NTD GC-MS method gave LODs as low as 0.04 nM and the P&T GC-FPD method 0.3 nM. Linearities ( $R^2$ ) for both techniques were > 0.99 for a concentration range of 0.5 to 10 nM.

In Figure 7, we present a visual comparison of the DMS measurements in each  $pCO_2$ group for the two analytical methods and a whole data method correlation. In Figures 7a, 7b, 7c, measurements provided by the NTD method are marked with filled cycles while the ones provided by the P&T method with star symbols. On the whole, both methods are in good agreement, with similar DMS concentration ranges (0.3 to 6 nM)by the NTD method and 0.34 to 6.18 nM by the P&T method), temporal variations and  $CO_2$  effect. Best agreement between the two methods was found for the higher DMS production group (low  $pCO_2$  treatment) with correlation coefficient  $R^2 = 0.81$ . A linear regression (Figure 2.7d) for the whole data set gave a total  $R^2 = 0.805$  correlation between the two methods. The derived slope shows a 13~% overestimation of the NTD over the P&T method. This is mainly caused by discrepancies in the first period of the experimental study when the NTD method measured consistently slightly higher (i.e. days 0 to 10). Possibly, this was caused by an early calibration error in one or both systems. Thereafter, both techniques showed good agreement. Overall, the comparison proves that the newly developed NTD GC-MS method, applied for the first time on seawater samples, produced similar results for DMS to an established P&T GC-FPD method.

## 2.4 Conclusion

This study details the development of a new NTD GC-MS method with focus on the effective sampling and analysis of the target atmospheric relevant VOCs: DMS, isoprene and  $\alpha$ -pinenes, out of seawater samples. The method efficiency, accuracy, sensitivity, linearity and repeatability have been demonstrated. The ability of the NTD method to perform aqueous phase measurements was tested in the field during a  $CO_2$  enrichment study where the target compounds were identified and successfully quantified. A DMS decrease was observed at high  $CO_2$  levels while isoprene showed no clear CO<sub>2</sub> correlation. Furthermore, an in-field method comparison proved that the first application of the NTD method on seawater samples provided similar results for DMS to an established P&T GC-FPD method. The NTD method delivers multiple VOC analysis, within 23 minutes with sensitivities comparable or even better to the conventional P&T and SPME methods. It has a fast sampling process and since it does not require a separate thermal desorption system it is easier to handle and may be assembled at lower cost. On the basis of our results, we recommend the new NTD GC-MS method as an alternative to the established techniques for the analysis of VOCs in seawater samples.

## A cknowledgements

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## 2.5 Supplementary Data

## Needle Trap Devices

Needle Trap Devices, product name "NeedleEx", are produced from Shinwa Industries Ltd. in Japan (contact person Mr. Ellwood Sean James). They are distributed from PAS Technology in Magdala, Germany (contact person Mr. Dietmar Hein, e-mail address: dietmar.hein@pas-tec.com).

## Method Evaluation

Additional information concerning the NTD method evaluation in Section 2.4.2: Selection of Purging Volume are given below:

- Searching for the appropriate purging volume, volumes ranging from 50 to 700 ml were examined. In Figure 2.8, the obtained peak areas are plotted against the purging volume, for all examined compounds.
- Calibrations at concentration levels between 0.07 to 5 nM where performed at short (100 ml) and long (400 ml) purging times. Table 2.5, presents the correlations coefficients  $(r^2)$  obtained for all examined tracers.

| Compound            | Linearity (100 ml) | Linearity (400 ml) |
|---------------------|--------------------|--------------------|
|                     | $r^2$              | $r^2$              |
| isoprene            | 0.987              | 0.968              |
| DMS                 | 0.999              | 0.991              |
| benzene             | 0.986              | 0.984              |
| toluene             | 0.956              | 0.967              |
| p-xylene            | 0.955              | 0.957              |
| $(-)\alpha$ -pinene | 0.964              | 0.971              |
| $(+)\alpha$ -pinene | 0.959              | 0.967              |

**Table 2.5:** Correlation coefficients  $(r^2)$  in the range of 0.07 to 5 nM corresponding to 100 ml and 400 ml purging volumes accordingly.


Fig. 2.8: Peak areas at different purging volumes for the examined VOCs

# Research Note: Effects of Ocean Acidification on Marine VOC Emissions

The increasing anthropogenic  $CO_2$  emissions in the atmosphere result in an increasing  $CO_2$  uptake by the ocean and thus to a more acidic ocean environment. The impacts of ocean acidification on marine organisms, ocean ecosystems and climate-relevant organic gas emissions are still poorly understood. An evaluation of the effect of ocean acidification on the production rates of various VOCs during a  $CO_2$  enrichment study, is discussed in this chapter.

# 3.1 Mesocosm CO<sub>2</sub> enrichment study - Norway 2011



Fig. 3.1: The 9 Mesocosms moored off-shore of the Raunefjord - Mesocosm schematic representation.

Mesocosms can be defined as experimental tools that bring a small part of the natural environment, encompassing a surface ocean ecosystem, under controlled conditions.



Fig. 3.2: Chl- $\alpha$  concentration levels for all nine mesocosm enclosures during the mesocosm study.

Mesocosm studies have therefore the advantage, compared to laboratory approaches, of maintaining a natural community under close to natural conditions, taking into account relevant aspects from the real world such as indirect effects, bioavailability, substance degradation, biological compensation and recovery. Mesocosms are currently the best available tool for evaluating the impacts of ocean acidification (Riebesell et al. (2008)). As part of this thesis, the effect of ocean acidification on the production of marine VOCs was studied during a mesocosm  $CO_2$  enrichment study, in a Norwegian Fjord (May-June 2011). Nine flexible, mesocosm enclosures, containing unfiltered fjord water, were moored off-shore of the Raunefjord (60° 15' 40" N, 5° 12' 0" E, water depth: 80 m), as shown in Figure 3.1. A mesocosm consists of a steel flotation frame combined with a flexible enclosure (polyurethane) with stabilizing rings. At the end, a sediment trap fits into the plastic enclosure. The flexible enclosure has a 2m diameter and a length of 25m (Figure 3.1 - on the right side). After the mesocosm deployment, the  $CO_2$  addition occurred in steps by injecting  $CO_2$  saturated seawater. VOC concentrations from low (280, 280, 360  $\mu$ atm), middle (560, 840, 1120  $\mu$ atm) and high pCO<sub>2</sub>  $(1400, 2000, 3000 \,\mu \text{atm})$  treated mesocosm enclosures were monitored for a period of 29 days. Fertilization with nitrate and phosphate was used (day 14) to trigger a phytoplankton bloom growth. As shown in Figure 3.2, Chl- $\alpha$  (data provided by Signe

Klavsen) showed a two stage bloom development. A natural bloom occured between days 2 - 8 and a second bloom was provoked by the additions of nutrients, days 16 - 24. The response of all mesocosm enclosures during the first blooming period was approximately the same, while in the second blooming phase lower CO<sub>2</sub> mesocosms (blue color) correlated with higher Chl- $\alpha$  concentrations. Pico/nanophytoplankton (i.e Synechococcus (0.6 - 1.6  $\mu$ m), picoeukaryotes (0.2 - 2  $\mu$ m), small nanoeukaryotes (2 - 6  $\mu$ m), big nanoeukaryotes (6 - 20  $\mu$ m), E.huxleyi(5 - 10  $\mu$ m) and crypophytes (2 - 20  $\mu$ m) count measurements were provided by Aud Larsen (University of Bergen, Norway) during the mesocosm study.

Using the NTD method, described in Chapter 3, DMS, isoprene and  $\alpha$ -pinene were identified and quantified in all 9 mesocosm enclosures. The findings for each species are given in more detail below.

# 3.2 Marine DMS

The ocean is a major source of Sulphur (S) to the atmosphere primarily in the form of Dimethyl Sulphide (DMS,  $(CH_3)_2S$ ). Marine DMS represents therefore a key pathway in the global biogeochemical sulphur cycle (almost 50% of the global biogenic sulphur emissions, Lana (2011)). A super-saturation of the surface ocean with DMS leads to a DMS flux from the ocean to the atmosphere, currently estimated to  $28.1 \times 10^6$  tonnes S yr<sup>-1</sup> (Carpenter et al. (2012)). In the atmosphere, DMS is oxidized to form sulphuric and methanesulphonic acids. These acids contribute to new particle formation and growth of cloud condensation nuclei (CCN) and thereby affect the radiative properties of the atmosphere by reflecting solar radiation and a possible negative feedback effect (Charlson (1987)).

In the ocean, DMS is produced by the breakdown of its precorsor, dimethyl sulphoniopropionate (DMSP), catalysed by the enzyme DMSP-lyase:

 $(CH_3)_2S^+CH_2CH_2COO^- \rightarrow (CH_3)_2S^+ CH_2CH_2COOH$ 

DMSP is synthesised by both macro and micro-algae in seawater for vital algaeprocesses like osmoregulation, cryoprotection and protection against grazing and oxidative stress (Liss (1997), Gattuso and Hansson (2011), Carpenter et al. (2012) and references therein). Coccolithophorids, especially the species Emiliania huxleyi, are consudered to be the main producer of DMS (see for example, Gabric et al. (2001)). In previous studies (Engel et al. (2005) and references therein), variations in  $CO_2$  levels showed changes in the net specific growth rates, the calcification of cells, the stoichiometry of elemental uptake and the accumulation and loss processes of E. huxleyi.



Fig. 3.3: (a) Mean DMS concentrations and their standard deviations for the three  $pCO_2$  groups (low, middle and high  $pCO_2$ ) during the course of the experiment, (b) mean DMS /  $pCO_2$  correlation for the nine mesocosm enclosures.

#### 3.2.1 DMS Concentration Levels during the Mesocosm Study 2011

DMS was found to be the most abundant marine organic compound identified in the mesocosm enclosures, at concentrations ranging from 0.3 to 6 nM. In Figure 3.3 (a), the mean DMS concentrations for the three  $pCO_2$  groups and their standard deviations are presented over a period of 29 days. The blue line corresponds to low (280 - 390  $\mu$ atm), the green to middle (280 - 390  $\mu$ atm) and red to high (280 - 390  $\mu$ atm)  $pCO_2$  levels. Over the course of the experiment, DMS showed a similar trend in all three  $pCO_2$  groups. One small concentration increase appeared on day 3 followed by a higher increase around day 15 lasting until the end of the experiment. Between days 8 and 29, a clear consistent concentration difference was observed between the three  $CO_2$  treatments. Significantly higher DMS concentrations were observed in the low  $pCO_2$ 



Fig. 3.4: (a) Mean Emiliania huxleyi counts (b) E.huxleyi / DMS correlation for the three  $pCO_2$  groups (low, middle and high  $pCO_2$ ) during the course of the experiment.

mesocosms, while higher  $pCO_2$  concentrations led to smaller DMS production. The effectiveness of  $CO_2$  in decreasing DMS emissions is represented nicely in Figure 3.3 (b) where the mean DMS concentration (for all 9 mesocosms) is plotted against the  $pCO_2$  concentration. This study suggests that a higher  $CO_2$  world would result in lower DMS emissions. A similar  $CO_2$  effect on DMS emissions has been reported in the majority of previous mesocosm studies (Hopkins et al. (2010), Avgoustidi et al. (2012)). In contrast, Vogt et al. (2008a) reported no significant  $CO_2$  effect while Wingenter et al. (2007) even a small increase of DMS emissions with increasing  $CO_2$  levels. These opposing responses to elevated  $CO_2$  could be a consequence of different compositions and abundances as well as different physical and biological processes in the examined mesocosms.

In Figure 3.4 (a), the E. huxley icounts for the three  $pCO_2$  groups (provided by Aud

Larsen) are presented. Comparing the DMS emissions with the E. huxleyi counts (Figure 3.4 (b)), a clear correlation is apparent for all  $CO_2$  treatments, indicating E.huxleyi as the main source of DMS in the ocean.

# 3.3 Marine Isoprene

Isoprene (C<sub>5</sub>H<sub>8</sub>), is the atmosphere's most strongly emitted VOC of biogenic origin (ca. 500 Tg C/yr). Based on in-situ measurements, satellite observations and modelling studies, global marine isoprene emissions are estimated between 0.10 - 1.68 Tg C yr<sup>-1</sup> (Gantt et al. (2009) and references therein). Isoprene has received increased attention due to its potential to form secondary organic aerosols (SOA) (Claeys et al. (2004), Kroll and Seinfeld (2008)), and therefore impact the radiation balance of the atmosphere, modify cloud microphysics, and participate in chemical transformations (Shaw et al. (2010)). These effects are predicted to be significant in remote and coastal regions of the atmosphere for areas where high isoprene production is expected (i.e coastal upwelling regions, wetlands).

Isoprene emitters include heterotrophic bacteria, seaweeds and marine phytoplankton with the latter being the most significant (Gantt et al. (2009), Shaw et al. (2010)). Laboratory studies have correlated isoprene emissions with 27 individual phytoplankton species (Shaw et al. (2010) and references therein). In Shaw (2001), among the examined phytoplankton species, species with larger cell volumes provided larger production rates per cell. Shaw et al. (2003) and Gantt et al. (2009) tested the impact of light and temperature on isoprene production rates by monocultures, finding similarities to terrestrial observations. In both studies, a rapid increase was observed at low light levels and a gradual increase with increasing irradiance until level off. The effect of ocean acidification on isoprene emissions was addressed for the first time in this study.

#### 3.3.1 Isoprene Concentration Levels during the Mesocosm Study 2011

Oceanic isoprene emissions have been accomplished for the first time during a  $CO_2$ enrichment study. Our isoprene results for the three  $pCO_2$  groups are presented in Figure 3.5 (a). Isoprene concentrations ranged between 0.02 and 0.42 nM. Differences in the concentration levels were apparent between the three  $CO_2$  treatments although low  $CO_2$  levels and high isoprene emissions did not correspond as clearly as in the case of DMS. At the beginning and end of the experiment, all  $CO_2$  treatments showed similar isoprene levels. During the intermediate period the middle and the low  $pCO_2$ groups provided higher isoprene emissions. Since isoprene is produced by most phytoplankton species, a direct link to one of them is difficult. After correlating the isoprene



Fig. 3.5: (a) Mean isoprene concentrations and (b) counts of big nanoeukaryotes for the three  $pCO_2$  groups (low, middle and high  $pCO_2$ ) during the course of the experiment.

data with counts of the different phytoplankton species measured during the campaign, an apparent similarity with the big nanoeukaryotes species (Figure 3.5 (b)) was observed, indicating big nanoeukaryotes as one of the main isoprene sources in this study. This observation is in agreement with previous observations of large cell species (Shaw (2001)), mentioned in the previous paragraph.

# 3.4 Marine Monoterpenes

Compared to DMS and isoprene, monoterpenes were until 2008 an undiscovered ocean product. In general, terpenoids are known to be produced in the ocean by micromacro algae, sponges and corals. These terpenoids though are thought to be complex terpenes (often acyclic and halogenated), rather than monoterpenes. This was because their synthesis in the ocean was believed to be driven by different mechanisms (despite the same precursors) than on land (Hay and Fenical (1988), Wise, M. L. (2003)). Recently, the first observation of monoterpenes (including (-)/(+)- $\alpha$ -pinene, limonene and p-ocimene) in laboratory experiments and also shipboard measurements, were reported by Yassaa et al. (2008). During a cruise across the Southern Atlantic Ocean, Yassaa et al. (2008) observed maximum levels of 100-225 pptv total monoterpenes when the ship crossed an active phytoplankton bloom. Considering the short lifetime of monoterpenes, this strongly suggested an oceanic source. The year after, Colomb et al. (2009) reported air mixing ratios up to 100 pptv of total monoterpenes (in regions of a phytoplankton bloom) during a cruise over the Southern Indian Austral Ocean. Modelled estimates by Luo and Yu (2010) using data from Yassaa et al. (2008), predict an oceanic monoterpene source of 29.5 Tg y<sup>-1</sup>. Based on the above, marine monoterpenes can be considered as a significant source of ocean carbon at the remote marine atmosphere with considerable impact on the formation of marine oxidants (including ozone) and secondary organic aerosols.

Due to limitation of measurements, the sources of monoterpenes in the ocean, is very uncertain. In the laboratory Yassaa et al. (2008) investigated 9 algae species, of which one Chlorophycae species, i.e Dunaliella tertiolecta showed at least three times higher emissions of total monoterpenes than the rest species (of which some Diatoms, Coccol-ithophorids and Cyanobacteria).

