Berichtsblatt

1. ISBN oder ISSN	2. Berichtsart (Schlussbericht oder Veröffentlichung) Schlussbericht

3. Titel
SO 218- SHIVA: Stratosphärisches Ozon: Halogen Einfluss in einer sich verändernden Atmosphäre

4. Autor(en) [Name(n), Vorname(n)]	5. Abschlussdatum des Vorhabens 31.03.2013
Quack, Birgit	6. Veröffentlichungsdatum
	7. Form der Publikation

8. Durchführende Institution(en) (Name, Adresse)	9. Ber. Nr. Durchführende Institution
GEOMAR, Helmholtz-Zentrum für Ozeanforschung Kiel Düsternbrooker Weg 20 24105 Kiel	10. Förderkennzeichen *) 03G0218A
	11. Seitenzahl 29 + 90 (englischer Anhang)

12. Fördernde Institution (Name, Adresse)	13. Literaturangaben 54
Bundesministerium für Bildung und Forschung (BMBF) 53170 Bonn	14. Tabellen 2 + 7
	15. Abbildungen 10 + 63

16. Zusätzliche Angaben: Der Abschlussbericht ist in deutscher Sprache verfasst, dem ein 90 -seitiger Anhang in Englisch beigefügt wurde, der 24 Berichte der an der Kampagne beteiligten internationalen Arbeitsgruppen enthält.

17. Vorgelegt bei (Titel, Ort, Datum) :Atmospheric Chemistry and Physics and Biogeosciences - Special Issues: SHIVA mehrere Veröffentlichungen sind in Vorbereitung

18. Kurzfassung: Auf der Forschungsseereise SO218-SHIVA im südchinesischen Meer und in philippinischen Gewässern von Singapur bis Manila vom 15. bis zum 29. November 2011 wurden im Rahmen des EU-Projektes SHIVA (Stratospheric Ozone: Halogens in a varying atmosphere) in interdisziplinärer Zusammenarbeit Produktion, Emission und Transport ozeanischer leichtflüchtiger Brom- und Jodverbindungen in bisher nicht untersuchten Küstenregionen des West-Pazifik erforscht. Die Kampagne fand zu Beginn der tropischen Hauptkonvektionszeit in dem Haupteintragsort troposphärischer Luftmassen in die Stratosphäre statt. Auf FS Sonne wurden das Meerwasser und die von ozeanischen Emissionen beeinflusste Luft analysiert. Mit dem deutschen Forschungsflugzeug Falcon, das zur gleichen Zeit auf Borneo (Miri, Malaysia) stationiert war, wurde versucht die gleichen Luftmassen zu analysieren, die schon auf FS Sonne beprobt wurden. Die Messungen biologischer, ozeanographischer und weiterer chemischer Parameter wurden im Ozean mittels in-situ Messungen und Fernerkundungsmethoden in Zusammenarbeit mit malaysischen und philippinischen Kollegen durchgeführt. Für küstennahe Untersuchungen wurden mehrere Probenahmen mit lokalen Booten von ortsansässigen Universitäten organisiert, sowie ein zweimaliger Probenaustausch zwischen den Booten und *FS Sonne* durchgeführt. Die Ergebnisse zeigten unter anderem generell hohe Konzentrationen brom- und jodhaltiger Verbindungen im Wasser, besonders in den flachen Schelfregionen und nah den Küsten. Dadurch dass die Gehalte der Spurenstoffe in der Atmosphäre eher niedrig waren, war das warme Meerwasser in dieser Region überall eine Quelle der natürlichen Halogenverbindungen für die Atmosphäre. Transportsimulationen zeigten, dass die großen ozeanischen Emissionen der leichtflüchtiger Brom- und Jodverbindungen im Vergleich zu andern Ozeanregionen (z.B. Ostatlantik), die auch Quellen für die tropische Tropopausen-Schicht und die darüber liegende Stratosphäre enthalten, zusammen mit starkem konvektivem Transport zu signifikanten Vorkommen in der Tropopausenregion und intensivstem Transport von Halogenen in die Stratosphäre führen. Ergebnisse der Seereise wurden auf internationalen Konferenzen vorgestellt und in begutachteten Zeitschriften veröffentlicht. Die Daten stehen zur weiteren Auswertung in Datenbanken zur Verfügung.

19. Schlagwörter
Wechselwirkungen Ozean/Atmosphäre, Gasaustausch, Spurengasemissionen, Stratosphäre, Transport, Ozon

20. Verlag	21. Preis

Document Control Sheet

1. ISBN or ISSN	2. type of document (e.g. report, publication) Final report
3. title SO 218- SHIVA: Stratospheric Ozone: Halogen Impacts in a varying atmosphere	
4. author(s) (family name, first name(s)) Quack, Birgit and SO218 cruise members	5. end of project 31 March 2013
	6. publication date
	7. form of publication
8. performing organization(s) (name, address) GEOMAR Helmholtz Centre for Ocean Research Kiel Düsternbrooker Weg 20 24105 Kiel Germany	9. originator's report no. 03G0218A
	10. reference no.
	11. no. of pages 29 + 90 (English appendix)
12. sponsoring agency (name, address) Bundesministerium für Bildung und Forschung (BMBF) 53170 Bonn	13. no. of references 54
	14. no. of tables 2 + 7
	15. no. of figures 10 + 63
16. supplementary notes The final report is written in German, and an appendix of 90 pages in English is attached wurde, which contains 24 reports from international work groups, who participated in the campaign.	
17. presented at (title, place, date) :Atmospheric Chemistry and Physics and Biogeosciences - Special Issues: SHIVA, articles are published and several are in preparation	

18. abstract

Within the frame work of the EU-project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) the research cruise SO218 of the German research vessel SONNE was organized and conducted by the GEOMAR Helmholtz Centre for Ocean research Kiel from 15 to 29 November 2011 in the South China and Sulu Sea. The RV Sonne (cruise SO218) sailed from Singapore to Manila (Philippines). The route incorporated 2 diurnal stations off the western coast of Borneo, 2 contacts with local boats from the universities in Kuching and Kota Kinabalu, and was overflown by the GERMAN research air craft Falcon from the DLR German Aerospace Center on 3 occasions. The cruise was mainly bound to investigate tropical trace gas emissions in Malaysian and Philippine waters of various biogeochemical regimes between Singapore and Manila (Philippines) and their contribution to stratospheric halogens. Partners on board were from the European project SHIVA - Stratospheric halogens in a varying atmosphere - (http://shiva.iup.uni-heidelberg.de/) and from Malaysia, the University of Malaya, Kuala-Lumpur (IOES) Universiti of Malaya, Sarawak (UNIMAS), Universiti of Malaya, Sabah) and the University of the Philippines Diliman, Quezon. During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed. Halocarbon concentrations were determined in water and air, and sea-to-air fluxes were calculated. Many other atmospheric trace gases, transport processes and various oceanic chemical, physical and biological parameters were also determined. The results show, that his region is a significant source region for marine brominated and iodinated very short-lived trace gases, above all bromoform ($CHBr_3$) and that significant and rapid transport of the gases occurs into the stratosphere.The data are available in databases for further evaluations.

19. keywords

Ocean/Atmosphere Interactions, Air/Sea Gas Exchange, Trace Gas Emissions, Transport, Stratosphere, Ozone

20. publisher	21. price

Abschlussbericht zum Projektantrag

SO218- SHIVA

Stratosphärisches Ozon:

Halogen Einfluss in einer sich verändernden Atmosphäre

(01.08.2011- 31.03.2013)

Forschungsexpedition mit FS Sonne

15. bis zum 29. November 2011

Singapur bis Manila (Philippinen)

Zuwendungsempfänger: GEOMAR Helmoltz-Zentrum für Ozeanforschung Kiel

Förderkennzeichen: 03G0218A

Verantwortlich für den Inhalt dieses Berichtes:

Dr. Birgit Quack, GEOMAR Helmoltz-Zentrum für Ozeanforschung Kiel

GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung
Projektträger Jülich Forschungszentrum Jülich
GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel
SHIVA

GEOMAR Helmholtz—Zentrum für Ozeanforschung Kiel
Düsternbrooker Weg 20
D-24105 Kiel
Tel: +431 6004206
Fax: +431 6004205
email: bquack@geomar.de

SO218-SHIVA: Stratosphärisches Ozon: Halogen Einfluss in einer sich verändernden Atmosphäre

I.1. Aufgabenstellung 4

I.2. Voraussetzungen unter denen das Vorhaben durchgeführt wurde 4

I.3. Planung und Ablauf des Vorhabens 5

Das an Bord durchgeführte Arbeitsprogramm: 6

I.4. Stand der Wissenschaft und Technik: Die Bedeutung von natürlichen Halogenverbindungen für das stratosphärische Ozon 8

I.5. Zusammenarbeit mit anderen Stellen (Nationale und internationale Einbindung) 13

II. 1. Verwendung der Zuwendung und das erzielte Ergebnis 15

II.2. Positionen des zahlenmäßigen Nachweises 22

II.3. Notwendigkeit und Angemessenheit der geleisteten Arbeit 23

II.4. Der voraussichtlichen Nutzens, insbesondere der Verwertbarkeit des Ergebnisses im Sinne des fortgeschriebenen Verwertungsplans 24