#### 3.4.1 $\alpha$ -pinene Concentration Levels during the Mesocosm Study 2011

During the Mesocosm 2011 campaign,  $\alpha$ -pinene (C<sub>10</sub>H<sub>16</sub>) was identified and quantified for the first time in seawater. The analytical column used (CYCLODEX-B), was able to separate the two  $\alpha$ -pinene enantiomers. The results obtained during the experiment, are presented in Figure 3.6. Concentration levels in the mesocosm enclosures ranged between 0.0041 to 0.063 nM for (-)- $\alpha$ -pinene and 0.002 to 0.055 nM for (+)- $\alpha$ -pinene. Despite the similar concentration levels of both enantiomers, their concentration trends are very different, indicating different emitting sources. For (-)- $\alpha$ -pinene (Figure 3.6 (a)) maximum concentration levels were observed at the beginning of the campaign, days 2-8, while for (+)- $\alpha$ -pinene (Figure 3.6 (b)) a big concentration increase appeared between days 8-15. The trend of the (-)- $\alpha$ -pinene shows similarities to the trend of the big nanoeukaryotes (Figure 3.5 (b)), while for (+)- $\alpha$ -pinene none of the examined phytoplankton species showed a corresponding trend. Interestingly here, all three CO<sub>2</sub> groups showed very similar concentration levels, indicating that the production of monoterpenes in the ocean would probably not be effected in a higher CO<sub>2</sub> world.



Fig. 3.6: Mean  $\alpha$ -pinene concentrations of the (+) (plot (a)) and the (-) (plot (b)) enantiomer for three  $pCO_2$  groups (low, middle and high  $pCO_2$ ) and their standard deviations during the course of the experiment.

# Introduction - Air-sea gas exchange

Over the last half century, the exchange of gases between atmosphere and ocean, two very important reservoirs in the global cycling of chemical species, has received increased attention. The ocean has been recognized to be an important source and sink for various important trace gases like  $CO_2$  (uptaking ~ 48% of the anthropogenic  $CO_2$  since the late 18th century (Sabine et al. (2004)),  $O_2$ , CO,  $CH_4$ , various volatile organic compounds (e.g., dms (precursor to cloud condensation nuclei (CCN)), acetone, methanol, acetaldehyde, isoprene), halogenated compounds (e.g., CH<sub>3</sub>I, CH<sub>3</sub>Cl, CHBr<sub>3</sub>), nitrous compounds (e.g., NH<sub>3</sub>, N<sub>2</sub>O, HNO<sub>3</sub>, NO), CFCs, particles but also anthropogenic tracers coming from ship emissions. Gas exchange is therefore of fundamental importance to lower and upper atmosphere processes, ocean biology, geochemical cycles, clouds, climate and human health (Williams (2004), Nightingale (2009), Carpenter et al. (2012), Doney et al. (2012)). Furthermore, the exchange of heat and momentum between ocean and atmosphere play a pivotal role in weather, global climate and the general circulation of the ocean and the atmosphere (Veron et al. (2011)). As shown in Figure 4.1, there are many processes in the open ocean that are thought to influence the air-sea gas transfer. Investigating the role of individual parameters is thus of great difficulty in the ocean. Over the last decades, several wind-wave tunnel experiments have been performed attempting to understand the mechanisms which control the transfer rates of the air-sea gas exchange, try to measure them and parameterize them. (Wanninkhof et al. (2009), Nightingale (2009)). Thanks to recent instrumental advances, various physical parameters can now be measured and phenomena such as surface waves, bubbles, droplets and surfactant layers can be better investigated (Jähne and Haussecker (1998), Jähne (2009), Veron et al. (2011)). So far, despite the numerous laboratory and oceanic gas exchange studies, a full understanding of the processes behind the air-sea gas exchange has still not been established.



Fig. 4.1: The air-sea flux of gases and the various processes that are believed to control these fluxes. (Illustration by Jayne Doucette, Woods Hole Oceanographic Institution)

# 4.1 Theoretical Background - The two layer concept of resistance to gas transfer at water surfaces



Fig. 4.2: Two layer Model: Liss & Slater, Nature 1974

The transfer of gases across air-water interphases occurs by way of molecular (molecular characteristics, small scale) and turbulent diffusion (turbulent motion, large scale). In the body of air and water, turbulent diffusion dominates. However, close to the interface the turbulent motion is suppressed and the exchange of mass depends on molecular diffusivity there (Donelan and Wanninkhof (2002)). This view has led to conceptual models of this process, like the widely used "Two layer model" proposed by Liss and Slater (1974) (see Figure 4.2). The boundary layers on either side of the interface are subdivided into a turbulent outer layer and an inner molecular layer. It is these two inner molecular layers that provide the main resistance to the transport of gases across the interface. This simplified model is physically not entirely realistic, though it helps to visualize processes at the interface and allows simplification of theoretical calculations of the gas exchange rates.

Based on Fick's first law, the flux of a tracer across one layer is equal to the concen-

tration difference across the layer,  $\Delta_c$  and the tracer's transfer rate through the layer,  $k \ (k = D \ (\text{diffusivity of gas in layer}) \ / \ z \ (\text{thickness of layer}))$ 

$$F = k\Delta c \tag{4.1}$$

The transfer rate (also termed transfer velocity), k is expressed in velocity units (i.e. cm/h) and is related to turbulent associated mechanisms (i.e., surface stress, surface roughness, waves - wave breaking, bubbles etc.) and tracer characteristics (i.e., solubility, diffusivity), as they can change the size of the molecular layers. The total velocity  $k_t$  of the transfer for any gas will be a combination of the individual velocities in each molecular layer.

# 4.2 Partition of the transfer

Mass (or more specifically molecular) boundary layers are formed in the air (~ 100 – 1000  $\mu$ m) and the water phase (~ 20 – 200  $\mu$ m) on opposite sides of the interface. At the surface itself, for gases obeying Henrys law, solubility equilibrium is established such that:

$$c_{\rm ws} = \alpha c_{\rm as}.\tag{4.2}$$

where  $\alpha$  is the dimensionless Ostwalds solubility and  $c_{as}$ ,  $c_{ws}$  the surface tracer concentrations at the air side and water side of the interface respectively. The flux of a tracer across the interface can be expressed from either a water (Eq. 4.3) or an air-side (Eq. 4.4) point of view, as follows:

$$F = k_{\rm tw} (\alpha c_{\rm a} - c_{\rm w}) \tag{4.3}$$

, or

$$F = k_{\rm ta}(c_{\rm a} - c_{\rm w/\alpha}) \tag{4.4}$$

where  $c_a$ ,  $c_w$  the bulk air and water phase concentrations and  $k_{tw}$  and  $k_{ta}$  the total transfer velocities for both perspectives. The total transfer velocity,  $k_t$  comprises of the individual transfer velocities in water  $k_w$  (as seen from a water side perspective) and air  $k_a$  (as seen from an air side perspective):

$$k_{\rm t,w} = \left(\frac{1}{k_{\rm w}} + \frac{\alpha}{k_{\rm a}}\right)^{-1},\tag{4.5}$$

$$k_{\rm t,a} = \left(\frac{1}{k_{\rm a}} + \frac{1}{\alpha k_{\rm w}}\right)^{-1},\tag{4.6}$$

The two forms of  $k_t$  differ by the solubility factor,  $\alpha$ . The ratio  $\alpha k_w/k_w$ , determines which boundary layer controls the transfer. As can be derived from Equation 4.5, a low solubility shifts control of the transfer process to the aqueous layer and a high solubility (Equation 4.6) shifts control of the transfer to the gas-phase boundary layer (Jähne and Haussecker (1998)). Tracers with very high solubility (i.e. water vapor, heat) are entirely controlled by the air-side layer (Figure 4.3 (A)) while the ones with very low solubility (i.e.  $CO_2$ ,  $N_2O$ ) by the water side layer (Figure 4.3 (B)). These two extreme cases are shown schematically in Figure 4.3. Of course for all tracers with intermediate solubility, the total transfer rate is related to both individual layer rates,  $k_w$  and  $k_a$ .



Fig. 4.3: The concentration profiles of the transfer process for (A) a very high soluble tracer (resistance only in the air side molecular layer) and (B) a very low soluble tracer (resistance only in the water side molecular layer

# 4.3 Open Research Questions and Thesis Goals

In the past, improvement toward a better understanding of the mechanisms controlling the air-sea gas transfer has been hindered due to poor measurement technology (Jähne and Haussecker (1998)). Recently, a much greater range of techniques has been available, which can provide measurements on much faster time scales; a so long significant barrier to the air-sea transfer rate measurements. Moreover, additional improvements in relevant research areas such as hydrodynamics, micrometeorology, optical and image processing have greatly assisted this endeavor. An integration of the newly available technologies is in focus of the current research, encouraging the investigation in the field of air-sea gas exchange. Six key air-sea gas exchange questions that need elucidation, follow in more detail:

1) Despite the numerous studies on measuring and parameterizing the water-side transfer coefficient,  $k_w$  as a function of wind speed, no unique relationship between k and wind speed is apparent. Latest studies support that the gas transfer is not simply a function of the wind speed but depends also on other parameters describing the near-surface turbulence (Jähne et al. (1987), Jähne and Haussecker (1998), Frew et al. (2004), Jähne (2009), Veron et al. (2011)).

- Wind-wave tanks provide an ideal environment to study the physical parameters influencing gas transfer. They enable setting and tuning of the environmental parameters, so that the process in question can be studied in great detail. Wind-wave tank studies could provide answers on how accurately the currently measured surface parameters can describe the effect of surface waves, surface turbulence on either side of the interface, bubbles, droplets, surfactants on the gas exchange rates.
- Once the critical parameters accounting for all critical processes effecting the gas exchange have been found, they can be used to provide a more efficient transfer velocity relationship.

2) Gas exchange rate measurements at the very low wind speed regime are hard to conduct, especially in the ocean. Exchange rates at this wind speed regime are therefore uncertain and rely on extrapolations that might not be accurately reproducing the gas exchange rates.

• The newest technology, used under controlled conditions provided by wind wave tanks can help in investigating the gas exchange rate at the very low wind speed regime.

3) The friction velocity, $u_*$  expressing the shear stress created on the water surface by the wind and the mean square slope,  $\sigma_s^2$  describing the "shape" of the wind field or in other words the surface roughness, are considered more suited variables to define phenomena such as waves and wave breaking, near surface turbulence, bubbles and surface films (Jähne et al. (1987), Jähne and Haussecker (1998), Frew et al. (2004), Jähne (2009), Veron et al. (2011)). • An intensive investigation of the air-sea gas exchange processes in terms of  $u_*$  and  $\sigma_s^2$  is required in order to evaluate the effect of both parameters on the air-sea gas transfer velocity and attempt a more physical parameterization. Here again, new technological approaches and state of the art wind wave tunnels can encourage such attempts.

4) The effect of solubility on the phase control of the transport process, is fundamental. So far though, tracers on the very low end of the solubility range have been extensively studied whereas only a few at the very high end. How medium solubility tracers behave can be presently only assumed from theoretical insights. The phase control of the transfer is of critical importance for accurate transfer rate predictions.

• Air sea gas exchange rate measurements should also involve medium solubility tracers in order to better understand and account for the effect of solubility. Important information concerning the phase control could be provided in this way.

# 5) The solubility influence on the phase control of the transfer rate has not been evaluated under varying wind speed conditions. Solubility has so far never been included in parameterizations.

• Studies of tracers covering a larger solubility range under various wind speed regimes should be performed so that the solubility effect under different turbulent conditions can be investigated. A parameterization that could include the solubility factor would represent a significant advance for transfer velocity predictions of any tracer.

# 6) Global models rely on efficient parameterizations of the air -sea gas exchange rates in order to account for the oceans effect as a source or a sick of various important trace gases (Pozzer et al. (2006), Saltzman (2009))

• Precise measurements and estimations provided by efficient parameterizations would greatly help future global model predictions. Global models would be able to account much more accurately for the influence of ocean trace gas fluxes on atmospheric processes, ocean biology, geochemical cycles, clouds, climate etc.

The motivation of the present thesis was developed from the above mentioned open questions considering the air-sea gas exchange rates. The annular wind wave canal facility "Aeolotron" in Heidelberg, Germany was chosen as the ideal place to conduct our air-sea gas exchange experiments. Numerous trace gases were carefully selected to encompass a wide solubility and diffusivity range, enabling investigation of the tracer properties' effect on the exchange rates. Gas exchange rates at challenging low wind speed ranges such as 0.8 m/s ( $u_{10}$ ) were accomplished. Gradually increasing wind speed regimes were studied extending up to 15 m/s ( $u_{10}$ ). The changing surface conditions (smooth to rough surface) were further investigated under surface film covered water surface. High resolution proton transfer reaction mass spectroscopy (PTR-MS) instrumentation as well as Fourier Transform infrared Spectroscopy (FTIR) were used for parallel air and water concentration measurements of 14 tracers. A mass balance procedure was used to derive the total transfer velocities for all examined tracers. Additional environmental condition as well as surface related parameters quantifications accompanied the transfer velocity measurements.

For the first time, such a comprehensive dataset has been collected, covering broad solubility and diffusivity ranges. State of the art concentration measurements in both air and water phase, provided high quality and reproducibility transfer rate estimations. Our results, open the possibility to investigate all the uncertain areas of air-sea gas exchange. A detailed examination of the effects of the various mechanisms on the measured gas exchange rates was accomplished and a new, more complete, total transfer velocity parameterization is proposed. One equation, that can provide the transfer velocity of any tracer and under clean and surfactant covered surfaces.

# Measuring air-sea gas exchange velocities in a large scale annular wind-wave tank

E. Mesarchaki<sup>1</sup>, C. Kräuter<sup>2</sup>, K. E. Krall<sup>2</sup>, M. Bopp<sup>2</sup>, F. Helleis<sup>1</sup>, J. Williams<sup>1</sup> and B. Jähne<sup>2,3</sup>

<sup>1</sup>Max-Planck-Institut für Chemie (Otto-Hahn-Institut) Hahn-Meitner-Weg 1, 55128 Mainz

<sup>2</sup>Institut für Umweltphysik, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany <sup>3</sup>Heidelberg Collaboratory for Image Processing, Universität Heidelberg, Speyerer Street 6, 69115 Heidelberg, Germany

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Summary. In this study we present gas exchange measurements conducted in a large scale wind-wave tank. Fourteen chemical species spanning a wide range of solubility (dimensionless solubility,  $\alpha = 0.4$  to 5470) and diffusivity (Schmidt number in water,  $Sc_w = 594$  to 1194) were examined under various turbulent ( $u_{10} = 0.8$  to  $15 \text{ m s}^{-1}$ ) conditions. Additional experiments were performed under different surfactant modulated (two different concentration levels of Triton X-100) surface states. This paper details the complete methodology, experimental procedure and instrumentation used to derive the total transfer velocity for all examined tracers. The results presented here demonstrate the efficacy of the proposed method, and the derived gas exchange velocities are shown to be comparable to previous investigations. The gas transfer behaviour is exemplified by contrasting two species at the two solubility extremes, namely nitrous oxide (N<sub>2</sub>O) and methanol (CH<sub>3</sub>OH). Interestingly, a strong transfer velocity reduction (up to factor of three) was observed for N<sub>2</sub>O under a surfactant covered water surface. In contrast, the surfactant affected CH<sub>3</sub>OH, the high solubility tracer only weakly.

# 5.1 Introduction

The world's oceans are key sources and sinks in the global budgets of numerous atmospherically important trace gases, in particular  $CO_2$ ,  $N_2O$  and volatile organic compounds (VOCs) (Field et al. (1998), Williams (2004), Millet et al. (2008), Millet et al. (2010), Carpenter et al. (2012)). Gas exchange between the ocean and the atmosphere is therefore a significant conduit within global biogeochemical cycles. Air-sea gas fluxes, provided either by direct flux measurements or accurate gas transfer parameterizations, are a prerequisite for global climate models tasked to deliver accurate future predictions (Pozzer et al. (2006), Saltzman (2009)).

The principles behind gas exchange at the air-sea interface have been reported in detail within previous reviews (Jähne and Haussecker (1998), Donelan and Wanninkhof (2002), Wanninkhof et al. (2009), Jähne (2009), Nightingale (2009)). A simplified conceptual model is generally accepted whereby mass boundary layers are formed on both sides of the interface. The transport of gases across the boundary layers is controlled by molecular motion, expressed by the diffusion coefficient D. The transfer velocity k(in cm h<sup>-1</sup>), of a gas across the surface is defined as the gas flux density F, divided by the concentration difference  $\Delta c$ , between air and water (henceforth named  $k_{\rm t}$  expressing the transfer through both boundary layers against the single air and water layer transfer,  $k_{\rm a}$  and  $k_{\rm w}$ , accordingly). Wind driven turbulence near the water surface (surface stress and roughness, waves, breaking waves, bubbles, spray etc.), influences the thickness of the mass boundary layers. Thus, the transfer velocity is related to the degree of turbulence on both sides close to the interface as well as the tracer characteristics i.e., their solubility and diffusion coefficient (Danckwerts (1951), Liss and Slater (1974)). The impact of wind driven mechanisms and diverse physiochemical tracer characteristics on the gas exchange rates can be studied in detail through transfer velocity measurements of individual species provided by the method proposed here. Such studies aim to cover poorly understood air-sea gas transfer regimes and provide direct tests for individual species and new insights into the theoretical background.

Gas transfer velocities have been determined in both field studies (using mass balance, eddy correlation or controlled flux techniques) and laboratory experiments described in previous gas exchange reviews (Jähne and Haussecker (1998), Donelan and Wanninkhof (2002), Wanninkhof et al. (2009), Jähne (2009), Nightingale (2009)) and references therein. Wind-wave tanks, in contrast with the open ocean, offer a unique environment for the investigation of individual mechanisms related to the air-sea gas exchange under controlled conditions.

Mass balance methods have been applied in the field using geochemical tracers (O<sub>2</sub>, <sup>14</sup>C, Radon, for instance in Broecker et al. (1985)) and dual tracer (SF<sub>6</sub>, <sup>3</sup>He, for instance in Watson et al. (1991), Wanninkhof et al. (1993)) techniques. The main drawback of these approaches was the temporal resolution which led to time constants in the order of



**Fig. 5.1:** Mass balances for the air and water-side. Naming convention is as follows: A: water surface area;  $V_{\rm a}$ : air volume;  $V_{\rm w}$ : water volume; k: gas transfer velocity,  $c_{\rm a}$ : air-side concentration;  $c_{\rm w}$ : water-side concentration;  $c_{\rm a}^i$ : input tracer concentration;  $c_{\rm a}^0$ : tracer concentration in the ambient air. The dotting denotes the time derivative of the related symbol.

days to weeks. The measurement frequency was too low to probe the fast variability of the physical parameters controlling the gas exchange (Jähne and Haussecker (1998)). Furthermore, the transfer velocity measurements were based primarily on sparingly soluble tracers, and very few experimental results of highly soluble trace gas transfer velocities are available.

In this study, gas-exchange experiments were performed in a state-of-the-art large scale annular wind-wave tank. An experimental approach based on mass balance has been developed, whereby air and water side concentrations of various tracers are monitored using instrumentation capable of on-line measurement. For the first time, parallel measurements of total air and water-side transfer velocities for 14 individual gases within a wide range of solubility, have been achieved. Supplementary parameters directly linked with the gas exchange velocitiess, such as friction velocity and mean square slope of the water surface, were additionally measured under the same conditions. This paper details the entire instrumental set-up and provides a validation of the overall operation and concept through transfer velocity measurements of nitrous oxide and methanol. These species are chosen as they bracket the wide range of solubilities among the investigated tracers and show clearly different gas exchange behaviours.

# 5.2 Method

In this study, total transfer velocities for low as well as medium to highly soluble tracers were determined using a mass balance approach. The wind-wave tank is interpreted in terms of a box model.

# 5.2.1 The box model

The basic idea of the box model method is the development of a direct correlation between the air and water-phase concentrations,  $c_{\rm a}$  and  $c_{\rm w}$ , and the desired transfer rates k of various tracers.

Figure 5.1 shows a schematic representation of the wind-wave tank in a box model (Kräuter (2011), Krall (2013)). Water and air-spaces are assumed to be two well-mixed separate boxes,  $V_{\rm w}$  and  $V_{\rm a}$  between which tracers can be exchanged only through the water surface, A. Further possible pathways of tracers entering or leaving the box are also shown in Fig. 5.1. Assuming constant volumes, temperature and pressure conditions, the mass balance for the air and the water phases of the box, yields for a water-side perspective:

$$V_{\rm a}\dot{c}_{\rm a} = Ak_{\rm tw}(c_{\rm w} - \alpha c_{\rm a}) + \dot{V}_{\rm a}^{i}c_{\rm a}^{i} - \dot{V}_{\rm a}c_{\rm a} + \dot{V}_{\rm a}c_{\rm a}^{0}$$
(5.1)

$$V_{\rm w}\dot{c}_{\rm w} = -Ak_{\rm tw}(c_{\rm w} - \alpha c_{\rm a}). \tag{5.2}$$

and an air-side perspective:

$$V_{\rm a}\dot{c}_{\rm a} = -Ak_{\rm ta}\left(c_{\rm a} - \frac{c_{\rm w}}{\alpha}\right) + \dot{V}_{\rm a}^{i}c_{\rm a}^{i} - \dot{V}_{\rm a}c_{\rm a} + \dot{V}_{\rm a}c_{\rm a}^{0}$$
(5.3)

$$V_{\rm w}\dot{c}_{\rm w} = Ak_{\rm ta}\left(c_{\rm a} - \frac{c_{\rm w}}{\alpha}\right). \tag{5.4}$$

where  $\alpha = c_w/c_a$ , denotes the dimensionless solubility and  $k_{tw}$ ,  $k_{ta}$  the total transfer velocities for a water and an air-sided viewer, respectively. The two transfer velocities differ by the solubility factor of the tracer (see Eq. (A1) in Appendix A).

The first term on the right hand side of each equation represents the exchange of a tracer from one phase to the other due to a concentration gradient. The second term stands for possible tracer input  $(\dot{V}_{a}^{i}c_{a}^{i})$ , the third term for possible tracer output (flushing/leaking term:  $\dot{V}_{a}c_{a}$ ) and the fourth term for possible tracer coming in through leaks from the surrounding room or through the flushing  $(\dot{V}_{a}c_{a}^{0})$ .

In the following sections, two different box model solutions, as used in this work for the low soluble tracers (water-side controlled: Sect. 5.2.2) and for the medium to high soluble tracers (air-side controlled: Sect. 5.2.3), are presented in detail. The simulated air/water concentration time series derived for a water ((b) and (c) in purple) and an air-side controlled ((d) and (e) in orange) tracer, are presented in Fig. 5.2. Three example wind speed conditions are assumed. The dashed lines indicate the change in wind speed and the grey background boxes the flushing periods.

#### 5.2.2 Water-side controlled tracers

The following approach was used for tracers with relatively low solubility ( $\alpha < 100$ ) for which the transfer velocity, k is mainly restricted due to the water-side resistance. Here, a low solubility tracer is dissolved in the water volume which is considered wellmixed. High tracer concentration in the water and very low concentrations in the air  $(c_a \simeq 0)$  direct the flux from the water to the air (evasion).

Figure 5.2 (b), shows the simulated air-phase concentration time series of an example water-side controlled tracer at three example wind speed conditions (given in Fig. 5.2



Fig. 5.2: Simulated concentration time series for an air-sided and a water-sided tracer in both air and water phase.

(a), change of wind speed is denoted with grey dashed lines). Each condition starts with a closed air-space tank configuration (closed box - no flushing, see more details in Sect. 5.3.2) where the air-side concentration, starting from circa zero, increases linearly with time, due to the water-to-air gas exchange. At time  $t_1$ , the air-space is opened (open box - flushing on, flushing time is denoted with grey background) and a drastic decrease is observed due to dilution of the air-space concentration with the relatively clean ambient air entering the facility. As indicated in the figure, the higher the wind speed the faster the concentration increase. Figure 5.2 (c) presents the water-phase concentration of the same tracer which in parallel starts from the highest concentration point and gradually decreases during the course of the experiment as more and more molecules escape the water to enter the gas-phase.

The ambient tracer concentration in the air entering the air-space through leaks or

during flushing can be safely assumed as negligible in comparison to the levels used for all examined tracers. Omitting parameter  $c_{\rm a}^0$ , simplifies the box model Eq. (5.1), which can be subsequently solved for  $k_{\rm tw}$  as follows

$$k_{\rm tw} = \frac{V_{\rm a}}{A} \cdot \frac{\dot{c}_{\rm a} + \lambda_{\rm f,x} c_{\rm a}}{c_{\rm w}} \cdot \frac{1}{1 - \alpha c_{\rm a}/c_{\rm w}}$$
(5.5)

where  $\lambda_{f,x} = V_a/V_a$  is the leak or flush rate for x being 1 or 2, accordingly. Applying Eq. (5.5), the instantaneous total transfer velocities  $(k_{tw})$  can be calculated from time resolved measurements of air and water-side concentrations.

#### 5.2.3 Air-side controlled tracers

In this approach, tracers with relatively high solubility ( $\alpha > 100$ ) for which k is expected to be controlled mainly by air-side processes, were used. Here, a relatively high solubility tracer is introduced with a constant flow to the air volume, continuously during the experiment. Due to low concentrations in the water volume, the net gas exchange flux is directed from the air to the water (invasion).

In Fig. 5.2 (d) the air-phase concentration of an example air-side controlled tracer is shown. During the closed air-space period ( $t_0$  to  $t_1$ ), the concentration increases exponentially, as a fraction of the air-space molecules transmit into the water due to air-water gas exchange. At  $t_1$ , the concentration reaches a steady state,  $SS_1$  where the input rate of the tracer is equal to the exchange rate between the two phases and the leak/flush rate.

At an equilibrium point, the concentration time derivative  $\dot{c}_{a}$  is approximately zero so that Eq. (5.3) can be written as

$$c_{\rm a} = \frac{\lambda_{\rm ta} \frac{c_{\rm w}}{\alpha} + \lambda^i c_{\rm a}^i}{\lambda_{\rm ta} + \lambda_{\rm f,x}}.$$
(5.6)

where  $\lambda_{ta} = \frac{A}{V_a} k_{ta}$  is the exchange rate and  $\lambda^i = \frac{\dot{V}_a^i}{V_a}$  the input rate. After  $SS_1$ , the facility is flushed with ambient air (open air-space) and the concentration decreases abruptly. Under these conditions  $(t_2)$ , a second steady state,  $SS_2$  is developed at a lower concentration range. In  $SS_1$ , a very small leak rate is present ( $\lambda_{f,1} \approx 0$ , leak rate) while in  $SS_2$  the leak rate is much larger due to the open air-space ( $\lambda_{f,2}$ , flush rate). Dividing the air-sided concentrations of the two steady states  $\frac{c_{a,1}}{c_{a,2}}$  (as given in Eq. (5.6)) and solving it with respect to the exchange rate, yields

$$\lambda_{\rm ta} = \frac{\lambda_{\rm f,2} c_{\rm a,2} - \lambda_{\rm f,1} c_{\rm a,1}}{(c_{\rm a,1} - c_{\rm a,2})}.$$
(5.7)

The total transfer velocities in the wind-wave tank box are calculated from

$$k_{\rm ta} = \frac{\lambda_{\rm ta} V_{\rm a}}{A}.\tag{5.8}$$

#### Leak and flush rate

In most wind-wave facilities, small air leaks are inevitable. The amount of tracer escaping the air-space of the facility needs to be monitored and corrected for, as described in Sects. 5.2.2 and 5.2.3. To measure the leak/flush rate  $\lambda_{f,x}$  for the open and closed configuration of the wind wave tank, a non-soluble tracer (here CF<sub>4</sub>) called a leak test gas, is used. Directly after closing the wind-wave tank, a small amount of the leak test gas is injected rapidly into the air-space. As the leak test gas is non-soluble, the water-side concentration  $c_w$  as well as the gas exchange velocity  $k_{ta}$  in Eq. (5.3) are equal to zero, reducing the air-side mass balance equation to

$$V_{\mathbf{a}}\dot{c}_{\mathbf{a}} = \dot{V}_{\mathbf{a}}^{i}c_{\mathbf{a}}^{i} - \dot{V}_{\mathbf{a}}c_{\mathbf{a}}.$$
(5.9)

After the initial injection, the input term  $\dot{V}_{a}^{i}c_{a}^{i}$  in Eq. (5.9) vanishes, yielding  $V_{a}\dot{c}_{a} = -\dot{V}_{a}c_{a}$ . This simple differential equation can be solved easily to

$$c_{\rm a}(t) = c_{\rm a}(0) \cdot \exp(-\lambda_{\rm f,x} \cdot t), \qquad (5.10)$$

where  $c_{\rm a}(0)$  is the concentration directly after the input of the leak test gas. Monitoring the concentration of the leak test gas over time and fitting an exponentially decreasing curve to this concentration time series, yields the leak/flush rate  $\lambda_{\rm f,x}$  of the system. In the "Aeolotron" facility, typical leak and flush rates were in the order of 0.05 to 0.4 h<sup>-1</sup> and 20 to 50 h<sup>-1</sup>, accordingly.

# 5.3 Experiments

#### 5.3.1 The "Aeolotron" wind-wave tank

The air-water gas exchange experiments were conducted in the large scale annular "Aeolotron" wind-wave tank at the University of Heidelberg, Germany (Figure 5.3). With an outer diameter of circa 10 m, a total height of approximately 2.4 m and a typical water volume of 18000 l, the "Aeolotron" represents the worldâs largest operational ring shaped facility. The chamber is mostly gastight, thermally isolated, chemically clean and inert. In Figure 5.3, a list of the main dimensions along with an aerial illustration of the facility are given. The tank is divided in 16 segments and an inner window extending through segments 16 - 4 allows visual access to the wind formed waves. The facility ventilation system consists of two grey tubes through which the air space can be flushed with ambient air at a rate up to  $50 h^{-1}$ . Two diametrically positioned ceiling mounted axial ventilators (segment 4 and 12) are used to generate wind velocities up to  $u_{ref} = 12 m s^{-1}$ .

In the facility, several ambient parameters are monitored. Temperature measurements are provided by two temperature sensors (PT-100) installed in the water and air phase

of segment 15 (at 0.5 and 2.3 m, respectively). On the ceiling of the same segment a fan-anemometer (STS 020) installed in the center line, determines the wind velocity. Two humidity sensors are mounted in segments 2 and 13 while the inner pressure is measured in segment 13. In the same segment, an optical ruler provides the water height. Segments 1 and 11 contain the tracer inlets for the air and water phase accordingly.

The annular geometry of the wind-wave tank, contrary to a linear geometry, permits homogeneous wave fields and unlimited fetch. The well mixed air-space (at few cm height above the surface) ensures no concentration gradients and therefore concentration measurements independent of the sampling height. On the other hand, the restricted size of the facility which leads to waves being reflected to the walls, results to a different wave field than on the open ocean.



**Fig. 5.3:** An aerial illustration of the "Aeolotron" tank and its main features. The numbers denote the segments. The axial fans producing the wind can be seen in the roof of segments 4 and 12. The air ducts supplying fresh air and removing waste air are shown in grey.

# 5.3.2 Tracers and Instrumentation

A series of 14 tracers covering a wide solubility ( $\alpha = 0.4$  to 5470) and diffusivity ( $Sc_w = 594$  to 1194) range, were selected for this study. Many of these tracers are very common in the ocean environment while the rest are used to extend the solubility and diffusivity ranges, a significant criterion for further physical investigations of the gas exchange mechanisms. Table 5.1 gives an overview of the examined tracers, with their

| Gas                     | Formula                       | М     | $lpha^1$                    | $Sc_a^{13}$ | $Sc_w^{13}$ |
|-------------------------|-------------------------------|-------|-----------------------------|-------------|-------------|
| methanol                | CH <sub>3</sub> OH            | 32.04 | $5293^{-2}$                 | 1.0268      | 671.04      |
| 1-butanol               | $C_4H_9OH$                    | 74.12 | $4712^{-3}$                 | 1.8198      | 1141.7      |
| acetonitrile            | $\rm CH_3CN$                  | 41.05 | $1609$ $^4$                 | 1.2957      | 832.07      |
| acetone                 | $(CH_3)_2CO$                  | 58.08 | $878.0^{4}$                 | 1.4921      | 880.53      |
| 2-butanone              | $C_2H_5COCH_3$                | 72.11 | $598.9^{3}$                 | 1.7344      | 1159.8      |
| acetaldehyde            | $CH_3CHO$                     | 44.05 | $378.7^{-5}$                | 1.0786      | 824.90      |
| ethyl acetate           | $CH_3C(O)OC_2H_5$             | 88.10 | $156.4^{6}$                 | 1.8183      | 997.46      |
| dms                     | $\mathrm{CH}_3\mathrm{SCH}_3$ | 62.13 | $16.62^{7}$                 | 1.4484      | 979.40      |
| benzene                 | $C_6H_6$                      | 78.11 | $5.672^{8}$                 | 1.6785      | 980.46      |
| toluene                 | $C_6H_5CH_3$                  | 92.14 | $4.529^{8}$                 | 1.8409      | 1176.3      |
| ${ m trifluoromethane}$ | $\mathrm{CHF}_3$              | 70.01 | $0.760^{9}$                 | 1.2132      | 747.50      |
| nitrous oxide           | $N_2O$                        | 44.01 | $0.676^{10}$                | 1.0007      | 593.90      |
| isoprene                | $C_5H_8$                      | 68.12 | $0.31^{11}$ - $0.69^{12}$ * | 1.6617      | 1193.9      |

**Table 5.1:** Molecular masses (M in g mol<sup>-1</sup>), dimensionless solubility ( $\alpha$ ) and Schmidt numbers in air ( $Sc_a$ ) and water ( $Sc_w$ ) for the investigated tracers at 20°C.