II.5. Während der Durchführung des Vorhabens bekannt gewordener Fortschritt auf dem Gebiet des Vorhabens bei anderen Stellen 25

II. 6. Die erfolgten und geplanten Veröffentlichungen des Ergebnisses 26

Publikationen in begutachteten Zeitschriften (Veröffentlicht und Geplant) 26

Präsentationen (Poster und Vorträge) 27

SO218-SHIVA: STRATOSPHÄRISCHES OZON: HALOGEN EINFLUSS IN EINER SICH VERÄNDERNDEN ATMOSPHÄRE

I.1. AUFGABENSTELLUNG

Im Rahmen des EU-Projektes SHIVA (Stratospheric Ozone: Halogens in a varying atmosphere) sollten in Feldstudien kurzlebige Substanzen mit klimasensitiven natürlichen Emissionen untersucht werden, im Besonderen waren ozeanische leichtflüchtige Brom- und Jodverbindungen in tropischen Regionen, die als Hauptquellorte für die Stratosphäre gelten, ein Ziel der Forschung. SHIVA- „Stratospheric halogens in a varying atmosphere“ beinhaltete ein aktuelles Forschungsthema der „World Meteorological Organzation“ (WMO) Ozonforschung und ist fest in internationalen Programmen verankert. Auf der Forschungsseereise SHIVA-Sonne im südchinesischen Meer und in philippinischen Gewässern von Singapur bis Manila vom 15. bis zum 29. November 2011 wurden in interdisziplinärer Zusammenarbeit Produktion, Emission und Transport der Verbindungen in bisher nicht untersuchten Küstenregionen des West-Pazifik erforscht. Die Kampagne fand zu Beginn der tropischen Hauptkonvektionszeit in dem Haupteintragsort troposphärischer Luftmassen in die Stratosphäre statt, wo marine Quellen mit Bedeutung für die Ozonschicht untersucht wurden. Auf FS Sonne wurden das Meerwasser und die von ozeanischen Emissionen beeinflusste Luft analysiert. Mit dem deutschen Forschungsflugzeug Falcon, das zur gleichen Zeit auf Borneo (Miri, Malaysia) stationiert war, wurde versucht die gleichen Luftmassen zu analysieren, die schon auf *FS Sonne* beprobt wurden. Anorganische Zersetzungsprodukte der Halogenverbindungen und der Spurengashaushalt der Atmosphäre mit anschließender Modellierung charakterisierten die chemische Transformation der ozeanischen Emissionen vom Erdboden bis in die tropische Tropopausenschicht und ihren Eintrag in die Stratosphäre. Die Messung biologischer, ozeanographischer und chemischer Parameter im Ozean mittels in-situ Messungen und Fernerkundungsmethoden in Zusammenarbeit mit malaysischen und philippinischen Kollegen wurden für Quellzuordnungen herangezogen. Für küstennahe Untersuchung wurden mehrere Probenahmen mit lokalen Booten von ortsansässigen Universitäten organisiert, sowie ein zweimaliger Probenaustausch zwischen den Booten und *FS Sonne* durchgeführt.

I.2. VORAUSSETZUNGEN UNTER DENEN DAS VORHABEN DURCHGEFÜHRT WURDE

Das EU- Projekt SHIVA (2009-2013), dessen zentraler Bestandteil die durchgeführte Forschungs-seereise SHIVA-Sonne war, beinhaltete einen aktuellen Forschungsschwerpunkt der Ozonforschung, der im letzten „Ozon-Bericht“ der WMO von 2011 hohe Priorität erhielt, wobei es um den Beitrag ozeanischer kurzlebiger Verbindungen zum stratosphärischen Brom und zur Ozonzerstörung geht. Dieser stratosphärische Bromeintrag wird aktuell weltweit mit etwa 5 ppt als Annahme in Klimachemiemodellen berücksichtigt, um den beobachteten Ozonabbau der mittleren Breiten simulieren zu können. Die Frage woher, wie schnell und in welchen Mengen dieses Brom in die Stratosphäre gelangt, ist bisher nicht geklärt. Vermutlich kommt dem Gebiet um den maritimen Kontinent im West Pazifik dabei die größte Bedeutung zu. In diesem Hauptkonvektionsgebiet finden ca. 60 % aller globalen Einträge troposphärischer Luftmassen in die Stratosphäre statt.

Die Seereise wurde zur Ermittlung der Emissionen im tropischen küstennahen Westpazifik für den bisher keine ozeanischen Messungen kurzlebiger Bromverbindungen und anderer halogenierter Kohlenwasserstoffe existierten, und ihres Transportes durch die Troposphäre bis in die Stratosphäre durchgeführt. Die ozeanischen Konzentrationsverteilungen und Emissionen der halogenierten Verbindungen und weiterer klimarelevanter Spurengase (DMS, CO_2, O_2, N_2O, CH_4) sowie der Phyto-planktongehalt des Meerwassers wurden ebenfalls bestimmt. In malaysischen und philippinischen

Gewässern wurden einige CTD-Stationen durchgeführt, um die chemische und biologische Produktion der Spurengase im Ozean (Vertikalprofile) und deren Gehalte und Quellen im Oberflächenwasser besser zu verstehen.

Die Vor- und Nachbereitung der Seereise war aus diplomatischen und logistischen Gründen aufwändig und erforderte mehrere Besuche in Malaysia, sowie eine Fahrtplanung und -durchführung, die neben den wissenschaftlichen Fragestellungen, Ausschlussgebiete, Piratenaktivitäten, Territorialstreitigkeiten, Küstenfischerei, sowie schwierige Passagen wegen unklarer oder zu flacher Bathymetrie berücksichtigen musste. Die kombinierte internationale Messkampagne mit FS Sonne, zusätzlich einigen kleinen küstennahen Einsätzen von Forschungsbooten, dem deutschen Forschungsflugzeug Falcon, sowie gleichzeitige Messungen vom Erdboden und vom All aus, wie sie im Westpazifik im Herbst 2011 durchgeführt wurde, ist sehr erfolgreich verlaufen.

Als Teil des EU-Projektes SHIVA, wurde für die Seereise ein Großteil der Kosten in dem EU- Projekt beantragt. Der BMBF-Antrag für die Expedition SO218- SHIVA beinhaltete die Reisekosten für zusätzliche, besonders für asiatische mitfahrende Wissenschaftler, sowie deren Logistik - und Verbrauchskosten, die im EU-Antrag nicht berücksichtigt waren. Es kam bei den beantragten Mitteln zwischen dem BMBF-Antrag „SO218-SHIVA“ und dem EU-Projekt SHIVA zu keinen Überschneidungen.

I.3. Planung und Ablauf des Vorhabens

Wissenschaftler aus 18 Einrichtungen in Europa und Asien erforschten im EU- Projekt SHIVA die natürlichen Ursachen für Ozonabbau, wobei das Helmholtz-Zentrum für Ozeanforschung Kiel (GEOMAR) die marinen Messungen der großen SHIVA-Kampagne im November 2011 koordinierte. Das Hauptarbeitsgebiet während der Seereise lag zwischen 0°/102°E und 14°N/120°E. Die Klimatologien beschreiben für den Winter in diesem Gebiet nordöstliche Winde mit mittleren horizontalen Windgeschwindigkeiten, die eine vom Schiff unkontaminierte Luftprobenahme ermöglichte. Durch das Gebiet wurde eine Route geplant, die den wissenschaftlichen Zielen entsprach und dabei nicht zu weit von der Borneo-Küste entfernt lag und nicht in chinesische, bzw. malaysisch-indonesische Gewässer vordrang. Die kontinuierliche Luft- und Meerwasserbeprobung fand in den Hoheitsgebieten Malaysias, Bruneis und der Philippinen statt. Über das Auswärtige Amt (Herr Mahrle) wurde am 10.Januar 2011 zusammen mit dem sogenannten EPU (Economic Planing Unit)-Proposal (verfasst vom SHIVA- Projektkoordinator Klaus Pfeilsticker) der diplomatische Antrag (Marine Scientific Research Application) an Malaysia eingereicht. Am 23. März 2011 wurde das Projekt im National Security Council von Malaysia beraten und grundsätzlich bewilligt. Am 10. Mai 2011 wurden die diplomatischen Anträge auf Meeresforschung an die deutschen Botschaften in Brunei und die Philippinen gesandt, die vor Antritt der Seereise alle bewilligt waren. Die Flug-Hoheitsgebiete sind von denen der marinen EEZ sehr verschieden, und Anträge für Fluggenehmigungen wurden für das Flugzeug von der DLR an die jeweiligen Staaten gestellt. In diesem Zusammenhang sei erwähnt, dass einem offiziellen Gesuch des BMBF um einen Begleitschutz - am 17. Februar 2011 über das Auswärtige Amt und die deutsche Botschaft in Kuala-Lumpur an Malaysia eingereicht- nicht stattgegeben wurde. Glücklicherweise kam es während der Forschungsssseereise zu keinerlei unliebsamen Begegnungen oder Zwischenfällen.
Vom 15. bis 29. November 2011 wurde die Expedition SO218 dann durchgeführt. Vom Starthafen Singapur aus operierte FS Sonne im Südchinesischen Meer und der Sulu See vor Malaysia, Brunei und den Philippinen und lief als Endhafen Manila (Philippinen) an. Das Schiff folgte einer Fahrtroute entlang der Schelfgewässer der West- und Nordküste Borneos, durch die tiefe Sulu See bis in Küstengewässer der Insel Luzon. Während der Fahrt wurden dreistündig Luft- und Wasserproben