 $^1$  values are taken from dispare sources therefore a 10 % uncertainty is to be expected

 $^{2}$  Schaffer et al. (1969), <sup>3</sup> Snider et al. (1985), <sup>4</sup> Benkelberg et al. (1995), <sup>5</sup> Betterton et al. (1988), <sup>6</sup> Janini et al. (1986), <sup>7</sup> Dacey et al. (1984), <sup>8</sup> Robbins et al. (1993), <sup>9</sup> Krall (2013), <sup>10</sup> Weiss and Price (1980), <sup>11</sup> Yaws and Pan (1992), <sup>12</sup> Sander (1999), <sup>13</sup> Yaws (1995), <sup>\*</sup> only available values at  $25\hat{A}^{\circ}C$ .

respective molecular masses, solubility and Schmidt numbers, Sc (the dimensionless ratio of the kinematic viscosity of water  $\nu$  and the diffusivity of the tracer D,  $Sc = \nu/D$ ) at 20.

All tracers were monitored on-line in both the air and the water-phase. The VOC measurements were performed using Proton Reaction Mass Spectrometry (PTR-MS) from Ionicon Analytik GmbH (Innsbruck, Austria) while for the halocarbons and N<sub>2</sub>O, two Fourier Transform Infrared (FT-IR) Spectrometers (Thermo Nicolet iS10) were used. As leak test gas, carbon tetrafluoride ( $CF_4$ ) was used. It was also measured by FT-IR spectrometry.

For the surfactant experiments, the soluble substance Triton X-100,  $C_{14}H_{22}O(C_2H_4O)_{9.5}$ (Dow Chemicals, listed  $M_r = 647 \,\mathrm{g}\,\mathrm{mol}^{-1}$ ) was used to cover the water surface. Triton X-100 was chosen because of its common use as a reference substance to quantify the surface activity of unknown surfactant mixtures found in the open ocean (Frew et al. (1995a), Cosovic and Vojvodic (1998), Wurl et al. (2011)).

The operation and sampling conditions for both phases are briefly described below. Additional instrumentation for substantial supplementary measurements follows.



Fig. 5.4: "Membrane equilibrator - PTRQ-MS" set-up schematic. The dark blue and orange lines represent the water and air loops of the system, accordingly.

#### Water-Phase Measurements

In the water-phase a PTR-Quadrupole-MS (water inlet in segment 3) and a FT-IR (water inlet in segment 6) were used to measure the concentration levels of the VOCs and the halocarbons and N<sub>2</sub>O respectively. Our instrumentation, which is normally suited only for air sampling, was combined with an external membrane equilibrator (the oxygenator "Quadrox" manufactured by Maquet GmbH, Rastatt, Germany) to establish equilibrium between the water concentration and the gas stream to be measured. In this way, water-side concentrations could be obtained and used for the calculation of the transfer velocities for the low solubility tracers (see Sect. 5.2.2).

#### Membrane equilibrator configuration

The membrane equilibrator device includes a thin gas permeable membrane capable of separating the gas from the liquid phase (commercially available and often used in medicine as a human lung replacement to oxygenate blood). Water from the "Aeolotron" is constantly pumped through the membrane device where gas exchange occurs, due to the partial pressure difference of the gases involved, until equilibrium between air and water is achieved (Henryâs law at constant temperature).

A detailed configuration of the membrane set-up in conjunction with the PTR-MS is shown in Fig. 5.4. The system consists of a water and an air loop, both constantly in contact with the membrane equilibrator. The dark blue lines represent the water loop where water was being pumped from the "Aeolotron" through the membrane and back into the facility, with a constant flow of  $3.4 \,\mathrm{L\,min^{-1}}$ . The light orange color lines represent the air loop which has a link to the PTRQ-MS instrument. A synthetic air inlet and an excess flow exhaust are used to regulate the flow inside the air loop constant at  $1 \,\mathrm{L\,min^{-1}}$  and the systems pressure at 1013 hPa. Part of the air that comes out of the equilibrator is driven to the PTRQ-MS for analysis, while the rest remains in the loop. The relative humidity in the equilibrated air increases after passing through the equilibrator, therefore the air tubing was heated to a few degrees above room temperature avoiding water condensation.

A similar set-up using a second membrane equilibrator was connected to the FT-IR instrument. The water flow was kept at a rate of about  $3 \text{ Lmin}^{-1}$ . Here the instrument's measuring cell was integrated into the air loop, removing the need for sample extraction, a synthetic air inlet and an exhaust. The air was circulated in the closed loop at a rate of approximately  $150 \text{ mLmin}^{-1}$ . Between the equilibrator and the measuring cell a dehumidifying unit containing phosphorous pentoxide was used to remove water from the air stream and in this way protect the optical windows of the IR measuring cell. The time constant of the membrane equilibrator was evaluated as described in Krall and Jähne (2014), providing a very fast responce of  $\simeq 1$  minute.

# PTRQ-MS configuration

The PTR-MS detection technique has been described in detail elsewhere (Lindinger et al. (1998)). The instrument's ion source produces an excess of primary ions  $(H_3O^+)$  which then undergo proton transfer reactions with the VOC molecules of the air sample (sampling flow: 30 ml min<sup>-1</sup>). Throughout the measurements, the drift pressure was kept to 2.1 mbar and the drift voltage at 600 V resulting to a field intensity (E/N) of 130 Td (Td =  $10^{-17}$ cm<sup>2</sup> V molecule<sup>-1</sup>). The SEV detector detected single ions with a dwell time of 1 second. During the experiments, 30 masses were monitored sequentially leading to a time resolution of 30 seconds. Possible mass overlapping was prevented with careful reselection of the analyzed compounds initial mass scans.

At high humidity levels, as was the case here, a significant number of primary ions react with the water molecules of the sampled air forming water clusters (De Gouw et al. (2007)). This complicates the determination of the instruments sensitivity for some species (Jobson and McCoskey (2010)), and therefore calibrations were performed at the same humidity levels as present in the experiments and exactly the same measuring set-up (see Fig. 5.4) was used. Known concentrations of low-solubility VOCs were

diluted in deionized water and then introduced into the water-phase of the facility, in precise volume quantities. To avoid losses of the investigated tracers into the air phase due to air-water gas exchange, the water surface was covered with a large amount of an organic surfactant (0.446 mg l<sup>-1</sup>, Triton X-100) and calm wind conditions were used to gently mix the air space. Under such conditions gas exchange rates were estimated to be negligible. Linear behavior was established for all low solubility tracers (dimensionless solubility < 20) examined at concentration levels between 0 and 7  $\mu$ mol l<sup>-1</sup>.

# FT-IR configuration

The key aspects of Fourier-Transform Infrared spectroscopy, or FT-IR spectroscopy, are described in detail in Griffiths (2007). In this study, a Nicolet iS10 (manufactured by Thermo Fischer Scientific Inc., Waltham, MA., USA) FT-IR spectrometer with a custom made measuring cell of approximately 5 cm length was used. About every 5 seconds, one infrared absorbance spectrum with wavenumbers between 4000 cm<sup>-1</sup> and  $650 \text{ cm}^{-1}$  with a resolution of  $0.214 \text{ cm}^{-1}$  was acquired. Six of these single spectra were averaged to minimize noise and stored for further evaluation, leading to a time resolution of about 1 spectrum every 30 seconds. These spectra were later converted to concentrations by first scaling reference spectra of all tracers used in height to best represent the measured spectra, and then using a calibration to calculate the concentration from the scaling factors. This procedure, as well as the estimation of the uncertainties in the concentration measurements is described in detail in Krall (2013).

# Air-phase Measurements

In the air-phase, a PTR- Time of Flight (ToF) - MS (inlet in segment 3) with a time resolution of 10 seconds provided very fast on-line measurements for the VOCs while a FT-IR (inlet in segment 2) with a time resolution of 30 seconds was in parallel monitoring the halocarbons and N<sub>2</sub>O. High time resolution measurements enabled a fast experimental procedure and at the same time high accuracy data analysis. Additionally, due to the fast on-line measurements, the transient response of the system could be followed very efficiently throughout the experimental procedure. Example air-side measurements are shown in Figure 5.6 for a water and an air-side controlled tracer.

# PTR-TOF-MS configuration

The ionization principle of the PTR-TOF-MS is the same as the PTRQ-MS, however, here a Time of Flight mass spectrometer is used. Protonated VOC ions are driven through a transfer lens system to the pulse extraction region of the TOF-MS where they are accelerated and detected according to their flight times. In this way, higher time and mass resolutions are achieved (Jordan et al. (2009), Graus et al. (2010)).

Throughout the measurements, the PTR-TOF-MS was configured in the standard V mode with a mass resolution of approximately 3700 m  $\Delta m^{-1}$ . The drift voltage was maintained at 600 V and the drift pressure at 2.20 mbar (E/N 140 Td). Mass spectra were collected over the range 10-200 m z<sup>-1</sup> and averaged every 10 seconds, providing a mean internal signal for each compound. After acquisition all spectrum files were mass calibrated using (H<sub>2</sub>O)H<sup>+</sup>, NO<sup>+</sup> and (C<sub>3</sub>H<sub>6</sub>O)H<sup>+</sup> ions to correct for mass peak shifting. For the data processing software from Ionicon and Tofwerk (MID Calculator and TOFDaqViewer) was used.

Calibrations in the air-phase were conducted under high humidity conditions equivalent to the sampling conditions during the experiments (85 - 90% rel. humidity). The desired mixing ratios (1-600 ppbv) were obtained by appropriate dilution of the multicomponent VOC gas standard with synthetic air. Linear responce was established for all examined tracers.

Parallel calibrations of both PTR-MS instruments showed similar sensitivities, hence no sensitivity correction was applied.

# FT-IR configuration

A second Thermo Scientific Nicolet iS10 FT-IR spectrometer was used to measure the air side concentrations. The measuring cell with a folded light path of a total length of 2 m, was kept at a constant temperature of 35 using a Thermo Nicolet cell cover. Air from the "Aeolotron" was sampled at a rate of  $150 \text{ ml min}^{-1}$  at segment 13. As with the water side instrumentation, water vapor was removed before entering the measuring cell using phosphorous pentoxide. The spectrometer settings, data acquisition as well as data processing was identical to the water side instrumentation, see Section 5.3.2.

# Error analysis

The individual total transfer velocity uncertainties were calculated applying the uncertainty propagation of error for uncertainties independent from each other to Equations 5.5, for the  $k_{tw}$  and 5.7, 5.8 for the  $k_{ta}$  accordingly.

The concentration uncertainties for the PTR-MS measurements were calculated using the background noise and the calibration uncertainty of each examined tracer. Relatively low uncertainties were obtained for the air-phase concentration levels  $SS_1$  and  $SS_2$  ranging between 1-1.5% and 1.5-2.5%, accordingly. The water-phase concentration uncertainty,  $\Delta c_w$  was estimated the same way and the uncertainties were between 6.5-8% for the concentration ranges used.

The uncertainties of the concentration measurement with the FT-IR spectrometers was found to be concentration dependent. All concentration uncertainties lie below 4 % for the typical concentrations measured in the described experiments.

The individual uncertainties for the leak and flushing rates of all conditions were in the order of 0.5% and 1% accordingly. Based on the geometrical parameters of the

facility the surface area uncertainty was calculated to be approximately 2% while a maximum of 3% is estimated for the volume uncertainty. For the solubility values provided by literature, accurate uncertainty estimations are difficult. Here we assume an uncertainty of 10% for all literature sources.

The overall estimated total transfer velocity uncertainties therefore ranged between 6-12 % and 6-20 % for the  $k_{ta}$  and  $k_{tw}$  values of all examined tracers respectively.

# Additional instrumentation

Supplementary measurements of wind driven, surface associated, physical parameters such as the mean square slope and the water-sided friction velocity, were additionally made in the "Aeolotron" wind-wave tank to enable further investigations of the physical mechanisms of air-water gas exchange.

The mean square slope measurements, reflecting the surface roughness conditions, were performed in parallel with the gas-exchange measurements using a color imaging slope gauge (CISG) installed in segment 13. The CISG device uses the refraction properties of light at the air-water boundary. A color coded light source was placed below the water while a camera observed the water surface from above. Using lenses to achieve a telecentric setup, a relationship between surface slope and the registered color can be determined. A more detailed description can be found in Rocholz (2008).

The water-sided friction velocity,  $u_{*,w}$  measurements, expressing the shear stress created on the water interface, were accomplished at a later stage using the same setting of the wind generator and the same surfactant coverage of the water surface. The momentum balance method was used as described in Bopp (2011) and Nielsen (2004). To apply this method, the friction between the water and the walls needs to be measured first. This is done by monitoring the decrease of the velocity of the water bulk after switching off the wind. In a stationary equilibrium, that is characterized by an equality of the momentum input into the water by the wind and the momentum loss due to friction at the walls, the friction velocity  $u_{*,w}$  can be calculated from the mean water velocity. The water velocity was measured using a three-axis Modular Acoustic Velocity Sensor (MAVS-3 manufactured by NOBSKA, Falmouth, MA, USA) installed in the center of the water channel in segment 4 of the "Aeolotron" at a water depth of around 50 cm.

# Experimental arrangement

The "Aeolotron" facility was filled to 1 m height ( $\sim 18 \text{ m}^3$  water volume) with clean deionized water. Diluted aqueous mixtures of low solubility tracers were introduced into the water-phase of the facility a day prior to an experiment and homogeneity was achieved using two circulating pumps. Before the beginning of each experiment (for the clean water surface cases) the water surface was skimmed to clean off any possible



Fig. 5.5: Schematic time series of the wind speed, flushing periods and air/water tracer inputs.

surface contamination. To do this, a small barrier with a channel is mounted between the walls of the tank, perpendicular to the wind direction while the wind is turned on at a low wind speed ( $u_{\rm ref} \approx 3 \text{ m s}^{-1}$ ). The wind pushes the water surface over the barrier into the channel removing any surfactant. A pump continuously empties the channel and drains the water contaminated with surface active materials.

Individual gas-washing bottles containing highly soluble tracers in liquid form were purged with a controlled flow of clean air that swept the air-tracer gas mixture into the air-phase of the facility. The bottles were kept in a thermostatic bath at 20 throughout the experimental procedure.

At the beginning of each experiment, the first wind speed condition was applied while the flushing of the air-space was turned on (open air-space) in order to achieve a background point for all tracers. Thereafter, the flushing was turned off (closed airspace) and the tracer concentration (air and water-side controlled) started to increase (see more in Sect. 5.2.3). Immediately after turning off the flushing, the leak test gas was introduced into the air-space. After the steady state point  $(SS_1)$  for the air-side controlled tracers was approached, the air-space was flushed once more with ambient air and an abrupt concentration decrease was observed. The same process was repeated for eight different wind speed conditions, progressing from lower to higher values. In Fig. 5.5 a time series of the experimental conditions; wind speed, flushing periods and air and water tracer inputs, are schematically represented. The obtained air-sided concentration time series over the eight wind speed conditions for a water (a) and an



Fig. 5.6: Air-side concentrations obtained for example water-side (a) and an air-side (b) controlled tracer through-out the experimental procedure.

air-sided (b) example tracer are given in Fig. 5.6.