gewonnen, die während zweier Tagesstationen am 18. und 21. November auf stündlichen Rhythmus vermehrt wurden. Es wurden zusätzlich an 14 Stationen ca. 40 Tiefenprofile mit der CTD und dem Kranzwasserschöpfer gefahren und mehr als 60 Radiosondierungen der Atmosphärenstruktur durchgeführt. So wurden atmosphärische und ozeanische Konzentrationen bromierter, jodierter und chlorierter Halogenkohlenwasserstoffe erhalten, um ihre marinen Emissionen berechnen zu können. Ebenso wurden physikalische Ozeanparameter, sowie Phytoplankton- und Zooplanktonspezies untersucht, um die Quellen der Verbindungen bestimmen zu können. Die ozeanischen Konzentrationen weiterer Spurengase wie Dimethylsulfid (DMS), Distickstoffoxid (N_2O) und Methan (CH_4), Kohlendioxid (CO_2) und Sauerstoff (O_2) wurden gemessen, um ihre Herkunft und Quellstärken in dieser Region sowie ihre Korrelationen mit den Halogenkohlenwasserstoffen zu analysieren. Meteorologische Parameter und atmosphärisches Ozon, sowie reaktive Halogenabbauprodukte, ebenso wie weitere atmosphärische natürliche und anthropogene Spurengase, vornehmlich als Verschmutzungsindikatoren wurden bestimmt.

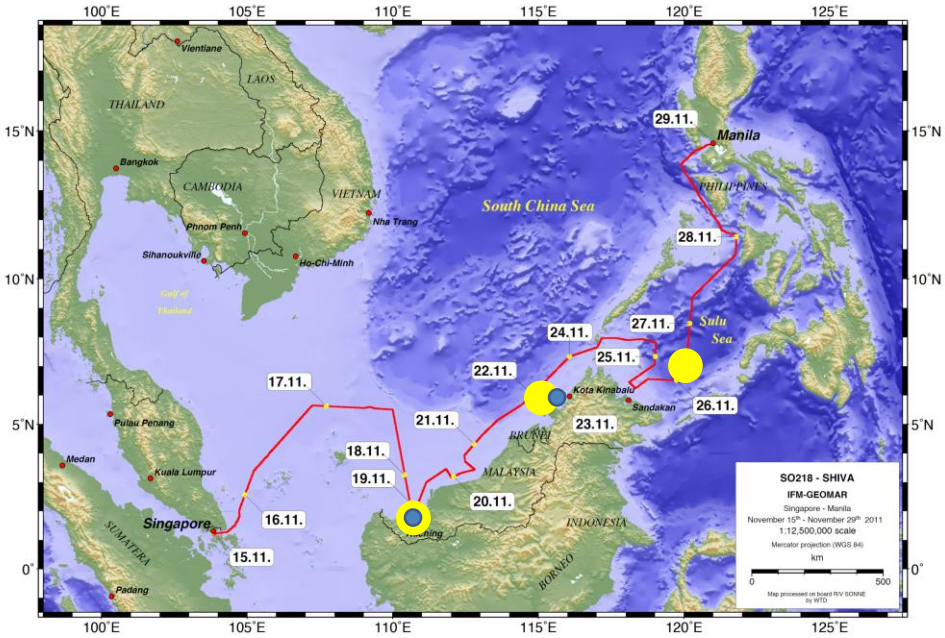


Abbildung 1: **SO218-FAHRTVERLAUF** FS Sonne Singapur-Manila (15-29 November 2011) mit Bootskontakten und Küstenprobenaustausch (blaue Kreise) und Überflüge von Falcon (gelbe Kreise).

DAS AN BORD DURCHGEFÜHRTE ARBEITSPROGRAMM:

- Kontinuierliche Meerwasserbeprobung mit eigenem Pumpsystem im hydrographischen Schacht zur Messung von Spurengasen, sowie hydrographischen und biologischen Parametern im Oberflächenwasser.
- Sammlung diskreter Luftproben auf dem Peildeck.
- Aerosolfilterproben der Atmosphäre auf dem Peildeck.
- Atmosphärenchemische und optische Messungen durch mehrere Sensoren auf Peildeck. Ballonaufstiege vom Hauptdeck des Schiffes.
- Messungen der Luft- und Meerwasserproben mit Gaschromatographie/ Massenspektrometriesystem (GC/MS).
- Massenspektrometrische Messungen der Atmosphäre in einem Laborcontainer auf dem Vordeck des Schiffes.
- In situ-Messungen von Ozean-optischen Eigenschaften und Phytoplankton.
- 11 flache und drei tiefe Stationen für CTD- und Wasserprobennahme.
- Koordination mit Flugzeugmessungen, des zeitgleich auf Borneo stationierten Forschungsflugzeuges DLR Falcon.
- Koordination des Treffens und Probenaustausches mit zwei küstennahen Booten

Für eine übersichtlichere Darstellung der Arbeiten während der Seereise wurden die TEILNEHMENDEN GRUPPEN in Arbeitsgruppen zusammengefasst:

	VW	Arbeitsgruppe	Teilnehmer	Teilnehmer	Funktion	Universität/ Institut	Methoden
	Verantwortliche/r Wissenschaftler/in (VW)	Nummer und Bezeichnung	Nachname	Vorname	Funktion	Universität	Methoden und Daten
	Schiff						meteorologische und ozeanographische Daten
			Quack	Birgit	leitende Wissenschaftlerin	IFM-GEOMAR	
		Beobachter Malaysia: Said Sapii, Beobachter Philippinen: Benjamin Z. Magura					
im Wasser	Quack	1a: Halogenierte Kohlenwasserstoffe (MS)	Hepach	Helmke	Studentin	IFM-GEOMAR	halogenierte Kohlenwasserstoffe in Wasser und Atmosphäre:
			Petrick	Gert	Techniker	IFM-GEOMAR	CH_3I, CH_2Cl_2, $CHCl_3$, CCl_4, (CH_3CCl_3), CH_2Br_2, (C_2HCCl_3),
		1b: Halogenierte Kohlenwasserstoffe (ED)	Qiang	Shi	Studentin	IFM-GEOMAR	$CHBrCl_2$, CH_2ClI, CH_2BrI, C_2Cl_4, $CHBr_2Cl$,
			Raimund	Stefan	Wissenschaftler	IFM-GEOMAR	$CHBr_3$, CH_2I_2
	Bracher	2a: Biologie; Pigmente	Altenburg Soppa	Mariana	Wissenschaftlerin	AWI- BREMERHAVEN	Pigmente, Bestrahlungsstärke, Strahlung
			Wiegmann	Sonja	Technikerin	AWI- BREMERHAVEN	Flowzytometrie,Chlorophyll-Fluoreszenz
			Cheah	Wee	Wissenschaftler	AWI- BREMERHAVEN	Mikroskopie; Fernerkundung
	Malaysia	2b: Biologie	Idid	Rizman	Wissenschaftler	U Malaya Kuala Lumpur	Biologie / ADCP/PAM/ Zooplanktonzusammensetzung
			Muhajid	Aazani	Wissenschaftlerin	UNIMAS Malaysia Sarawak	Biologie, (Satelliten-)fernerkundung, Molekularbiologie
	Phillippinen		Palermo	Joseph	Wissenschaftler	University of the Philippines Diliman	Biologie/Flow-Cam/ , Phytoplanktonzusammensetzung,
	Marandino	3a: OVO, C	Zindler	Cathleen	Student/in	IFM-GEOMAR	OVOC: Aceton, Acetaldehyde, Propanal, Butanal, Butanon
	Quack	3b: Ox, Nuts	Marandino	Christa	Studentin	IFM-GEOMAR	Nährstoffe und sauerstoff (+ Atmosphärenproben)
		3c: N_20, CH_4, DMS					ozeanische Spurengase (N_20, CH_4, DMS)
	Körtzinger	4: P_{CO2}, P_{O2}, S,T	Müller	Christian	Student	IFM-GEOMAR	P_{CO2}/ P_{OXYGEN};CTD (Temp., Sal.);FREON; Probennahmen Gasdruck: Druck aller Gase im Merrwasser, DIC, Alkalinität
in Luft	Krüger	5: Radiosonde	Krüger	Kirstin	Wissenschaftler/in	IFM-GEOMAR	Schiff und Flugzeugkoordination, Radiosonde (60)
			Immler	Franz	Wissenschaftler/in	IFM-GEOMAR	DISDROMETER, Regensensor (Niederschlag, Tröpfchengröße)
			Fuhlbrügge	Steffen	Student	IFM-GEOMAR	Co, Wasserdampf, O_3 Sonden (Cirruswolken, Feuchtigkeit)
	Atlas	6: Luftprobennahme	Wittke	Franziska	Studentin	IFM-GEOMAR	> 50 atmosphärische Spurengase: halogenierte KWs, Alkane (200) Zusammensetzung der Aerosole: Br, I, Nährstoffe, N_2O, CH_4,
	Pfeilsticker	7: CE- DOAS	Lampel	Johannes	Student	Uni Heidelberg	MAX DOAS: BRO, IO; Cavity ring down : IO
	Harris/ Kreher	8: µ- DIRAC	Kinzel	Julian	Wissenschaftler/in	Cambridge/NIWA/ IFM-GEOMAR	µ-DIRAC: kontinuierliche atmosphärische halogenierte KWs
	Schlager	9: CO, CO_2, CH_4, O_3	Sentian	Justin	Wissenschaftler/in	University Malaysia Sabah	PICARRO: CH_4, CO_2, O_3; CO
			Abdullah	Nur Aleesha	Wissenschaftler/in	Malaysian meteorologische Abteilung	
	Voigt	10a: CIMS, Br	Jurkat	Tina	Studentin	DLR	
		10b: IO, OH, Hox	Schäuble	Dominik	Wissenschaftler/in	DLR	CIMS: atmosphärische Spurengase Br, HBr. BrO
	Heard	10c: Containerinformation	Ingham	Trevor	Wissenschaftler/in	Uni Leeds	LIF: IO
			Bunyan	Hannah	Studentin	Uni Leeds	
	Baker	11: Aerosole				UEA Norwich	Chlor , Brom und Iodgehalt von Aerosolen

Tabelle 2: Arbeitsgruppeneinteilung auf SHIVA-Sonne (Singapur- Manila, November 2011).

Da mit FS Sonne nicht so nah an die Küsten (Fischerei, Bohrtürme, Piraterie) herangefahren werden kann (>20m Tiefe), und hohe Konzentrationen der kurzlebigen Verbindungen in Küstennähe erwartet wurden und besonders der Gradient zwischen küstennahen und offeneren Gewässern für weitere Modellrechnungen von Interesse waren, wurden mit Wissenschaftlern der ortsansässigen Universitäten in Kuching (UNIMAS/ Sarawak, Dr. Lim Po Teen), in Kota-Kinabalu (UMS/Sabah, Prof. Dr. Ann Anton) und in Kuala-Lumpur (UM, Prof. Phang Sew Moi) für einige Küstenstellen lokale Bootseinsätze durchgeführt. Auf diesen Bootseinsätzen sollten die Wissenschaftler alle 5km von der Küste entfernt Wasserproben nehmen, die dann bei einem kurzen Treffen zwischen FS Sonne und dem Universitätsboot ausgetauscht werden sollten. Im Gegenzug dazu sollten die ortsansässigen Wissenschaftlern Wasserproben von der offenen See erhalten. So wurden am 19. November 2011 während zweier Stunden küstennahe Proben beim Treffen mit einem örtlichen Boot der Universität in Kuching und am 22. November mit einem Boot der Universität Kota Kinabalu ausgetauscht. Die vorher geplanten Besuche der malaysischen Wissenschaftler an Bord von FS Sonne konnte an beiden Stationen aus Sicherheitsgründen nicht durchgeführt werden (starker Schwell und Unfallgefahr durch die Bauart der malaysischen Boote). FS Sonne wurde dreimal vom Forschungsflugzeug Falcon, das während der Kampagne in Miri (Borneo) stationiert war, zur Interkalibrierung und zur Verfolgung identischer Luftmassen tief überflogen (siehe Abbildung 1). Im Mai 2012 fand ein Auswertetreffen am GEOMAR in Kiel statt, auf dem gemeinsame Publikationen geplant und besprochen wurden.

I.4. Stand der Wissenschaft und Technik: Die Bedeutung von natürlichen Halogenverbindungen für das stratosphärische Ozon

Die im Frühjahr über den Polen auftretende chemische Ozonabnahme wird hauptsächlich durch anthropogen emittierte Chlor- und Bromfluorkohlenwasserstoff verursacht. In den mittleren Breiten bestimmt ebenfalls die Zufuhr von Halogenen den stratosphärischen Ozonhaushalt und die starke Ozonabnahme. Neuen Erkenntnissen zur Folge spielen hier auch natürliche Halogenkohlenwasserstoffe eine Rolle (Salawitch et al., 2005, 2006; WMO, 2007). Neue Ergebnisse zeigen, dass in der unteren Stratosphäre höhere Konzentrationen reaktiven Broms auftreten, als durch die Emissionen der langlebigen, meist anthropogenen Spurengase erklärt werden können (Dorf et al., 2005, Dorf et al., 2006, WMO 2011). Unter Berücksichtigung von 5 ppt zusätzlichem reaktiven Brom kann in Chemietransportmodellen (CTM) die beobachtete Ozonabnahme in mittleren Breiten simuliert werden (Salawitch et al., 2005; WMO, 2011; Sinnhuber et al 2009). Als Hauptverdächtige für dieses Brom gelten ozeanische Emissionen kurzlebiger Bromverbindungen, insbesondere von Bromoform- ($CHBr_3$) und Dibrommethan (CH_2Br_2) (Quack und Wallace, 2003) (Abbildung 2), die laut Modellstudien einen großen Anteil an den +5 pptv Totalbromgehalt in der Stratosphäre haben (Hossaini et al 2010; Gettelman et al 2009; Aschmann et al 2009) oder sogar komplett die zusätzlichen 5 pptv Brom in der Stratosphäre verursachen (Liang et al.,2009) können.

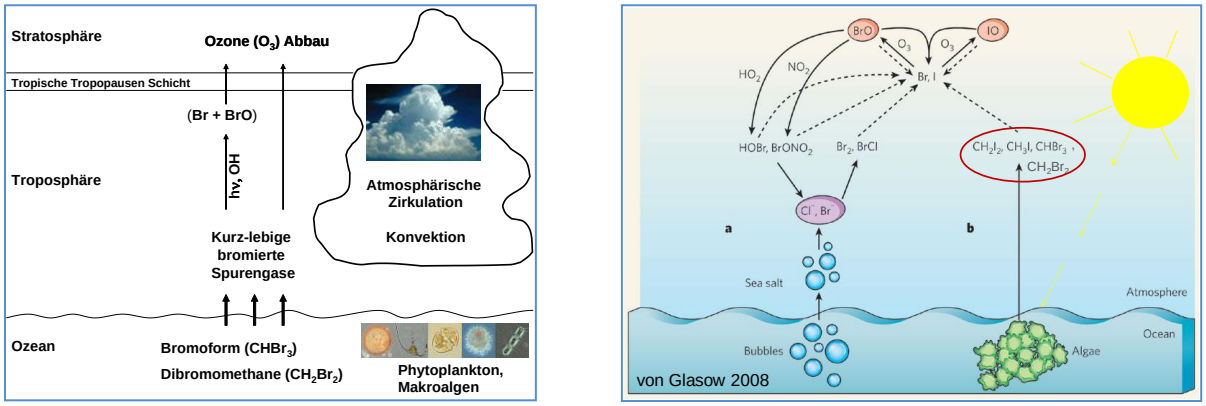


Abbildung 2: Ozeanische Quellen kurzlebiger Halogenkohlenwasserstoffe und ihre Wirkungen in der Atmosphäre. Rechte Abbildung von Glasow (2008).

Ein großer Anteil der ozeanischen Emissionen befinden sich in tropischen Regionen, wobei stark lokalisierte Quellregionen in Küstennähe, im äquatorialen Atlantik und im nordwestafrikanischen Auftriebsgebiet vor Mauretanien identifiziert wurden (Quack et al., 2004; Quack et al., 2007a; Butler et al., 2007). Die ozeanischen Quellen sind weitgehend unerforscht, werden jedoch im Allgemeinen mit biologischer Produktion in Verbindung gebracht. Eine wichtige Produzentenrolle von bromierten Verbindungen spielen küstennahe Makroalgen (Carpenter und Liss, 2000), jedoch auch die Produktion der Hauptverbindung Bromoform ($CHBr_3$) in der Oberfläche des offenen Ozeans, wie es im tropischen und subtropischen Atlantik gefunden wurde (Quack et al., 2004, 2007a, b). Die Beziehung der Produktion zur Phytoplanktonverteilung ist bis heute unklar. Als Faktoren, die die ozeanischen Konzentrationen beeinflussen, kommen unter anderem der Küstenabstand und die Wassertiefe, die Spezieszusammensetzung und Lebenszyklen des Phytoplankton, Wassertemperatur sowie Vermischung und Gasaustausch in Frage.

Auch jodierte Kohlenwasserstoffe, wie Jodmethan (CH_3I) können eine Bedeutung für die Ozonchemie (Solomon et al., 1994, Vogt et al., 1999, Tegtmeier et al., 2013) und für weitere chemische Prozesse in der Atmosphäre haben (Kolb, 2002, O'Dowd et al., 2002). Die Hauptquelle für atmosphärisches Jodmethan ist die Emission aus dem Ozean, wobei die Produktionswege im Ozean nur zu 10%

aufgeklärt und photochemische sowie biologische Ursachen haben können (Richter und Wallace, 2004). Simultane Messungen der halogenierten Spurengase in der Atmosphäre und im Ozean sind rar (WMO, 2011) und bisher nur in wenigen Veröffentlichungen zu finden, an denen wir maßgeblich beteiligt sind. Daher besitzen wir ausgewiesene Expertise in diesem ozeanischen, atmosphärischen und analytischen Wissenschaftsbereich. Die simultanen Messungen sind notwendig, um die ozeanischen Emissionen berechnen zu können, von denen große Mengen durch Konvektionsprozesse in die obere Atmosphäre transportiert werden können. Eine Messkampagne, die sowohl die ozeanischen Emissionen mittels der Untersuchungen auf einem Forschungsschiff, als auch ihre Transportwege durch die Atmosphäre mit Flugzeugmessungen bis in die Stratosphäre untersucht, war bisher noch nicht durchgeführt worden.