The wind speed varied from very low values  $(u_{\rm ref} = 0.74 \,\mathrm{m\,s^{-1}})$ , equivalent to  $u_{10} = 0.79 \,\mathrm{m\,s^{-1}})$  up to higher ones  $(u_{\rm ref} = 8.26 \,\mathrm{m\,s^{-1}})$ , equiv.  $u_{10} = 14.6 \,\mathrm{m\,s^{-1}})$ . At the very beginning of the experiment, hardly any surface movement was seen. As the experiment progressed, the first capillary waves became apparent and started breaking above  $u_{\rm ref} = 4.8 \,\mathrm{m\,s^{-1}}$ . Reaching larger wavelengths, wave braking and bubble formation was observable only at the very last wind speed condition.

The experimental procedure described above was repeated four times at clean surface conditions for all tracers listed in Table 1. Three further repetitions were accomplished with a surfactant (Triton X-100) covered water surface. The surfactant concentration in the fifth repetition was  $0.033 \text{ mg L}^{-1}$  while in the last two a larger amount of  $0.167 \text{ mg L}^{-1}$  was used.

Despite the well reproduced experimental conditions, small variations between the repetitions were observed. Table 2 displays a mean value of the main measured parameters along with the standard deviation, expressing the extent of variability between the repetitions, of each case. For the last condition of the clean case only three repetitions are used to derive the mean values, as in repetition three the wind speed was accidentally set to the wrong value. Also in repetition two, the  $\sigma_s^2$  values observed in conditions 4, 5, 6 were significantly lower and therefore omitted from the averaging. Here we assume that the water surface was probably insufficiently skimmed before the experiment or that surfactant material might have entered the facility during the flushing phases. In the low surfactant case (case 2), no  $u_{*,w}$  measurements were performed. The low surfactant case  $u_{*,w}$  values used for data plotting (Section 5.4.2) are interpolated between the clean and the heavy surfactant cases. In the higher surfactant case (case 3), the first condition was omitted for reasons of experimental simplicity while  $\sigma_s^2$  are available
only for one repetition.

**Table 5.2:** Reference velocities,  $u_{ref}$  (ms<sup>-1</sup>), friction velocities,  $u_{*w}$  (cms<sup>-1</sup>), mean square slope,  $\sigma_s^2$ , air temperature,  $t_{air}$  (°C), water temperature,  $t_{water}$  (°C) mean values and % standard deviations, as quantified in the "Aeolotron" facility for 1: clean surface experiments, 2: surface covered with 0.033 mgl<sup>-1</sup> Triton X-100, 3: surface covered with 0.167 mgl<sup>-1</sup> Triton X-100.

| Case  | Parameter            | cond.1      | cond.2      | cond.3      | cond.4      | cond.5      | cond.6      | cond.7      | cond.8      |
|-------|----------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|       | $u_{ref}$ (±%)       | 0.744 (1.3) | 1.421 (0.5) | 2.052 (0.3) | 2.674 (0.5) | 3.621 (0.1) | 4.805 (0.3) | 6.465 (0.2) | 8.256 (0.1) |
|       | $u_{*w}$ (±%)        | 0.071 (1.5) | 0.156 (0.7) | 0.251 (0.4) | 0.361 (0.6) | 0.559 (0.2) | 0.856 (0.6) | 1.369 (0.3) | 2.048 (0.1) |
| 1     | $\sigma_s^2$ (±%)    | 0.002 (1.7) | 0.007 (1.4) | 0.013 (1.2) | 0.016 (0.5) | 0.024 (2.2) | 0.046 (2.0) | 0.078 (3.0) | 0.118 (6.3) |
| (× 4) | $T_a \ (\pm\%)$      | 21.29 (1.5) | 21.18 (1.5) | 21.09 (1.6) | 20.99 (1.6) | 20.88 (1.6) | 20.75 (1.6) | 20.59 (1.7) | 20.50 (1.8) |
|       | $T_w (\pm \%)$       | 19.30 (1.7) | 19.37 (1.8) | 19.41 (1.8) | 19.41 (1.8) | 19.39 (1.8) | 19.34 (1.9) | 19.29 (2.0) | 19.26 (2.1) |
|       | $u_{ref}$ (±%)       | 0.800 ( - ) | 1.460 ( - ) | 2.091 ( - ) | 2.717 ( - ) | 3.650 ( - ) | 4.851 ( - ) | 6.502 ( - ) | 8.288 ( - ) |
|       | $u_{*w}(\pm\%)$      | -           | -           | -           | -           | -           | -           | -           | -           |
| 2     | $\sigma_s^2$ (±%)    | 0.002 ( - ) | 0.002 (-)   | 0.002 (-)   | 0.008 ( - ) | 0.010 ( - ) | 0.020 ( - ) | 0.071 (-)   | 0.111 ( - ) |
| (× 1) | $T_a \ (\pm\%)$      | 22.11 ( - ) | 22.04 ( - ) | 21.94 ( - ) | 21.77 ( - ) | 21.64 ( - ) | 21.44 ( - ) | 21.19(-)    | 21.11 ( - ) |
|       | $T_w (\pm \%)$       | 19.80 ( - ) | 19.88 ( - ) | 19.93 ( - ) | 19.93 ( - ) | 19.93 ( - ) | 19.90 ( - ) | 19.88 ( - ) | 19.85 ( - ) |
|       | $u_{ref}$ (±%)       | -           | 1.451 (1.2) | 2.075 (0.0) | 2.707 (0.6) | 3.667 (0.3) | 4.913 (0.4) | 6.615 (0.2) | 8.371 (0.0) |
|       | $u_{*w} \ (\pm\%)$   | -           | 0.105 (1.7) | 0.175 (0.1) | 0.260 (0.9) | 0.421 (0.4) | 0.680 (0.7) | 1.132 (0.4) | 1.713 (0.0) |
| 3     | $\sigma_s^2~(\pm\%)$ |             | 0.002 (-)   | 0.002 ( - ) | 0.002 (-)   | 0.005 ( - ) | 0.007 (-)   | 0.040 ( - ) | 0.096 ( - ) |
| (× 2) | $T_a \ (\pm\%)$      | -           | 21.51 (1.4) | 21.59 (1.3) | 21.60 (1.0) | 21.53 (0.9) | 21.51 (0.6) | 21.34 (0.7) | 21.22 (0.9) |
|       | $T_w (\pm \%)$       | -           | 19.83 (0.5) | 19.86 (0.6) | 19.90 (0.7) | 19.94 (0.6) | 19.95 (0.7) | 19.95 (0.7) | 19.95 (0.7) |

### 5.4 Results

The total transfer velocities for the examined 14 tracers reported in Table 5.1, were derived in all conducted experiments. In this work, two contrasting tracers at opposite ends of the solubility spectrum, N<sub>2</sub>O ( $\alpha = 0.67$ ) anticipated as an only water-side controlled tracer (i.e.  $k_{tw} \sim k_w$ ) and CH<sub>3</sub>OH ( $\alpha = 5293$ ) similarly anticipated as an only air-side controlled (i.e.  $k_{ta} \sim k_a$ ), are presented in more detail. In this way, we intend a validation of the efficacy of the above described methods and apparatus and subsequently a comparison with previous air-sea gas exchange studies. A full investigation of the mechanisms influencing the gas-exchange transfer and their relationship to individual gases over a broad solubility range will be presented in separate publications.

#### 5.4.1 Gas-Exchange Transfer Velocities

In Figs. 5.7 and 5.8, we present the experimentally obtained  $k_{tw}$  for N<sub>2</sub>O and the  $k_{ta}$  for CH<sub>3</sub>OH as a function of  $u_{*,w}$  for all clean water surface experiments. In both figures, square symbols are used to present the transfer velocities corresponding to repetition 1, circles for repetition 2, triangles for repetition 3 and diamonds for repetition 4. Vertical bars in light red give the individual transfer velocity uncertainty (see Sect.



Fig. 5.7: Total transfer velocity of N<sub>2</sub>O of four clean case repetitions plotted against  $u_{*,w}$ .

5.3.2) and the horizontal bars the uncertainty of the  $u_{*,w}$  measurements. Here, a mean value of the uncertainties as estimated by Bopp (2011) (approximately 12%) was applied. The  $u_{*,w}$  measurements were not conducted in parallel with the transfer velocity measurements but in a later experiment using similar conditions. Moreover, the conducted  $u_{*,w}$  measurements did not cover very low wind speed conditions such as the one used for the measurement of the first transfer velocity point. An extension of the  $u_{*,w}$  -  $u_{ref}$  relationship, as derived from the higher wind speed measurements, embraces a big uncertainty; therefore a total 30% uncertainty was estimated for the first point.

Small variations between the transfer velocity values for the same condition extending the given uncertainty bars were occasionally observed. A more apparent example is the lower transfer velocity points (circles) at conditions 4, 5 and 6 which arise as a result of the lower  $\sigma_s^2$  values observed in repetition 2 (as described in Sect. 5.3.2). This effect could be taken as an indication that only one physical parameter is not enough to effectively describe the complicated process of the air-sea gas exchange. As the experimental conditions used in the four repetitions were similar but not identical (see Table 5.2), a four replicate mean value calculation was avoided and instead a fit though all points is chosen (black dashed line). Despite the non-identical conditions,



Fig. 5.8: Total transfer velocity of  $CH_3OH$  of four clean case repetitions plotted against  $u_{*,w}$ .

the transfer velocity values are reproducible.

As indicated in Fig. 5.7, the  $k_{tw}$  increases nonlinearly with  $u_{*,w}$ . The correlation could be described as linear up to  $u_{*,w} = 0.86 \text{ cm s}^{-1}$  (equiv.  $u_{10} = 7.3 \text{ m s}^{-1}$ ) while above this point, a faster increase is observed. This sudden increase in the so far linear tendency can be attributed to various water surface effects, which are not going to be discussed here.

The air-sided transfer velocities  $k_{\rm ta}$  (Figure 5.8) in contrast, increase linearly ( $R^2 = 0.99$ ) with  $u_{\rm *,w}$  throughout the examined velocity range ( $u_{\rm *,w} = 0.07 - 2.06 \,{\rm cm \, s^{-1}}$  equiv.  $u_{10} = 0.8 - 14.6 \,{\rm m \, s^{-1}}$ ). As it appears from Fig. 5.8, the first transfer velocity values of CH<sub>3</sub>OH (i.e. those at the lowest turbulent condition) are slightly underestimated relative to the linear trend ( $\simeq 10\%$ ). This could be explained due to the inefficiently mixed air-space caused by the lower turbulence conditions applied.

Overall, the observed trends and transfer velocity magnitudes of both  $k_{tw}$  and  $k_{ta}$  are in good agreement with observations made by previous studies. A more detailed comparison with literature follows in Sect. 5.4.3.



Fig. 5.9: Effect of the two different surfactant surface coverages on the total transfer velocities of  $N_2O$  and  $CH_3OH$ .

#### 5.4.2 Effect of Surfactants

After obtaining clear, reproducible transfer velocity trends for a clean water surface, the effect of a surfactant was evaluated using two different surfactant (Triton X-100) concentrations. As expected, the surfactant layers decrease the transfer velocity of the tracers and also the surface stress,  $u_{*,w}$ . In Fig. 5.9, the transfer velocities of all seven experiments are presented against  $u_{*,w}$  for N<sub>2</sub>O and CH<sub>3</sub>OH. The clean water surface results are given in red, the results obtained using 0.033 mg L<sup>-1</sup> Triton X-100 in green and the one using 0.167 mg L<sup>-1</sup> Triton X-100 in blue. In both cases, reduced transfer velocities were observed which became more prominent as the surfactant concentration increased. In addition, the surfactant decreased the transfer velocity best at low wind speeds, becoming ineffective under higher turbulent conditions.

The surfactant effect shows significant differences between the two contrasting tracers. In the case of  $N_2O$ , the effect extends up to a factor of three for the lower wind speed range and still remains around a factor of one at the higher examined wind speeds where waves, wave breaking and bubbles are present. The observed trend though shows that at higher wind speed regimes (above the studied regime) no surfactant effect would be seen. The surfactant effect in case of CH<sub>3</sub>OH is significantly weaker, as here the exchange is mainly controlled by the air-side boundary layer.

#### 5.4.3 Comparison with previous studies

The gas transfer velocities of weakly soluble tracers has been extensively studied over the previous years. Numerous  $k_w$  parameterizations are available, derived from experimental (laboratory and field) measurements as well as physical models. In Fig. 5.10,



Fig. 5.10: Comparison between the  $k_{tw}$  measurements of N<sub>2</sub>O (red circles) and previous  $k_{w}$  parameterizations. The colored lines corespond to: LM\_86: Liss and Merlivat (1986), C\_94: Clark et al. (1994), WM\_99:Wanninkhof and McGillis (1999), N\_00: Nightingale et al. (2000), M\_01: McGillis et al. (2001), M\_04: McGillis et al. (2004), Ho\_06: Ho et al. (2006), and W\_09:Wanninkhof et al. (2009).

a selection of some representative, experimentally derived parameterizations (colored lines), are used for comparison with the  $k_{\rm tw}$  (here  $k_{\rm tw} \sim k_{\rm w}$ ) measurements of N<sub>2</sub>O (red points). The transfer velocities are plotted against the wind speed at 10 meters height,  $u_{10}$ .

Looking at the lower wind speed range (0.7 to  $4 \text{ m s}^{-1}$ ) an obvious spread between the various  $k_w$  predictions can be observed extending through more than two orders of magnitude. Transfer velocity measurements at the very low wind speed regions are difficult to conduct and therefore the extended fits based on higher wind speed ranges can lead to incorrect estimations. An evaluation of the previous studies though, is not the objective of this publication. Here, we aim to highlight the huge disagreement in the lower wind speed regime that leads to great uncertainty in the predicted  $k_w$ values. The projected absolute quantity differences to the atmospheric budgets though are estimated to be small since the fluxes themselves are small. One target of this study was to tackle the challenging measurements at the low wind speed end in order



Fig. 5.11: Comparison between the  $k_{ta}$  measurements of CH<sub>3</sub>OH (red circles) and previous  $k_a$  parameterizations. The colored lines correspond to: L\_73: Liss (1973), MY\_83: Mackay and Yeun (1983), D\_91 using the MW and D\_91\* using the  $Sc_a$  and a Smith et al. (1975) derived drag coefficient term: Duce et al. (1991), J\_10: Jeffery et al. (2010).

to achieve a better indication of the corresponding gas-exchange behavior. The middle wind speed range seems to be well represented in all studies. At the higher wind speed range, a smaller spread was observed especially above  $12 \,\mathrm{m\,s^{-1}}$ . This spread, a little more than an order of two, can lead to great discrepancies in the atmospheric budgets of the related tracers as the corresponding transfer velocities are much larger there.

The transfer velocities obtained in this study, show a closer agreement with the Clark et al. (1994) parameterization apart from the first wind speed condition. There, our results agree better with Nightingale et al. (2000).

In contrast to the weakly soluble, high soluble tracers have received much less attention. In Fig. 5.11, the total transfer velocity measurements of CH<sub>3</sub>OH (here  $k_{ta} \sim k_a$ ) are compared with some available tunnel (Liss (1973), Mackay and Yeun (1983)) and model (Duce et al. (1991), Jeffery et al. (2010))  $k_a$  parameterizations. It is worth mentioning that the measurements of this study do not include any correction regarding an extra turbulent resistance in the air-space. As indicated in Fig. 5.11, the increasing trend of the transfer velocity with the wind speed observed in this study is similar to the previous parameterizations. The scatter among the different studies is here occasionally much larger and extends through the entire range of the examined wind speeds. A closest agreement is achieved between the experimental  $k_{\rm ta}$  values of CH<sub>3</sub>OH and the two laboratory derived parameterizations Liss (1973) and Mackay and Yeun (1983).

### 5.5 Conclusion

This study has demonstrated that the "Aeolotron" wind-wave tank in combination with the adopted box model methodology, experimental procedure and instrumentation are capable of generating reliable and reproducible gas transfer velocities for species spanning a wide range of solubilities. The molecules nitrous oxide and methanol have been used to exemplify the behavior of sparingly soluble and highly soluble species. These represent cases of a water-side and an air-side layer control, as described in Sect. 6. Small differences between the obtained transfer velocity values of the four repetitions of the clean case, indicate that various physical parameters should be taken into account in future parameterizations in order to produce better transfer velocity estimations. The complete dataset for all species (including the intermediate cases of both layer control) along with the available micro-scale surface property parameters, extending over a low to medium wind speed regime, can be used to generate a generalized parametrization for the total transfer velocity. The derivation of this expression, which will be invaluable to future modeling efforts, will be presented in a separate publication.

Particularly interesting are the effects on the gas transfer velocity induced by the addition of a surfactant. Despite the surface micro-layer being commonly present on the ocean, its effect on air-sea gas transfer is poorly understood and there is a paucity of data both from the laboratory and the field. The impact of the surfactant is markedly different on the two tracers shown here. A strong reducing effect (up to a factor of three) was observed for the water-side controlled tracer, N<sub>2</sub>O while in the case of CH<sub>3</sub>OH, the surfactant showed a very weak impact.

We maintain that it is important to monitor the transfer process in both the water (using water-side controlled tracers) and the air-phase layer (using air-side controlled tracers) in order to develop a true enduring and generally applicable model for air-sea gas transfer. Previous attempts of generating expressions for  $k_a$  and  $k_w$  correspond reasonably well with the results produced here. In case of  $k_w$ , at low wind speeds there is a wide spread in the literature values, with this study corresponding most closely with those of Clark et al. (1994) and Nightingale et al. (2000). At high wind speeds the previous parameterizations are divided into three groups and this study lies in the central group. In case of  $k_a$ , the literature spread is occasionally larger with our results lying nearer to Liss (1973) and Mackay and Yeun (1983).

This study, based on data from the worldâs largest annular wind-wave facility, derived from advanced analytical technology which has been set-up to monitor the gas concentration changes in both the air and the water-phase simultaneously at unprecedented measurement frequency, has proven to produce high quality transfer velocity measurements. On the basis of our results, we recommend the proposed methodology for future air-sea gas exchange measurements.

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### Appendix A

#### Relationship between air-sided and water-sided variables

The experimentally calculated water-sided total transfer velocities,  $k_{tw}$  were converted to the equivalent air-sided total transfer velocities,  $k_{ta}$  using:

$$k_{\rm ta} = \alpha k_{\rm tw}.\tag{5.11}$$

Air-sided friction velocities can be converted to water-sided friction velocities by

$$u_{*\mathrm{w}} = \sqrt{\frac{\rho_{\mathrm{a}}}{\rho_{\mathrm{w}}}} u_{*\mathrm{a}}.$$
(5.12)

### A ppendix B

 $u_{10}$  derivation using  $u_{*a}$ 

The wind speed at a height of 10 meters,  $u_{10}$  is calculated from its relationship with the air-sided friction velocity and the drag coefficient,  $C_d$  using

$$C_{\rm d} = \frac{u_{*{\rm a}^2}}{u_{10^2}} \tag{5.13}$$

Here, the Smith et al. (1975) empirical relationship between the drag coefficient and the wind speed was used

$$10^3 C_{\rm d} = 0.63 + 0.066 u_{10} \tag{5.14}$$

### Appendix C - Naming conventions

- $k_{\rm w}$  transfer velocity in water for a water sided viewer
- $k_{\rm a}$  transfer velocity in air for an air sided viewer
- $k_{\rm tw}$  total transfer velocity for a water sided viewer
- $k_{\rm ta}$  total transfer velocity for an air sided viewer
- $c_{\rm w}$  water side concentration
- $c_{\rm a}$  air side concentration
- $V_{\rm w}$  water volume
- $V_{\rm a}$  air volume
- A water surface
- $\lambda_{\rm f,1}$  leaking rate
- $\lambda_{\rm f,2}$  flushing rate
- $\alpha = \frac{c_{\rm w}}{c_{\rm a}}$  dimensionless solubility
- $Sc_{\rm w}$  Schmidt number in water
- $Sc_{\rm a}$  Schmidt number in air
- M molecular mass
- $u_{*,w}$  water sided friction velocity
- $u_{*,a}$  air sided friction velocity
- $u_{\rm ref}$  reference wind speed
- $\sigma_{\rm s}^2$  mean square slope
- $u_{10}$  wind speed at 10 m height

# A universal, experimentally derived air-water transfer model for any gas under clean and surfactant covered surfaces

E. Mesarchaki<sup>1</sup>, F. Helleis<sup>1</sup>, K. E. Krall<sup>2</sup>, C. Kräuter<sup>2</sup>, B. Jähne<sup>2,3</sup>, and J. Williams<sup>1</sup>

 $^1\mathrm{Max}\mathchar`-Planck-Institut$ für Chemie (Otto-Hahn-Institut) Hahn-Meitner-Weg 1, 55<br/>128 Mainz

<sup>2</sup>Institut für Umweltphysik, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany <sup>3</sup>Heidelberg Collaboratory for Image Processing, Universität Heidelberg, Speyerer Street 6, 69115 Heidelberg, Germany

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Summary. Total transfer velocity measurements of 14 individual trace gases, spanning a wide solubility and diffusivity range, were used for the derivation of a Total Transfer Velocity (TTV) parameterization. The impact of friction velocity,  $u_*$  and mean square slope,  $\sigma_s^2$  on the total transfer rates was investigated at various wind speeds rates ( $u_{10}$  ranging between 0.8 to  $15 \text{ m s}^{-1}$ ) under clean and surfactant covered surfaces (Triton X-100 with film thicknesses of  $0.033 \text{ mg} \text{l}^{-1}$  and  $0.167 \text{ mg} \text{l}^{-1}$ ). Friction velocity was determined as the ideal parameter to express the wind driven turbulence while a negative exponential relationship between the water-side Schmidt number exponent,  $n_w$  and the  $\sigma_s^2$  could optimally describe the associated water surface conditions. A combination of both  $u_*$  and  $\sigma_s^2$  variables, was found to reproduce faithfully the air-water gas exchange process. The TTV model results correlated linearly ( $R^2 = 0.99$ ) with and the experimental data by a factor of  $\sim 1$ .

### 6.1 Introduction

Gas fluxes across the ocean-atmosphere (O-A) interface can significantly impact biogeochemistry and climate on local to global scales, making them a key element of global models. Presently, O-A fluxes are only poorly quantified in models, preventing valuable present and future environmental predictions. One of the main limiting factors to an efficient quantification of the O-A fluxes, is the absence of a "universal" air-sea gas transfer parameterization. Ideally, such a parameterization could be related to the inherent properties of the molecule (i.e solubility, diffusivity) and the appropriate physical variables closely linked to the gas exchange process.

Air-water gas fluxes are usually derived based on a two surface distributed boundary layer concept (Liss and Slater (1974)) as:

$$F = k_{\rm tw}(\alpha c_{\rm a} - c_{\rm w}) = k_{\rm ta}(c_{\rm a} - c_{\rm w}/\alpha) \tag{6.1}$$

where c is the bulk gas concentration in the air (a) or the water (w) phase,  $\alpha$  the dimensionless solubility and  $k_{tw}$  the total gas transfer velocity, expressing the velocity of a gas travelling through both air and water boundary layers.

Wind speed, an obvious driving force enhancing gas exchange, is easily measurable in the field and the laboratory and is also available in global data sets. Numerous studies have empirically parameterized air-sea gas transfer as a function of wind speed at ten meters height,  $u_{10}$  (Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999), Nightingale et al. (2000), McGillis et al. (2001), McGillis et al. (2004), Nightingale (2009)). Despite the numerous efforts linking k and  $u_{10}$  great dissimilarities occur, particularly at low and high wind speed regimes. This indicates that  $u_{10}$ , clearly missing significant wind related processes, is not the ideal variable on which to parameterize air-sea gas exchange and that a more physically based transfer velocity relation is needed.

Wind driven shear stress expressed by the friction velocity,  $u_*$  and surface roughness provided by the mean square slope,  $\sigma_s^2$  are considered more suitable variables to define phenomena such as waves and wave breaking, near surface turbulence, bubbles and surface films (Jähne et al. (1987), Jähne and Haussecker (1998), Frew et al. (2004), Jähne (2009), Veron et al. (2011)). Friction velocity relations reproduce nicely the turbulent process but they fail in the presence of microscale breaking and/or surfactant films. Mean square slope, shows a better correlation with k under such conditions (Jähne (1984), Hara et al. (1995), Frew (1997), Bock et al. (1999), Zappa et al. (2002), Zappa et al. (2004), Frew et al. (2004)) though still not entirely able to account for the gas exchange process. Clearly, both  $u_*$  and  $\sigma_s^2$  are related to the air-water gas transfer velocity but taken singly, each cannot describe the complete process.

To date, interest in parameterizing gas exchange transfer has been focused on the water side transfer velocity,  $k_w$  while relatively few  $k_a$  relations are available. Each of these relations  $(k_w, k_a)$  has been derived from measurements of single tracers. Gases of significant environmental importance such as CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> with  $\alpha < 10$  have been widely used to provide water-side layer transfer velocities (as here  $k_w = k_{t,w}$ ) while water vapour and heat with  $\alpha > 1000$  the air-side layer ones ( $k_a = k_{t,a}$ ). Intermediate solubility gases, are restricted by both boundary layers and therefore their transfer velocity depends on both  $k_w$  and  $k_a$ . Within this category are numerous ocean associated Volatile Organic Compounds (VOCs) (e.g acetone, acetaldehyde), halogenated compounds (e.g bromoform, CHBr<sub>3</sub>, diiodomethane, CH<sub>2</sub>I<sub>2</sub>), sulphur-containing (e.g dimethyl sulphide, DMS) and nitrogen containing compounds (e.g ammonia, NH<sub>3</sub>). Currently, the  $k_t$  estimation for such tracers inevitably includes a big uncertainty as it is based on the selection of two independently derived transfer velocity parameterizations (example schemes Pozzer et al. (2006), Johnson (2010)). An experimentally derived gas transfer parameterization over a wide range of solubilities and Schmidt numbers has been, until this study, unavailable.

In this paper, we present our gas exchange measurements performed in a large scale wind-wave tunnel (methodology described in Mesarchaki et al. (2014)). Total transfer velocities of 14 individual trace gases, within a wide range of solubility and diffusivity, were obtained at wind speeds  $(u_{10})$  between 0.8 and  $15 \text{ m s}^{-1}$ . The complete data set is used to evaluate the total transfer velocity dependence on solubility and Sc. The role of  $u_*$  and  $\sigma_s^2$  in describing gas transfer, under clean and surfactant covered surfaces, was investigated in detail. Finally, our findings were combined to provide an empirical, physically based total transfer velocity parameterization.

| Gas               | Formula             | М     | α           | $Sc_a$ | $Sc_w$ |
|-------------------|---------------------|-------|-------------|--------|--------|
| methanol          | $CH_3OH$            | 32.04 | 5293        | 1.0268 | 671.04 |
| 1-butanol         | $C_4H_9OH$          | 74.12 | 4712        | 1.8198 | 1141.7 |
| acetonitrile      | $CH_3CN$            | 41.05 | 1609        | 1.2957 | 832.07 |
| acetone           | $(CH_3)_2CO$        | 58.08 | 878.0       | 1.4921 | 880.53 |
| 2-butanone        | $C_2H_5COCH_3$      | 72.11 | 598.9       | 1.7344 | 1159.8 |
| acetaldehyde      | CH <sub>3</sub> CHO | 44.05 | $250^{-1}$  | 1.0786 | 824.90 |
| ethyl acetate     | $CH_3C(O)OC_2H_5$   | 88.10 | 156.4       | 1.8183 | 997.46 |
| dms               | $CH_3SCH_3$         | 62.13 | 16.62       | 1.4484 | 979.40 |
| benzene           | $C_6H_6$            | 78.11 | 5.672       | 1.6785 | 980.46 |
| toluene           | $C_6H_5CH_3$        | 92.14 | 4.529       | 1.8409 | 1176.3 |
| trifluoromethane  | $CHF_3$             | 70.01 | 0.760       | 1.2132 | 747.50 |
| nitrous oxide     | $N_2O$              | 44.01 | 0.676       | 1.0007 | 593.90 |
| isoprene          | $C_5H_8$            | 68.12 | $0.50^{-1}$ | 1.6617 | 1193.9 |
| pentafluoroethane | $CF_3CHF_2$         | 120.0 | 0.415       | 1.5106 | 1027.0 |

**Table 6.1:** Listed molecular masses (M in  $\text{gmol}^{-1}$ ), dimensionless solubility ( $\alpha$ ) and Schmidt numbers in air ( $Sc_a$ ) and water ( $Sc_w$ ) for the investigated tracers at 20 °C.

Table adapted from Mesarchaki et al. (2014), <sup>1</sup> modelled, this study

### 6.2 Experimental background: Wind-Wave tank experiments

The air-water gas exchange experiments described here, were performed in the world's biggest operational annular wind-wave tank "Aeolotron" at the University of Heidelberg, Germany. The tank has an outer diameter of 10 m, a height of 2.4 m and is typically filled with 180001 of water. Invasion and evasion experiments based on a mass balance approach were conducted using air and water phase concentration measurements provided by high temporal resolution Proton Reaction Mass Spectrometry (PTR-Q-MS and PTR-TOF-MS) and Fourier Transform Infrared Spectrometry (FTIR) instrumentation. Total transfer velocity measurements, for 14 individual trace gases within a wide range of solubility and diffusivity have been achieved. The examined tracers along with their chemical properties are listed in Table 5.1. Supplementary parameters, such as the reference wind speed, air and water temperature, humidity, friction velocity and the mean square slope, were recorded. The experimental set-up and measurement method are described in detail in Mesarchaki et al. (2014).



**Fig. 6.1:** Experimental  $k_{ta}$  for a selection of investigated tracers as a function of  $u_{*w}$ , at a clean water surface.

Four replicate experiments at a clean water surface were performed, where the total transfer velocity  $k_t$  of all examined tracers was estimated for eight different wind speed conditions, equivalent  $u_{10}$  between 0.8 to  $15 \,\mathrm{m\,s^{-1}}$ . In Figure 6.1, the experimentally obtained  $k_{ta}$  (total transfer velocity as seen from an air-side perspective) for a selection of trace gases are plotted as a function of the friction velocity  $u_{*w}$ . For clarity reasons, tracers with overlapping  $k_{ta}$  were ommitted from the figure. The different tracer gases are displayed with different colors related to their solubility range. Vertical error bars express the individual transfer velocity uncertainties and horizontal bars the uncertainty of the  $u_{*w}$  measurements,  $\sim 12\%$  (mean value of the uncertainties given in Bopp (2011)). For this parameter, greater uncertainty values (30%) are estimated in case of the first wind condition as result of extrapolation (see Mesarchaki et al. (2014)). For all tracers, greater turbulent conditions lead to higher  $k_{ta}$  observations. The obtained  $k_{ta}$ s for the various tracers match closely the solubility differences. Total transfer velocity variations of up to three orders of magnitude were obtained between the examined gas tracers (i.e. methanol - isoprene). Looking at the low solubility tracers a clear jump of the  $k_{ta}$  values is to be observed at friction velocities higher than 1 cm s<sup>-1</sup> (equivalent  $u_{10} = 6 \,\mathrm{m \, s^{-1}}$ ). This jump becomes smaller and smaller as the solubility increases and it disappears completely for the very high solubility tracers.

Among the four experimental repetitions, repetition 2 showed slightly lower  $k_{ta}$  values at the examined 4, 5 and 6 wind speed conditions (more apparent for all low and medium solubility tracers). For these conditions, lower  $\sigma_s^2$  values were also observed indicating the significance of the  $\sigma_s^2$  parameter in effecting the gas exchange rates.

Further investigation of the same tracers at a film covered water surface, was achieved using a soluble surfactant Triton X-100,  $(C_2H_4O)_n$ . Experiments with two different surfactant film thicknesses of  $0.033 \,\mathrm{mg}\,\mathrm{l}^{-1}$  (1 replicate) and  $0.167 \,\mathrm{mg}\,\mathrm{l}^{-1}$  (2 replicate experiments) were conducted at similar wind speed conditions to the clean case experiments, omitting the slow step of condition one. In Figure 6.2, the % decrease in the clean water surface  $k_{ta}$  caused by the surfactant layer (here  $0.167 \,\mathrm{mg}\,\mathrm{l}^{-1}$ ) is shown as a function of  $u_{*w}$ . Here again, the presented tracers are selected so that they do not overlap and that the effect of the surfactant film is clearly represented. As between 'clean water surface' and 'film covered surface' experiments the recorded  $u_{*w}$  values were systematically lower (under the same wind speed settings), no direct transfer velocity comparison of the two cases (clean/surfactant covered) was possible (see more in Section 6.3.4). Comparable conditions, for the range  $u_{*w} \sim 0.25$  to  $1.7 \,\mathrm{cm}\,\mathrm{s}^{-1}$ , were obtained by fitting the individual tracers against  $u_*$  and interpolating the  $k_{ta}$  values for the missing turbulent conditions. Therefore, Figure 6.2 represents an estimate of the expected  $k_{ta}$  decrease induced by a  $0.167 \,\mathrm{mg}\,\mathrm{l}^{-1}$  surfactant layer.