Die tropische Tropopausenschicht (Tropical Tropopause Layer: TTL) in ca. 14 -18 km Höhe ist das Eintrittstor für Spurengase in die Stratosphäre (Abbildung 3).

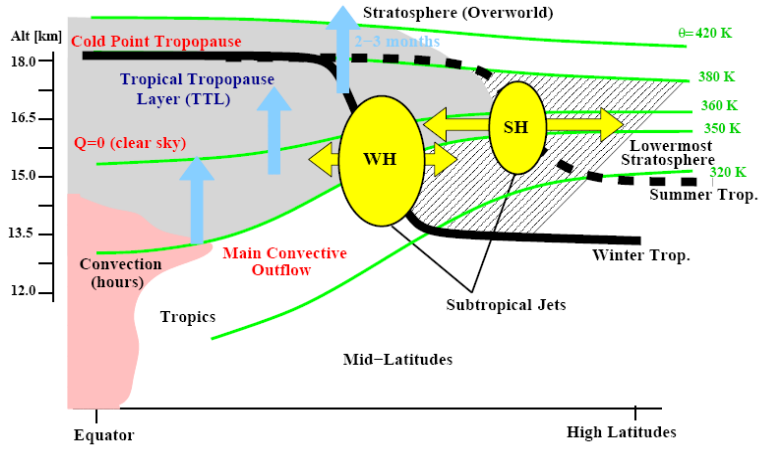


Abbildung 3: Die atmosphärische Zirkulation von Spurengasen. Schema von Transportprozessen, die die Tropische Tropopause mit der Stratosphäre verbinden (Konopka et al., 2007).

Die dynamischen und mikrophysikalischen Prozesse in der TTL, die die konvektionsgetriebene Troposphäre, mit zum Teil sehr schnellen Aufstiegsgeschwindigkeiten (einige m/s) von der darüber liegenden Stratosphäre (15-50 km Höhe) mit langsamen, strahlungsgetriebenen Vertikalbewegungen (mm/s) trennt, sind von großer Bedeutung für den Spurengaseintrag und die chemische Zusammensetzung der Stratosphäre. Mit neuen Methoden konnten realistischere Verweildauern in der TTL berechnet werden (Krüger et al. 2008, 2009), die zu einer besseren Abschätzung der absoluten Transportwege der sehr kurzlebigen Gase führen können (WMO, 2011). Dadurch ergibt sich eine genauere Aussage über die Eintragsorte von Luftmassen in die Stratosphäre (Krüger et al, 2008) und über die Form der Spurengase, die die Stratosphäre entweder als sog. Quell- oder Primärgase (mit Lebenszeiten von einigen Wochen) oder sog. Sekundärgase erreichen, die durch homogene und heterogene atmosphärenchemische und mikrophysikalische Prozesse innerhalb von Wolken aus den Quellgasen entstehen (WMO, 2007). Der westliche Pazifik wurde als Sektor für den Haupteintragsort von Luftmassen innerhalb der TTL im nordhemisphärischen Winter identifiziert (Fueglistaler et al, 2004; Bonazzola und Haynes 2004; Krüger et al, 2008). In diesem Gebiet sind auch die schnellen Aufstiegszonen der vorherrschenden tropischen Konvektionstürme lokalisiert (Abbildung 4).

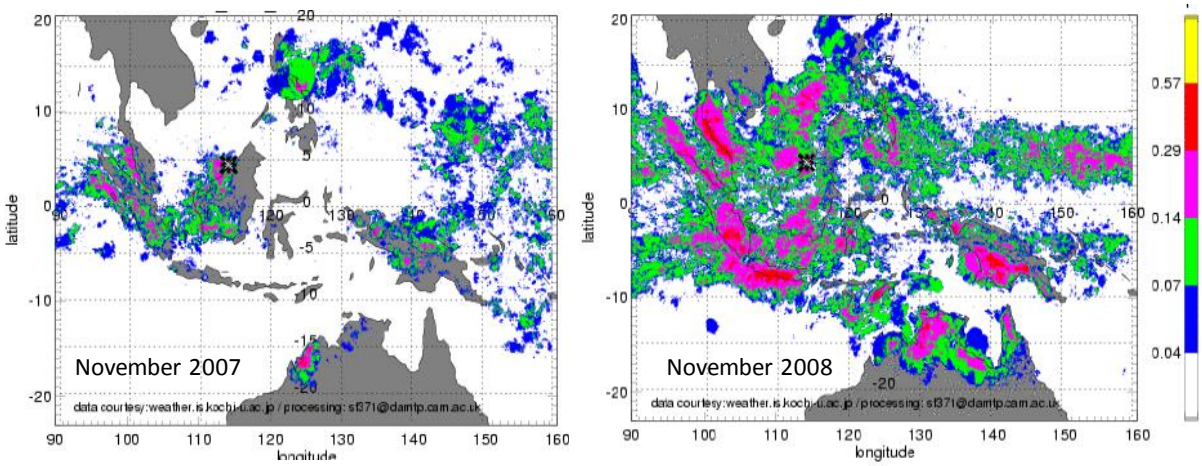
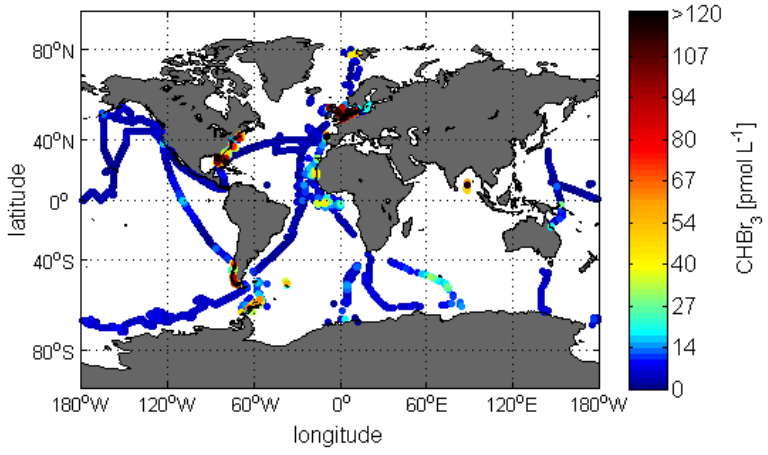


Abbildung 4: Beispiel des vertikalen Luftmassentransports in die die tropische Tropopausenschicht im November der beiden Jahre 2007/2008. Dargestellt ist die Konvektionswahrscheinlichkeit p. (Fueglistaler personal communication).

Marine Emissionen in der Nähe des Maritimen Kontinent (Bezeichnung des inselreichen Gebietes des tropischen Südwest Pazifik, 90°E - 150° E) waren unbekannt, da es aus diesem Gebiet bisher keine ozeanischen Messungen gab (Abbildung 5). Es konnte vermutet werden, dass die Gewässer um den west-pazifischen maritime Kontinent durch seinen Reichtum an makroalgenreichen Küsten und Organismen in Korallenriffen, von denen viele durch ihren Enzymgehalt an Haloperoxidasen (Gribble, 2000) als mögliche Halogenkohlenwasserstoffproduzenten in Frage kommen und durch seine hohen Wassertemperaturen eine bedeutende Quellregion für die Atmosphäre, sowohl für die bromierten Verbindungen, als auch für die anderen Verbindungen darstellt .



.

Abbildung 5: Messungen von Bromoform im Meerwasser (Daten aus http://halocat. geomar.de, initiiert in May 2009).

Resultierend aus den allerersten Messungen dieser Verbindungen im Westpazifik (140°-150°E) auf einem Transit mit FS Sonne über 60 Breitengrade (TransBrom) im Jahr 2009 (Quack und Krüger, 2010, Krüger und Quack, 2013) bestätigte, dass der Westpazifik ein Haupteintragsgebiet für kurzlebige marine Bromverbindungen in die Stratosphäre darstellt (Tegtmeier et al., 2012). Aus dem globalen Hauptkonvektionsgebiet und dem Haupteintragsort troposphärischer Luftmassen in die Stratosphäre im tropischen Westpazifik existierten bisher nur die ozeanischen Messungen dieser ersten Sonne Expedition TransBrom-Sonne (Oktober, 2009, Abbildung 5), die während einer niedrigeren

Aktivität der atmosphärischen Konvektion, in einem weitgehend biologisch ärmeren und küstenfernen Seegebiet des Westpazifik stattfand (Quack und Krüger, 2010, Krüger und Quack, 2013). Nun sollte die SHIVA-SONNE Kampagne in der Hauptkonvektionszeit in biologisch reicheren und küstennäheren Gewässern durchgeführt werden, die zudem auch zu Beginn der Hauptkonvektionszeit lag.