As indicated in Figure 6.2, the surfactant effect is relatively strong at low turbulent conditions while weakens with increasing turbulence. Tracers with solubility  $\alpha < 100$ ,



**Fig. 6.2:** % decrease in  $k_{ta}$  under a 0.167 mgl<sup>-1</sup> surfactant layer as a function of  $u_{*w}$ .

for which the transfer velocity is mainly controlled by the water phase molecular layer, show a very strong (up to 70% decrease in  $k_{ta}$ ) but also similar response to the surfactant layer. Though for  $\alpha > 100$ , the effect is different for every tracer, becoming less pronounced with increasing solubility.

### 6.3 Total Transfer Velocity (TTV) Model

#### 6.3.1 Theoretical basis: Gas transfer velocity across the air-water interface

A common approach shared by all conceptual models (diffusion models such as, Yaglom and Kader (1974), Deacon (1977), Coantic (1986) or surface renewal models such as, Münnich and Flothmann (1975), Csanady (1990)), expresses the dependence of the transfer velocity through a molecular boundary layer, k as a function of two factors; the transfer resistance provided by the layer,  $\beta$  and the layer thickness, z.

$$k = f(\frac{1}{\beta}, z). \tag{6.2}$$

Factor  $\beta$ , is usually considered as a dimensionless constant. The resistance though, is expected to be different for media with different viscosities, v. The layer thickness,

z depends on the tracers' molecular diffusivity in the medium (D) and the turbulent intensity applied to the layer (Q).

$$k = f(\frac{1}{\beta}, D, v, Q) \tag{6.3}$$

or

$$k = f(\frac{1}{\beta}, Sc^{-n}, Q) \tag{6.4}$$

where Sc is the Schmidt number expressing the dimensionless ratio of the kinematic viscosity to the molecular diffusivity of the gas (Sc = v/D). The Schmidt number exponent n, accounts for the effect of the surface conditions (smooth to wavy surfaces) on the turbulent processes of the layer (Jähne and Haussecker (1998), Jähne (2009)). Intense turbulence conditions and high diffusivity (low Sc) reduce the thickness of the mass boundary layer.

The total transfer velocity,  $k_t$  (transfer through both mass boundary layers) is of greater complexity as both individual transfer velocities (in water,  $k_w = f\left(\frac{1}{\beta_w}, Q, Sc_w^{-n_w}\right)$  and in air,  $k_a = f\left(\frac{1}{\beta_a}, Q, Sc_a^{-n_a}\right)$ ) contribute to the transfer. The degree to which each layer contributes to the  $k_t$  will depend on the tracerâs solubility,  $\alpha$  (dimensionless solubility) as indicated by the partition equations:

$$k_{\rm ta} = \left(\frac{1}{k_{\rm a}} + \frac{1}{\alpha k_{\rm w}}\right)^{-1},\tag{6.5}$$

$$k_{\rm tw} = \left(\frac{1}{k_{\rm w}} + \frac{\alpha}{k_{\rm a}}\right)^{-1} \tag{6.6}$$

in air and water accordingly (Liss and Slater (1974)). The two  $k_t$  forms are related by the solubility factor

$$k_{\rm ta} = \alpha k_{\rm tw} \tag{6.7}$$

#### 6.3.2 Modeling the gas transfer velocity with wind stress

The water surface friction velocity,  $u_{*,w}$  is predominantly used by conceptual models to express the turbulence at the water boundary layer. Deacon (1977) based on the formulation of Reichardt (1951), suggested a proportional relationship between the gas transfer coefficient in the water,  $k_w$  and the water friction velocity,  $u_{*w}$  over smooth water surfaces (4 - 10 m s<sup>-1</sup>):

$$k_{\rm w} = \frac{1}{\beta} u_{\rm *w} S c_{\rm w}^{-n} \tag{6.8}$$

where  $1/\beta = 1/12.1$  and n = -2/3

Münnich and Flothmann (1975), predicted the same expression using the surface

renewal model approach (Danckwerts (1951)) and suggested:  $1/\beta = 1/16$  and n = -1/2 for wavy surfaces. Thereafter numerous studies followed, which adapted this relation, providing various numeric solutions for  $\beta$  and n.

Considering the same structural form for  $k_{\rm w}$  and assuming an analogous concept for the  $k_{\rm a}$  (also supported by the tendency of our  $k_{\rm ta}$  measurements), we assembled the basis of our total transfer velocity (TTV) model equation (for an air-side perspective) with respect to  $u_{*,w}$ :

$$k_{\rm ta} = \left(\frac{1}{\frac{1}{\beta_{\rm a}}u_{*,{\rm a}}Sc_{\rm a}^{-n_{\rm a}}} + \frac{1}{\alpha(\frac{1}{\beta_{\rm w}}u_{*,{\rm w}}Sc_{\rm w}^{-n_{\rm w}})}\right)^{-1},\tag{6.9}$$

Friction velocity in air and water are related via the density of both mediums,  $\rho_{a}$  and  $\rho_{w}$ :

$$u_{*\mathrm{w}} = \sqrt{\frac{\rho_{\mathrm{a}}}{\rho_{\mathrm{w}}}} u_{*\mathrm{a}} \tag{6.10}$$

Using our complete data set (see section 6.2), we attempted a better understanding and subsequent estimation of the unknowns in equation 6.9:  $\beta_{\rm a}$ ,  $n_{\rm a}$ ,  $\beta_{\rm w}$ ,  $n_{\rm w}$ . The underlying concept of this work differs from previous studies as here the  $\beta$  and nparameters are derived from a compilation of 14 tracers (covering a wide range of solubility and diffusivity numbers) under various wind stress and surface roughness cases.

### 6.3.3 Wave formation and Schmidt number exponent dependence

Wave formation has been broadly studied as an additional enhancement mechanism to the transfer velocity (for instance, Jähne et al. (1987), Agarwal et al. (1992), Hering et al. (1998), Zappa et al. (2001), Frew et al. (2004), Zappa et al. (2004)). Wind waves cause significant dissimilarities between air and water-sided turbulent processes.

In the air boundary layer (~  $100 - 1000 \,\mu$ m), waves are not expected to affect significantly the turbulent processes (Jähne and Haussecker (1998)). In agreement with the no-wave effect concept, a Schmidt number exponent of 2/3 was found to be most appropriate for the TTV model in reproducing the experimental results.

Contrary to the air, in the water boundary layer (~  $20 - 200 \,\mu$ m), wind generated waves enhance nonlinearly the turbulent effect through numerous mechanisms altering the wind wave field. Caused by the turbulent effect, a "wilder" transport process in the water boundary layer is observed. This phenomenon has been so far reproduced by a decrease of the Schmidt number exponent, n from 2/3 (smooth surface) to 1/2 (rough surface). In Jähne and Haussecker (1998), the Schmidt number exponent plotted against  $u_{*,w}$  and  $\sigma_s^2$  shows a gradual rather than a sudden transition from 2/3 to 1/2. Similar observations were found in Krall (2013) plotting n against  $u_{10}$ . A linear transition of the Schmidt number exponent from 2/3 to 1/2 values was examined, where the TTV model reproduced satisfactory the measured  $k_t$  values. Though, the resultant  $k_{ta}$  were found to slightly underestimate the measurements for the high soluble tracers and did not reproduce the curving between the  $k_{ta}$  and the  $u_{*,w}$  seen in the experimental data satisfactory.

Using the derived  $\beta_{\rm a}$  and  $\beta_{\rm w}$  of the previous run (made with a linear Schmidt number exponent transition) and a  $n_{\rm a}$  of 2/3 to the TTV model, the unknown  $n_{\rm w}$  was provided. In Figure 6.3, the resulting  $n_{\rm w}$  values are plotted against mean square slope,  $\sigma_s^2$  for the examined low solubility tracers, for which the transfer is mainly controlled by the water-side layer and therefore the influence of  $n_{\rm w}$  on the  $k_{\rm t}$  is more weighted. The mean square slope, a measure of the nonlinearity of the wind wave field, is chosen as a better suited parameter to describe the surface conditions and thus the  $n_{\rm w}$ , as also suggested by Jähne and Haussecker (1998).



**Fig. 6.3:** Calculated Schmidt number exponent,  $n_{\rm w}$  plotted as a function of  $\sigma_s^2$ .

A negative exponential relationship between the two parameters was found to fit very well the calculated  $n_{\rm w}$  values (see Eq.6.11). An additional parameter, c was applied to the negative exponential relation to account for the lower  $n_{\rm w}$  values observed at  $\sigma_s^2$ values above 0.07 (clean water surface equivalent  $u_{*,w} \sim 1 \,\mathrm{cm}\,\mathrm{s}^{-1}$ , above which a clear step in the  $k_{\rm t}$  was also observed, see Section 6.2, Figure 6.1). Nielsen (2004) and Krall (2013), who calculated  $n_{\rm w}$  using the Schmidt number scaling equation, observed also lower  $n_{\rm w}$  values ( $n_{\rm w} < 0.5$ ) at similar turbulent conditions. The increase of  $k_{\rm t,w}$  above  $u_{*,w} \sim 1 \,\mathrm{cm}\,\mathrm{s}^{-1} / u_{10} \sim 6 \,\mathrm{m}\,\mathrm{s}^{-1}$ , which dependably leads to a decrease in the  $n_{\rm w}$ , could be a result of microscale wave braking and bubble production, apparent phenomena at these wind speed conditions becoming more regular the higher the wind speed (as also previously seen by Jessup et al. (1997)).

$$n_{\rm w} = \frac{1}{2} + \left(\frac{2}{3} - \frac{1}{2}\right) \exp(-32\,\sigma_{\rm s}^2) - c \tag{6.11}$$

where

$$c = \left(\frac{0.05}{exp\left(\frac{0.07 - \sigma_{\rm s}^2}{500}\right) + 1}\right). \tag{6.12}$$

With Schmidt number exponents provided by Eq. 6.11 - 6.12, the TTV equation (Eq.6.9) provided values of  $\beta_{\rm a} = 0.60208$  and  $\beta_{\rm w} = 7.841$  with uncertainties of 0.47% and 1.65%, accordingly. Considering the above, for clean water surfaces, Eq. 6.9 can be finalized to:

$$k_{\rm ta} = \left(\frac{1}{\frac{1}{0.6}u_{*,\rm a}Sc_{\rm a}^{-2/3}} + \frac{1}{\alpha(\frac{1}{7.84}u_{*,\rm w}Sc_{\rm w}^{-n_{\rm w}})}\right)^{-1},\tag{6.13}$$

where

$$n_{\rm w} = \frac{1}{2} + \left(\frac{2}{3} - \frac{1}{2}\right) exp(-32\,\sigma_{\rm s}^2) - \left(\frac{0.05}{exp(\frac{0.07 - \sigma_{\rm s}^2}{500}) + 1}\right).\tag{6.14}$$

Figure 6.4, presents the correlation between the total transfer velocities,  $k_{ta}$  calculated by Eq. 6.13 - 6.14 and the experimentally derived ones. Model and data (376 points) are correlated by a factor of 1.0015 providing a linearity of  $R^2 = 0.99$  and Pearson's number of Pr = 0.996 within the examined wind speed range  $u_{ref} = 0.74$  to 8.26 m s<sup>-1</sup> equivalent  $u_{10} = 0.78$  to 14.6 m s<sup>-1</sup>. Each tracer is given with a different color, based on the solubility color-coding used in the previous figures (see Section 6.2). As indicated in the figure, all tracers appear nicely on the 1:1 line at all examined wind speed conditions. For some repetitions the first point (lowest wind speed) of many tracers is overestimated by the TTV model. As mentioned before, at the first wind speed condition, larger  $u_{*,w}$  uncertainties are expected due to extrapolation. For the high soluble tracers a  $\sim 10\%$  understimation of the experimentally derived  $k_t$  is expected as a result of inefficient air space mixing (Mesarchaki et al. (2014)). Moreover, as  $u_{*,w}$ was not measured in parallel but subsequently using the same wind speed conditions, small differences between the repetions caused by differences in the  $u_{*,w}$  values at any wind speed condition can not be corrected for by the TTV model.

The experimental total transfer velocities were derived at 20°C. Therefore, the Sca, Scw, and dimensionless solubility values,  $\alpha$  in Eq.6.13, were also provided in 20 (as given in Table 5.1). In the case of isoprene, no  $\alpha$  values at 20°C, are available in the literature. Instead two quite different values 0.31 (Yaws and Pan (1992)) and



Fig. 6.4:  $k_{ta}$  correlation between the TTV model and the experimental data for a clean water surface.

0.69 (Sander (1999)) are proposed at 25°C. Based on our evaluation, a solubility of  $\alpha = 0.5$  was found to fit better the experimental data and was used to cover for the missing solubility at 20°C. Also for the molecule of acetaldehyde, assuming that the experimentally obtained transfer velocities are not put into question, a lower solubility was found to reproduce the measurements better than the available literature values. Here, higher solubility numbers such as 378.7 (Betterton et al. (1988)) bring the transfer velocities points of acetaldehyde slightly out of the 1:1 line, though this effect is so that strong as to affect the result given in Equation 6.13.

#### 6.3.4 Surfactant effect on the transfer velocity

As has been seen in many studies (for instance, Broecker (1978), Jähne et al. (1987), Frew (1997)) and also in this study (Section 6.2, Figure 6.2), surfactant layers can reduce significantly the gas transfer velocity. The existence of surface films changes the hydrodynamic properties of the water surface, reducing surface stress and roughness. Figure 6.5, shows the effect of surfactant films on the  $u_{*,w}$  and  $\sigma_s^2$  under the same wind speed conditions  $(u_{ref})$ , as estimated in the "Aeolotron" wind wave tank during the gas exchange experiments. In both figures, values obtained under a clean water surface are given with red, under  $0.033 \text{ mg} \text{l}^{-1}$  Triton-X100 covered surface with green and under  $0.167 \text{ mg} \text{l}^{-1}$  covered surface with blue. The presented uncertainties were obtained as the standard deviation of the mean value at each condition. The  $u_{*,w}$  values for the thin surfactant case (0.033 mg l<sup>-1</sup> Triton-X100), are interpolated between the two other cases, as no measurements were available for this case (presented with light green).



Fig. 6.5: Effect of surface films on the friction velocity and the mean square slope, for: clean water surface (red), surface covered with  $0.033 \text{ mg} \text{ l}^{-1}$  Triton-X100 (green) and  $0.167 \text{ mg} \text{ l}^{-1}$  Triton-X100 (blue).

As indicated in Fig. 6.5, the two parameters,  $u_{*,w}$  and  $\sigma_s^2$ , behave differently under the effect of surfactant films. A surfactant covered surface seems to effect much greater the mean square slope parameter and less the friction velocity. In both cases, the lower the wind speed settings the greater the surfactant impact.

When using the TTV equation (Eq. 6.9), the effect of surface films on the turbulence (change in  $u_{*,w}$ ) and the surface conditions (change in  $\sigma_s^2$  in Eq. 6.14) is already taken into account. The remaining uncertainty lie in the expected impact of a surfactant film on the resistance provided by the layer, parameter  $\beta_w$  in water and  $\beta_a$  in air. To investigate this, the  $k_{t,a}$  of our 14 tracer compilation as measured during a series of surface films experiments, of which one experimental repetition with 0.033 mg l<sup>-1</sup> and 2 repetitions with 0.167 mg l<sup>-1</sup> Triton-X100, were used in combination with the proposed TTV parameterization (Equation 6.9).