In der Schiffskampagne und anschließender Auswertung und Modellierung der Ergebnisse sollte in Zusammenarbeit mit atmosphärischen Dynamikern und Chemikern geklärt werden, wie stark der Beitrag der dortigen Emissionen am Halogengehalt in der Stratosphäre ist. Weiterhin sollten die biologischen Quellen auch für andere reaktive Spurengase in der Atmosphäre bestimmt werden. Aus dem Bereich des „maritimen Kontinent“ lagen bisher keine ozeanischen Messungen klimarelevanter Spurengase vor. Die kombinierte internationale Messkampagne mit einem großen und mehreren kleinen Forschungsschiffen, einem Forschungsflugzeug sowie gleichzeitige Messungen vom Erdboden und vom All aus, wie sie im Westpazifik für den Herbst 2011 zur Untersuchung der ozeanischen Emissionen an halogenierten Kohlenwasserstoffen, ihren atmosphärischen Transportwegen sowie die Auswirkung dieser Verbindungen für die globale Ozonschicht im Rahmen des EU-SHIVA Projektes geplant war, und erfolgreich durchgeführt wurde, ist bisher weltweit einmalig.

Literatur

Aschmann, J., B. M. Sinnhuber, E. L. Atlas, and S. M. Schauffler (2009), Modeling the transport of very short-lived substances into the tropical upper troposphere and lower stratosphere, Atmos. Chem. Phys. 9, 9237 - 9247.

Bonazzola, M., and P. H. Haynes (2004), A trajectory-based study of the tropical tropopause region, J. Geophys. Res., 109, D20112, doi:10.1029/2003JD004356.

Butler, J. H., D. B. King, J. M. Lobert, S. A. Montzka, S. A. Yvon-Lewis, B. D. Hall, N. J. Warwick, D. J. Mondeel, M. Aydin, and J. W. Elkins (2007), Oceanic distributions and emissions of short-lived halocarbons, Global Biogeochem. Cycles, doi:10.1029/2006GB002732.

Carpenter, L. J., and P. S. Liss (2000), On temperate sources of bromoform and other reactive organic bromine gases, Journal of Geophysical Research-Atmospheres, 105, 20539 - 20547.

Dorf, M., H. Bösch, A. Butz, C. Camy-Peyret, M. P. Chipperfield, A. Engel, F. Goutail, K. Grunow, F. Hendrick, S. Hrechanyy, B. Naujokat, J.-P. Pommereau, M. Van Roozendael, C. Sioris, F. Stroh, F. Weidner, and K. Pfeilsticker (2005), Balloon-borne stratospheric BrO measurements: comparison with Envisat/SCIAMACHY BrO limb profiles, Atmos. Chem. Phys., 6, 2483 - 2501.

Dorf, M., J. H. Butler, A. Butz, C. Camy-Peyret, M. P. Chipperfield, L. Kritten, S. A. Montzka, B. Simmes, F. Weidner, and K. Pfeilsticker (2006), Long-term observations of stratospheric bromine reveal slow down in growth, Geophys. Res. Lett., 33, doi: 10.1029/- 2006GL027714.

Dorf, M., A. Butz, C. Camy-Peyret, M. P. Chipperfield, L. Kritten, and K. Pfeilsticker (2008), Bromine in the tropical troposphere and stratosphere as derived from balloon-borne BrO observations, Atmos. Chem. Phys., 8, 7265 - 7271.

Gettelman, A., P. H. Lauritzen, M. Park, J. E. Kay (2009), Processes regulating short-lived species in the tropical tropopause layer, J. Geophys. Res., 114, D13303, doi:10.1029/2009JD011785.

Fueglistaler, S., H. Wernli, and T. Peter (2004), Tropical troposphere-to-stratosphere transport inferred from trajectory calculations, J. Geophys. Res., 109, D03108, doi:10.1029/2003JD004069.

Kolb, C.E. (2002), Iodine’s air of importance, Nature, 417, 597 – 598.

Konopka P., G. Günther, R. Müller, F. H. S. dos Santos, C. Schiller, F. Ravegnani, A. Ulanovsky, H. Schlager, C. M. Volk, S. Viciani, L. L. Pan, D.-S. McKenna, and M. Riese (2007), Contribution of mixing to upward transport across the tropicaltropopause layer (TTL) Atmos. Chem. Phys., 7, 3285 – 3308.

Krüger, K., S. Tegtmeier, and M. Rex (2008), Long-term climatology of air-mass transport through the Tropical Tropopause Layer (TTL) during NH winter, Atmos. Chem Phys., 8, 813 – 823.

Krüger, K., S. Tegtmeier, and M. Rex (2009), Residence Time in the TTL, Atmos. Chem. Phys., 9, 3985 6717 – 6725.

Krüger, K. and Quack, B.(2013) Introduction to special issue: the TransBrom Sonne expedition in the tropical West Pacific, Atmos. Chem. Phys., 13, 9439-9446, doi:10.5194/acp-13-9439-2013.

Liang, Q., R. S. Stolarski, S. R. Kawa, J. E. Nielsen, J. M. Rodriguez, A. R. Douglass, D. R. Blake, E. L. Atlas, and L. Ott, (2009), Finding the missing stratospheric Bry: a global modeling study of CHBr3 and CH2Br2, Atmos. Chem. Phys. Discuss., 9, 23623-23664.

O'Dowd, C. D., J. L. Jiminez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffmann (2002), Marine aerosol formation from biogenic iodine emissions, Nature, 417, 632 – 636.

Quack, B., and E. Suess (1999), Volatile halogenated hydrocarbons over the western Pacific between 43° and 4°N, J. Geophys. Res., 104, D1, 1663 – 1678.

Quack, B., and D. W. R. Wallace (2003), Air-sea flux of bromoform: Controls, rates, and implications, Global Biogeochemical Cycles, 17.

Quack, B., E. Atlas, G. Petrick, V. Stroud, S. Schauffler, and D. W. R. Wallace (2004), Oceanic bromoform sources for the tropical atmosphere, Geophysical Research Letters, 31.

Quack, B., E. Atlas, G. Petrick, and D. W. R. Wallace (2007), Bromoform and dibromomethane above the Mauritanian upwelling: Atmospheric distributions and oceanic emissions, J. Geophys. Res., 112, D09312, doi:10.1029/2006JD007614.

Quack, B., I. Peeken, G. Petrick, and K. Nachtigall (2007), Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling. J. Geophys. Res., 112, C10006, doi: 10.1029/2006JC003803.

Quack, B, and K. Krüger eds (2010), FS Sonne Fahrtbericht/Cruise report TransBrom Sonne, Tomakomai, Japan- Townsville, Australia, 09.10.-24.10.2009, IFM-GEOMAR Report No. 37, ISSN Nr.: 1614 – 6298.

Richter, U., and D. W. R. Wallace (2004), Production of methyl iodide in the tropical Atlantic Ocean, Geophys. Res. Lett., 31, L23S03, doi:10.1029/ 2004GL020779.

Salawitch, R. J. (2006), Atmospheric chemistry - Biogenic bromine, Nature, 439, 275 - 277.

Salawitch, R. J., D. K. Weisenstein, L. J. Kovalenko, C. E. Sioris, P. O. Wennberg, K. Chance, M. K. W. Ko, and C. A. McLinden (2005), Sensitivity of ozone to bromine in the lower stratosphere, Geophysical Research Letters, 32.

Sinnhuber, B.-M., N. Sheode, M. Sinnhuber, M. P. Chipperfield, and W. Feng (2009), The contribution of anthropogenic bromine emissions to past stratospheric ozone trends: a modelling study, Atmos. Chem. Phys., 9, 2863 – 2871.

Solomon, S., R. R. Garcia, and A. R. Ravishankara, (1994) On the role of iodine in ozone depletion, J. Geophys. Res., 99, D10, 20,491 – 20,499.

Tegtmeier, S., Krüger, K., Quack, B., Atlas, E. L., Pisso, I., Stohl, A., and Yang, X., (2012) : Emission and transport of bromocarbons: from the West Pacific ocean into the stratosphere, Atmos. Chem. Phys., 12, 10633-10648, doi:10.5194/acp-12-10633-2012

Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A., Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F. (2013): The contribution of oceanic methyl iodide to stratospheric iodine, Atmos. Chem. Phys. Discuss., 13, 11427-11471, doi:10.5194/acpd-13-11427-2013.

Vogt, R., R. Sander, R. von Glasow, and P. J. Crutzen (1999), Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, J. Atmos. Chem., 32, 375 – 395.

Von Glasow, R. (2008), Atmospheric chemistry: Sun, sea and ozone destruction. Nature, 453 (7199). pp. 1195 - 1196.

WMO (2007), Scientific assessment of ozone depletion: 2006, Global ozone research and monitoring project, 498 pp, World Meteorological Organization, Geneva.

WMO (2011), Scientific assessment of ozone depletion: 2010, Global ozone research and monitoring project, 112 pp, World Meteorological Organization, Geneva.

Yokouchi, Y., H. Li, T. Machida, S. Aoki, and H. Akimoto (1999), Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform, J. Geophys. Res., 104(D7), 8067–8076.

I.5. ZUSAMMENARBEIT MIT ANDEREN STELLEN (NATIONALE UND INTERNATIONALE EINBINDUNG)

Die Ausfahrt SO218 (SHIVA-Sonne), auf der ein großer Teil der Zusammenarbeitskosten mit den malaysischen Wissenschaftlern vom BMBF unterstützt wurde, war Bestandteil des EU-Projektes SHIVA (Stratospheric halogens in a varying atmosphere, Grant: 226224).

Teilnehmer der Fahrt und auch des Projektes SHIVA sind an weiteren nationalen und internationalen Projekten beteiligt, von denen einige im Folgenden aufgelistet sind:

- EU: SCOUT-O3 (Stratospheric-Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere-O3)
- EU: COST-Action 735 (Tools for Assessing Global Air-sea fluxes of Climate Gases)
- SPARC (Stratospheric Processes And their Role in Climate)
- CCMVal (coupled Chemistry-Climate Model Validation/ Stratospheric Processes and their Role in Climate (CCMVal/ SPARC)-Initiative)
- IGBP/ IGAC/ SOLAS (Surface Ocean Lower Atmosphere Study)
- BMBF-Verbundprojekt: SOPRAN (Surface Ocean Processes in the Anthropocene)
- IGAC/SOLAS/ HIT (Halogens in the Troposphere)
- WGL-Projekt: TransBrom,
- BMBF-Programm ROMIC: Role of the middle atmosphere in climate

An der Forschungsreise nahmen neben den an Bord befindlichen Wissenschaftlern, unter anderem folgende Institutionen und Partner mit der aufgeführten Beteiligung als hauptverantwortliche Wissenschaftler teil:

AWI BREMERHAVEN Alfred-Wegener-Institute für Polar und Meeresforschung, Fachbereich. Klima. Bussestraße 24, D- 27570 Bremerhaven.de, email: Astrid.Bracher@awi.de

Prof. Dr. Astrid Bracher, Phytooptics und Planktongemeinschaften

Dr. Rüdiger Röttgers (GKSS) Satellitenfernerkundung

Dr. Cecile Dupouy, (Centre d'Océanologie de Marseille) Ozeanoptik

DLR Deutsches Zentrum fuer Luft-und Raumfahrt (DLR), Oberpfaffenhofen, D-82234 Wessling, email: tina.jurkat@dlr.de, hans.schlager@dlr.de

Dr. Hans Schlager, Flugzeugkoordination und Tracer Experiment

GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel , Düsternbrooker Weg 20, D-24105 Kiel, Tel: +431 6004206, Fax: +431 6004205, email: bquack@ geomar.de; kkrueger@geomar.de

Prof. Dr. Doug Wallace (now at Halifax) - jodierte Halogenkohlenwasserstoffe

Dr. Carsten Schirnick (GEOMAR) - Datenbanken und Datenmanagement

Prof. Dr. Arne Körtzinger (GEOMAR)- gelöstes CO_2 / O_2/ Gesamtgas

Dr. Hermann Bange (GEOMAR)- Spurengase im Ozean DMS, N_2O, CH_4

IUP BREMEN Institut für Umweltphysik, Universität Bremen, Otto-Hahn-Allee 1, D-28359 Bremen, Deutschland, folkard@iup.physik.uni-bremen.de

Prof. Dr. John P. Burrows (Universität Bremen) Satellitenfernerkundung

IUP HEIDELBERG Institut für Umweltphysik, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, email: johannes.lampel@iup.uni-heidelberg.de

Prof. Dr. Ulrich Platt (Universität Heidelberg)-MAX DOAS-reaktive Spurengase

Prof. Dr. Klaus Pfeilsticker (Universität Heidelberg)-SHIVA Projektkoordinator

MMD Malaysian Meteorological Department, Jabatan Meteorologi Malaysia, Kementerian Sains, Teknologi dan Inovasi, Nur Aleesha Abdullah, email: aleesha@met.gov.my

NHD-Malaysia National Hydrographic Centre-Malaysia, Comannder Zaid Sapii, email: zaidsapii@gmail.com

NIWA Lauder, Central Otago, New Zealand, Karin Kreher,

Dr. Karin Kreher (NIWA/Lauder- New Zealand),

PHILIPPINE-NAVY ENS Benjamin Zambrano Magura, email: mantarayz12@yahoo.com

RSMAS MIAMI Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, email: eatlas@rsmas.miami.edu

Prof. Dr. Elliot Atlas (RSMAS, Miami)- Atmosphärische Spurengase aus Kanistern

UEA University of East Anglia, Norwich, NR4 7TJ, UK, email: alex.baker@uea.ac.uk

Dr. Alex Baker (UEA), Aerosole

UM Institute of Biological Sciences, Faculty of Science, 50603 Kuala Lumpur, Dr. Mohammed Rizman Idid, email: rizman@um.edu.my

Prof. Phang Siew Moi (UM Kuala-Lumpur, Malaysia) - Küstenboote und Biologie

Prof. Azizan Abu Samah (UM, Kuala-Lumpur, Malaysia) - Projektkoordination

UM SABAH Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu, Sabah, email: aanton@ums.edu.my

Prof. Ann Anton (UMS Kota-Kinabalu, Malaysia) - Küstenboote und biologische Arbeiten

UNI LEEDS School of Chemistry, University of Leeds, LS2 9JT, UK, email: t.ingham@leeds.ac.uk

UCAM University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, neil@atm.ch.cam.ac.uk

UNIMAS Department of Aquatic Science, Faculty of Resource Science & Technology, University Malaysia Sarawak, 94300 Kota Samarahan, Sarawak Malaysia, Aazani Mujahid, email: maazani@frst.unimas.my

Dr. Lim Po Teen (UNIMAS Kuching, Malaysia) - Küstenboote und biologische Arbeiten

UNI MAINZ Institute for Analytical Chemistry, D-55128 Mainz, Thorsten Hoffmann, Ru-Jin, Huang, email: rujin@uni-mainz.de

UPHI Biological Oceanography and Modeling of Ecosystem Lab., The Marine Science Institute, University of the Philippines, Diliman, Quezon City, 1101 Philippines, email: jaydeepalermo@gmail.com

weitere Projekte und Partner auf der SHIVA-homepage: http://shiva.iup.uni-heidelberg.de/links.html

Die Forschungsfahrt war ein wesentlicher Bestandteil des EU-Projektes SHIVA, dass im Rahmen des 7. Forschungs Rahmenprogramm der EU (SHIVA- Halogen Impacts in a Varying Atmosphere) die koordinierte Probennahme im tropischen West-Pazifik auf einem Forschungsschiff mit dem gleichzeitigen Einsatz eines Forschungsflugzeuges vorsah. Es fand eine enge Kooperation mit Wissenschaftlern des GEOMAR im Rahmen des BMBF-Verbundprojektes SOPRAN statt, die sich mit den ozeanischen Emissionen klimarelevanter Spurengase beschäftigen, da es aus diesem Ozeangebiet bisher kaum Messdaten gibt. Aufgrund der Einmaligkeit des Forschungsvorhabens bestand großes Interesse von Wissenschaftsgruppen sich an der Schiffskampagne im tropischen Westpazifik zu beteiligen, die zu einem über das Kernthema hinausreichenden Erfolg der Forschungsseereise beigetragen haben.

II. 1. VERWENDUNG DER ZUWENDUNG UND DAS ERZIELTE ERGEBNIS

Die SO218 Fahrt des Forschungsschiffes SONNE führte vom Starthafen Singapur, Abfahrt am 15.11.2011, bis nach Manila, Philippinen, Ankunft am 29.11.2011 (Abbildung 1). Alle Luftfrachten, Chemikalien und der bestellte flüssige Stickstoff wurden bis kurz vor Abfahrt in Singapur pünktlich geliefert. Somit konnte die Zeit im Hafen gut genutzt werden, um fast alle Instrumente dort aufzubauen. Der unermüdliche Einsatz der 25 Wissenschaftler an Bord, die von der Besatzung tatkräftig unterstütz wurden, ermöglichte es, dass bereits beim Auslaufen die meisten der 70 Mess-, Analyse- und Probenahmesysteme liefen, die einen einmaligen Datensatz produzierten, da in diesen Gewässern die meisten der auf SO218 untersuchten Parameter (unterschiedlichste Spurengase und physikalische Eigenschaften in Atmosphäre und Ozean, sowie biologische Eigenschaften des Wassers) noch nie untersucht worden waren.

Die Instrumente konnten schon beim Einlaufen in malaysische Gewässer vier Stunden nach Abfahrt in Singapur erste Daten aufzeichnen. Nach sechzehn Stunden Fahrtzeit führte die SO218 Route über einen Nordschlenker durch Indonesisches Gewässer, in denen keine Wasserproben gewonnen wurden, zur malaysischen Westküste von Borneo. Nach einer Tagestation trafen wir, wie verabredet am Samstag, den 19. November in der Mittagszeit ein lokales Fischerboot, besetzt mit vierzehn malaysischen, deutschen und englischen Wissenschaftlern und einem Fernsehteam (Abbildung 6). Seegangsbedingt konnte das kleine Fischerboot leider nicht längsseits gehen, so dass die Gäste nicht an Bord kommen konnten. Die Proben von fünf küstennahen Stationen konnten jedoch erfolgreich

ausgetauscht werden und wurden an Bord dann direkt auf biologische und chemische Parameter untersucht, um den Gradienten der Spurengaskonzentrationen zwischen offener See und Schelfgebiet zu bestimmen.

Abbildung 6: Küstenboot mit malaysischen Kollegen aus Kuching mit küstennah gewonnenen Proben.

Gleichzeitig überflog das Forschungsflugzeug der DLR (Deutsche Luft- und Raumfahrt) FALCON dessen Standort extra für diese Kampagne nach Miri auf Borneo verlegt wurde, die Sonne (Abbildung 7) und beprobte die Atmosphäre im Tiefflug neben der SONNE, etwa in gleicher Höhe, in der an Bord auch Spurengase aus der marinen Grenzschicht beprobt wurden.