Considering the resistance provided by the air-phase layer, the derived  $\beta_a$  value showed, as expected, no surfactant effect i.e  $\beta_a = 0.6$  = clean water surface, for both examined surface film thicknesses. In contrast, both thin and thick film experiments provided a higher  $\beta_w$  number i.e  $\beta_w = 11.5$ , indicating a stronger resistance provided by the water



Fig. 6.6:  $k_{ta}$  correlation between the TTV model and the experimental data for a water surface covered with 0.033 mg l<sup>-1</sup> Triton-X100.

phase layer in the presence of surface films. Surprisingly, the same number did fit ideally for both  $0.033 \,\mathrm{mg}\,\mathrm{l}^{-1}$  and  $0.167 \,\mathrm{mg}\,\mathrm{l}^{-1}$  Triton-X100 surfactant additions, signifying that it is not the thickness of the surfactant layer that diminishes the resistance but rather the existence of the film layer itself which acts as a "coat" apart from reducing surfaces' hydrodynamic properties also adds an extra resistance to the transfer. Another interesting observation was that the surfactant related  $\beta_{\rm w}$  provided a good correlation with the experimentally derived  $k_{\rm ta}$  up to roughness values of  $\sigma_s^2 = 0.07$ (translating to reference wind speed,  $u_{ref} = 6.3 \,\mathrm{m \, s^{-1}}$  for the low and  $u_{ref} = 7.0 \,\mathrm{m \, s^{-1}}$ for the high surfactant case). Above this point, as is clearly presented in Figure 6.5 (b), the surfactant is probably very well mixed with the water and does not affect the surface roughness any more. Consequently, above  $\sigma_s^2 = 0.07$ , the clean case  $\beta_w$  reproduced much better the experimental total transfer velocities. The transition from the surfactant  $\beta_{\rm w}$  to the clean surface  $\beta_{\rm w}$  arises later when the surfactant layer is thicker. Figures 6.6 and 6.7, present model-data correlations for the  $0.033 \,\mathrm{mg}\,\mathrm{l}^{-1}$  and  $0.167 \,\mathrm{mg}\,\mathrm{l}^{-1}$  Triton-X100 cases, respectivelly. In the low surfactant addition (Fig.6.6), model and data correlated by a factor of 1.0656 ( $R^2 = 0.983$  and Pr = 0.992) within the examined wind speed range  $u_{ref} = 1.46$  to  $8.3 \,\mathrm{m \, s^{-1}}$  equivalent  $u_{10} = 0.6$  to  $12.9 \,\mathrm{m \, s^{-1}}$ . For the high surfactant addition (Fig.6.7), model and data correlated by a factor of



Fig. 6.7:  $k_{ta}$  correlation between the TTV model and the experimental data for a water surface covered with  $0.167 \text{ mg l}^{-1}$  Triton-X100.

1.135 ( $R^2 = 0.99$  and Pr = 0.994) within the wind speed range  $u_{ref} = 1.4$  to 8.37 m s<sup>-1</sup> equivalent  $u_{10} = 1.27$  to  $12.7 \text{ m s}^{-1}$ . In both cases  $\beta_a = 0.6$  and  $\beta_w$ :  $11.5 < \sigma_s^2 = 0.07 > 7.841$ . The correlation factor for the high surfactant case, shows a small overestimation of the transfer velocities by the TTV model (13%). This overstimation is caused mainly by the higher values estimated by the TTV model at the fifth wind speed condition for all tracers. This could be a result of a slightly wrong measurement of the  $u_{*,w}$  or the  $\sigma_s^2$  at this condition but it is definetly not tracer related. Here again, small differences between the two repetitions, caused by differences in the  $u_{*,w}$  cannot be account for by the TTV model.

### 6.4 Further air-sea gas exchange insights

The correlation of the TTV model to the experimental data derived in the "Aeolotron" tank, for both the clean and also the surfactant covered water surface cases, inspires great confidence in the accuracy of the gas exchange process representation by the proposed parameterization. Having estimated the impact of the microscopic surface

parameters on the gas transfer across the interface, further examination of the influence of each individual layer on the transfer of various tracers can be attained.

Tracers with very high or very low solubility are controlled by the air or the water phase layer, respectively. In these cases, the individual transfer velocity through the not-controlling phase has no contribution to the total transfer velocity. Tracers with solubility in between these two extreme cases, can be controlled by the one or the other phase (or both of them) and still have both individual transfer velocities contributing to the total transfer. Using the findings of this study, interesting information can be obtained concerning the phase control as well as the exact contribution of each layer to the total transfer velocity for any tracer.

#### 6.4.1 Phase control of the transfer

The controlling phase of the transfer process, can be determined by the ratio:  $\alpha k_w / k_a$ . The dominant layer depends therefore mainly on the solubility of the tracer though in some cases (medium solubility tracers), the control can be also influenced by turbulence, changing surface conditions and surfactant films. Ratio values > 1, indicate an airside control while < 1, a water-side control. In Figure 6.8,  $\alpha k_w / k_a$  is plotted with respect to the solubility for many of the investigated tracers plus water vapor which was included to provide an extreme high solubility example (dimentionles solubility,  $\alpha \sim 60000$ ). A coloured bar gives the  $u_{*,w}$  values for the examined turbulent range. Plot (a) corresponds to a clean water surface and (b) to a 0.167 mg l<sup>-1</sup> Triton-X100 covered surface. In both figures, the same  $u_{*,w}$  is used providing a direct correlation of the two cases. To do this, the surfactant solution of the TTV model (Section 6.3.4) was extrapolated to lower  $u_{*,w}$  values.

As indicated by both plots, the  $\alpha k_w / k_a$  ratio gives different values at different turbulent conditions. For gases lying on the "one" line, turbulent intensity can switch phase control. The  $\alpha k_w / k_a$  ratio variability with respect to turbulence, changes behavior in presence of a surfactant film (here 0.167 mgl<sup>-1</sup> Triton-X100). The surfactant depresses significantly the mean square slope (see Figure 6.5(b)) keeping it to its lower value up to  $u_{*,w} \sim 0.55 \,\mathrm{cm \, s^{-1}}$ . Up to this point, no significant changes in the  $\alpha k_w / k_a$ numbers are observed. Above this point though, larger changes in increasing  $\sigma_s^2$  lead also to greater variations in the  $\alpha k_w / k_a$  ratio.

Taking acetone as an example, under a clean water surface (Figure 6.8, plot (a)), transfer is controlled by the water phase layer up to  $u_{*,w} \sim 0.1 \,\mathrm{cm \, s^{-1}}$  (equivalent  $u_{10} = 1.0 \,\mathrm{m \, s^{-1}}$ ) while above this point acetone becomes air-side controlled. When the surface is covered with a surfactant film (Figure 6.8, plot (b)), acetone remains water-side controlled up to  $u_{*,w} \sim 0.4 \,\mathrm{cm \, s^{-1}}$  (equivalent  $u_{10} = 3.8 \,\mathrm{m \, s^{-1}}$ ).

#### 6.4.2 Influence of the individual k on the $k_t$

In this section, the the exact contribution of each boundary layer to the total gas transfer is examined. In Figure 6.9, the % percent of each individual k to the  $k_t$  is plotted against solubility for the same tracers presented in Fig 6.8. The green color shows the % percent of  $k_w$  to the  $k_t$  and the orange color the % percent of  $k_a$  to the  $k_t$ . A  $u_{*,w}$  shade bar in each color gives the turbulent intensity corellated with each point. As seen for the phase control, turbulence changes the impact of each individual k on the  $k_t$ . Though, closer to the solubility extremes, the k impact on  $k_t$  remains the same for all examined turbulent conditions. Two interesting medium solubility examples are acetone and acetaldehyde. In a clean water surface, at very low turbulent conditions, both individual k values  $(k_w, k_a)$  contribute equally to the total transfer of acetone, while at higher turbulence the impact of  $k_a$  is clearly dominating (~ 75 %). Dissimilarly for acetaldehyde,  $k_t$  is approximately equally influenced by  $k_w$  and  $k_a$  at high turbulent conditions while at low turbulence  $k_w$  dominates. In the presence of surface films (here 0.167 mg l<sup>-1</sup> Triton-X100), the k contributions to the  $k_t$  differ from those observed for a clean water surface though again not in case of extreme solubility where the effect of turbulence on the percent of each individual k on the  $k_t$ , is not significant (Figure 6.9, plot (b)).

### 6.5 Conclusion

In this study, experimentally derived total transfer velocities are presented for a series of tracers as obtained from a state of the art wind-wave tank, at wind speeds  $(u_{10})$  between 0.8 and  $15 \,\mathrm{m\,s^{-1}}$ . The experimental data were used to derive a total transfer velocity (TTV) parameterization. The quality of the final parameterization is ultimately a function of the comprehensiveness, precision and accuracy of the underlying dataset. The solubility parameter is for the first time included in a gas exchange parameterization. The unique approach of this work, using a compilation of 14 tracers with different chemical identities to provide a TTV equation, rather than one tracer providing an individual transfer velocity  $(k_w \text{ or } k_a)$  relation, strengthens the reliability of our model and at the same time proves its applicability to any tracer within the examined solubility range ( $\alpha = 0.4$  to 5470).

The wind-wave tank was verified as an ideal environment to investigate the effect of wind and surface film related processes on the gas transfer. High time resolution gas exchange measurements under controlled conditions (wind speed, temperature, etc.), as well as the availability of friction velocity and mean square slope quantifications, enabled a much better understanding of the gas exchange process.  $u_{*,w}$  was determined as the ideal parameter to express the wind driven turbulence in the boundary layers. A negative exponential relationship between the water-side Schmidt number exponent,  $n_w$ 

and the  $\sigma_s^2$  could optimally describe the associated water surface conditions changing gradually from a smooth (2/3) to rough a (1/2) status. A TTV parameterization combining both  $u_{*,w}$  and  $\sigma_s^2$  parameters was found to reproduce best the experimentally derived  $k_{t,a}$ .

For a clean case surface, the TTV model correlated linearly with the experimental  $k_{t,a}$  by a factor of 1.0015 ( $R^2 = 0.99$ ,  $\Pr = 0.996$ ). In the presence of surface films, an increase in the resistance provided by the water boundary layer,  $\beta_w$  was observed up to  $\sigma_s^2 = 0.07$ , above which value the surfactant does not seem to effect the surface roughness or water layer resistance any more. Good model-data correlations were obtained for a 0.033 mg l<sup>-1</sup> Triton-X100 (correlation factor = 1.0656,  $R^2 = 0.983$ ,  $\Pr = 0.992$ ) and 0.167 mg l<sup>-1</sup> Triton-X100 (correlation factor = 1.135,  $R^2 = 0.99$ ,  $\Pr = 0.994$ ) covered surfaces. Due to the limited number of surfactant experiments in this work, further gas exchange investigation using alternative surfactant layers and concentrations is needed for confirmation of the findings presented here.

Our study demonstrates that the suggested TTV parameterization along with adequate measurements of  $u_{*,w}$  and  $\sigma_s^2$  over the examined wind speed range, faithfully reproduces the total transfer velocity of any gas under clean and surfactant covered surfaces. In this way, we wish to encourage future investments in improving the measuring technology used in wind-wave tanks and especially in the ocean for measuring  $u_{*,w}$  and  $\sigma_s^2$ .

We consider the application of the TTV parameterization in an ocean-atmosphere environment promising as even if wind-wave tunnels cannot entirely reproduce the oceanic sea state, the controlling gas exchange mechanisms are believed to be accounted for properly. For ocean  $k_t$  estimations, the salinity impact should be taken into account by the use of salt water derived Schmidt numbers and solubilities.

As presented in the last part of this work, the proposed model can be also applied in order to evaluate the impact of solubility, turbulence and surface films on the phase control of the transfer but also the individual k contribution to the  $k_t$  for a desired tracer.

We recommend the TTV model as a great tool for regional and global models, providing accurate total transfer velocity estimations for any tracer and any sea status, simplifying the calculation process and eliminating inevitable calculation uncertainty connected with the selection or combination of different parameterizations.

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Fig. 6.8: The  $\alpha k_w / k_a$  ratio as a function of solubility for a  $u_{*,w}$  range between 0.07 and 2.06 cm s<sup>-1</sup>. Plot (a) corresponds to a clean water surface and (b) to a 0.167 mgl<sup>-1</sup> Triton-X100 covered surface.



**Fig. 6.9:** The individual k impact on the  $k_t$  as a function of solubility for a  $u_{*,w}$  range between 0.07 and 2.06 cm s<sup>-1</sup>. Plot (a) corresponds to a clean water surface and (b) to a 0.167 mgl<sup>-1</sup> Triton-X100 covered surface.

# Conclusions

This thesis details the development of a new NTD GC-MS method with focus on the effective sampling and analysis of the target atmospheric relevant VOCs: DMS, isoprene, benzene, toluene, p-xylene, (+)- $\alpha$ -pinene and (-)- $\alpha$ -pinene, out of seawater samples. Laboratory evaluation and consequent field application indicated that the proposed method can be used successfully in place of the traditionally used extraction techniques (P&T, SPME) to extend the suite of species typically measured in the ocean and improve detection limits (obtained LODs were in the range of some pM for all examined compounds).

During a mesocosm  $CO_2$  enrichment study (Raunefjord, Norway), DMS, isoprene and  $\alpha$ -pinene were identified and quantified in seawater samples of present and future  $CO_2$  levels. The most abundant identified marine VOC was DMS at concentrations ranging from 0.3 to 6 nM. Isoprene was the second most abundant tracer (0.02 to 0.42), followed by (-)  $\alpha$ -pinene (0.0041 to 0.063 nM) and (+)  $\alpha$ -pinene (0.002 to 0.055 nM).

Ocean DMS emissions showed a clear drop with increasing CO<sub>2</sub> (DMS/CO<sub>2</sub> correlation  $R^2 = 0.96$ ) indicating an expected lower oceanic DMS production in the future. Good correlation was also observed between DMS and the phytoplankton species E. huxleyi (~  $R^2 = 0.8$ ) which was likely the main source of DMS in this study. In the case of isoprene, higher emissions were observed for the low and middle CO<sub>2</sub> levels, though this trend was not as clearcut as that of DMS. Similarities between the trends of isoprene and the phytoplankton species: "big nanoeukaryotes", were observed. According to this, big nanoeukaryotes, were likely one of the main isoprene sources in this study. This outcome is in agreement with previous laboratory observations. The  $\alpha$ -pinene compound ((-)  $\alpha$ -pinene and (+)  $\alpha$ -pinene), showed no CO<sub>2</sub> effect. The two enantiomers showed different temporal production trends, indicating different emission sources. For (-)  $\alpha$ -pinene similarities were observed with the big nanoeukaryotes while for (+)  $\alpha$ -pinene no correlation could be found among the examined phytoplankton species.

Successful air-water gas transfer velocity measurements were performed in a large scale wind wave tank, using state of the art measuring technologies. The adopted method-

ology, experimental procedure and instrumentation were proven capable of generating reliable and reproducible gas transfer rates for 14 individual tracers over a wide range of solubilities and diffusivities. Total transfer velocity measurements were performed at eight different wind speed conditions, starting from the very low wind speed regime  $u_{10}$ = 0.8 m s<sup>-1</sup> (experimentally un-explored wind speed region of previous studies) developing gradually to higher winds up to  $15 \text{ m s}^{-1}$ . Cases of clean and surfactant covered water surfaces (using a soluble surfactant Triton X-100,  $(C_2H_4O)_n$ ) were examined. The derived transfer velocities correlated well with previous  $k_w$  and  $k_a$  parameteri-

zations. Through this comparison though, the need for a more accurate air-sea gas exchange equation possibly based on surface related parameters (e.g friction velocity,  $u_*$  and mean square slope,  $\sigma_s^2$ ) rather than the wind speed at ten meters height,  $u_{10}$ , was evidently demonstrated.

A much better understanding of the gas exchange process was enabled using the obtained high quality transfer rate measurements and the available friction velocity and mean square slope quantifications. The role of  $u_*$  and  $\sigma_s^2$  in defining phenomena such as waves and wave breaking, near surface turbulence, bubbles and surface films was recognised as very significant.  $u_{*,w}$  was determined as the ideal "turbulent" parameter while  $\sigma_s^2$  showed an optimal description of the related surface conditions. In this way, the present work highlights the need for improved measuring technology providing easier and more accurate measurements of  $u_{*,w}$  and  $\sigma_s^2$  in the laboratory and especially in the ocean.

For the first time, a Total Transfer Velocity (TTV) model provided by a compilation of 14 tracers and a combination of both  $u_{*,w}$  and  $\sigma_s^2$  parameters, is proposed. The TTV model correlated linearly with the experimental data by a factor of 1.0015 ( $R^2 = 0.99$ , Pr = 0.996) under a clean water surface and factors of 1.0656 ( $R^2 = 0.983$ , Pr = 0.992) and 1.135 ( $R^2 = 0.99$ , Pr = 0.994) under 0.033 mgl<sup>-1</sup> and 0.167 mgl<sup>-1</sup> Triton-X100 covered surfaces, respectively. Through the proposed TTV parameterization, a new physical perspective is presented which has proven to be a faithful representation for any tracer within the examined solubility range (i.e  $\alpha = 0.4$  to 5470).

The development of such a comprehensive air-sea gas exchange parameterization represents a highly useful tool for regional and global models, providing accurate total transfer velocity estimations for any tracer and any sea status, simplifying the calculation process and eliminating inevitable calculation uncertainty connected with the selection or combination of different parameterizations.

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