Abbildung 7: Grenzschichtmessungen von Falcon und Überflug vor Kuching (Fotos von Torsten Bierstedt und Johannes Lampel).

Auch in Kota Kinabalu konnten küstennahe Proben am 22. November an Bord genommen werden, wobei auch dieses Mal der Seegang und die Bauart des Bootes ein sicheres Anlegen an der SONNE verhinderte. Beim zweiten Besuch der FALCON am 22. November 2011 wurde im Tiefflug wieder nahtlos an unsere Probenahme angeschlossen, während beim dritten Besuch im Nordosten Borneos Profile in der oberen Troposphäre, ohne Sichtkontakt mit Sonne geflogen wurden (Abbildung 7).

Während der dreizehneinhalb Tage dauernden Reise wurden rund um die Uhr in ein bis dreistündigem Rhythmus Wasser-, Luft-, Phyto- und Zooplanktonproben untersucht, sowie mehrere chemische und physikalischen Parameter von Atmosphäre und Meerwasser kontinuierlich aufgezeichnet. Auf 14 Stationen wurden 26 CTD Profile gefahren und 40 Außenbordseinsätze von Lichtmessinstrumenten und Planktonnetzen durchgeführt. Mehr als 3000 Wasserproben wurden gewonnen, in denen mehr als 40 verschiedene chemische und biologische Parameter- entweder direkt an Bord oder später in den

Heimatlaboren analysiert wurden. Mit 73 Radio- und 6 Ozonsonden, 400 Kanister- und Direktluftproben, sowie 9 kontinuierlich messenden optischen Systemen und Massenspektrometern wurde der Spurengasgehalt der Luft untersucht.

Die gewonnen Daten führten schon zu interessanten Ergebnissen (Anhang: Report 1-14 (24 Reports) gemeinsamen Auswertungen, Präsentationen und Publikationen (siehe II.6) und bilden auch weiterhin eine gute Grundlage für zukünftige Arbeiten (II.4). Im Folgenden wird eine Übersicht in deutscher Sprache über die Ergebnisse der beteiligten Arbeitsgruppen gegeben, deren ausführliche Berichte (Reports 1 bis 14, 24 Berichte) in englischer Sprache im Anhang zu finden sind. Diese Art der Präsentation wurde gewählt, um dem internationalen Charakter der Expedition Rechnung zu tragen und eine Art Abschlussdarstellung für alle an der Seereise beteiligten Gruppen zu erhalten, die weitere gemeinsame Auswertungen und Kooperationen unterstützen soll. Am 15. September wurde auch der endgültige Abschlussbericht für das EU-Projekt SHIVA in Brüssel eingereicht, in den Ergebnisse dieser Arbeiten einflossen.

Die regelmäßigen Luftanalysen und Radiosondenaufstiege an Bord der Sonne (**Anhang Report 5**) die eine eher spurengasarme Luft mit Kontaminationsereignissen zeigten (**Anhang Report 6,8,9,10a**). wurden durch eine intensive Analyse ozeanischer Parameter ergänzt. Die Analyse der marinen Spurengase in der Wassersäule zeigte erhöhte Konzentrationen der jodierten und bromierten Verbindungen (**Anhang Report 1**). Beide Tatsachen führen bei einer variablen Windgeschwindigkeit meist zu einem erhöhten Fluss der Verbindungen aus dem Meerwasser (**Anhang Report1**). Aufgrund der starken konvektiven Aktivität wurden schnelle und starke vertikale Transporte der Luftmassen in der marinen Grenzschicht bis in die Stratosphäre modelliert (**Anhang Report 14)** und gemessen (**Anhang Report 10b**), die bestätigten, dass die Region Quellen mariner halogenierter Spurengase für die Stratosphäre besitzt. Die Tiefenprofile des Meerwassers an den Stationen zeigten große Unterschiede in der Schichtung, als auch in der Tiefe und relativen Lage des Chlorophyllmaximums. Dadurch konnten Aussagen über die Herkunft der marinen halogenierten Spurengase getroffen werden (**Anhang Report 1**).

Mittels zweier unabhängiger Messsysteme (Purge- und Trap Gaschromatographie) wurden die marinen und die atmosphärischen Konzentrationen von Jodomethan, Dichlormethan, Chloroform, 1,1,1 – Trichlorethan, Tetrachlorkohlenstoff, 1,1,2 – Trichloroethen, Dibrommethan, Dichlorobrom-methan, Chlorjodmethan,1,1,2 –Trichlorethan, Dibromchlormethan, Brojodomethan, Bromoform, Dijodmethan an Bord der Sonne analysiert. Die Ergebnisse zu den **Halogenierten Kohlenwasser-stoffen in Meerwasser und Atmosphäre (Dr. Birgit Quack, Dr. Stefan Raimund, Helmke Hepach, Qiang Shi, Gert Petrick)** zeigen unter anderem generell hohe Konzentrationen brom- und jodhaltiger Verbindungen im Wasser, die in den flachen Schelfregionen und nah den Küsten stellenweise stark erhöht waren und ihre Quellen in Küstennähe und unterhalb der ozeanischen Deckschicht besaßen (**Anhang Report 1**). Dadurch dass die Gehalte der Spurenstoffe in der Atmosphäre eher niedrig waren, war das warme Meerwasser in dieser Region überall eine Quelle der natürlichen Halogenverbindungen für die Atmosphäre, die im Verlauf weniger Stunden in die mittlere und obere Troposphäre transportiert werden können (**Anhang. Report 5, 14**).

Das Ziel der **Beobachtung der globalen Phytoplanktonverteilung und Produktivität mit Hilfe von in situ Messungen und Satellitenfernerkundung (Ozeanoptik) (Prof. Dr. Astrid Bracher, Dr. Rizman Idid, Dr. Aazani Mujahid, Dr. Joseph Palermo)** war es durch die kombinierte Nutzung von Techniken der Satellitenfernerkundung und in-situ Messungen der Ozeanoptik, der Phytoplankton-produktivität und Zusammensetzung, Abschätzungen der globalen Primärproduktion und Verteilung wesentlicher Phytoplankton-Gruppen, besonders in Küstenregionen zu verbessern (**Anhang Report**

2a) Die Messungen werden als Referenzspektren für Satellitendatenauswertungen, Strahlungstransportrechnungen und ebenso für die Validation der Algorithmen und Modelle genutzt.

Die Messungen des AWI wurden dabei durch Messungen der malaysischen Universitäten UM in Kuala-Lumpur (Dr. Rizman Idid: Phytoplanktonbiomassemessungen und Primärproduktionsbestimmung durch fluorometrische Methoden: PAM, Turnerfluorimeter, Phytoplankton und Zooplanktondiversitätsbestimmungen durch Mikroskopie und Zählung der Netzfänge) UNIMAS Kuching (Dr. Aazani Mujahid: morphologische und molekularbiologische Charakterisierung der Phytoplankton und Bakteriendiversität, DNA-Proben, CTD, Chl-a: Satellit/in-situ Vergleiche) , UMS Kota-Kinabalu (Prof. Dr. Ann Anton: Biogeographische Herkunft und phylogenetische Beziehungen of Cochlodinium polikrikoides) University of the Philippines Diliman, Quezon (Dr. Joseph Palermo: Phytoplanktonspezies und Zusammensetzung mit FlowCam und Infinity ME.) ergänzt (**Anhang Report 2b, 2c,2d, 13 a, 13b, 13c**). Die biologischen Analysen vertieften das Verständnis über die Quellen und Senken der halogenierten und der andern beprobten Spurengase im Ozean.

Der Zusammenhang zwischen den Gemeinschaften des Zooplanktons und des Phytoplanktons sollten im Hinblick auf die Hauptspezies und taxonomischen Gruppen charakterisiert werden. Zum Sammeln und Filtern der Zooplanktonproben wurden Planktonnetze benutzt. Die Proben sollten zur morphologischen Identifikation in mit Formalin gepufferten Seewasser und zur molekular/ genetischen Untersuchungen in Alkohol aufbewahrt werden. Aus Sicherheits- und Lufttransport Gründen wurde auf den Kauf von Formalin verzichtet und auf Wunsch des malaysischen Kollegen unvergällter Alkohol in Singapur bei der Firma Merck beschafft. Bisher wurden die Proben leider nicht ausgewertet.

Ozeanische und besonders küstennahe Emissionen der **Klimarelevanten Spurengase: DMS, N_2O und CH_4 in Ozean und in der Atmosphäre (Dr. Christa Marandino, Dr. Cathleen Zindler, Dr. Hermann W. Bange)** die direkt und indirekt das Erdklima und die Chemie der Erdatmosphäre entscheidend beeinflussen, sind eine starke Quelle für die Troposphäre. Es wurden Messungen dieser Gase in den Küstenregionen und flachen Schelfgebieten des Südchinesischen Meers und der Sulusee durchgeführt, um die Quellstärke dieser Region und damit ihre Rolle für den atmosphärischen Haushalt von DMS, N_2O und CH_4 abschätzen zu können. Es wurden starke Quellen aller Gase besonders an der Küste Borneos (**Anhang Report 3**) gefunden.

Kohlendioxid und Sauerstoff (Dr. Tobias Steinhoff, Prof. Dr. Arne Körtzinger) wurden im Gebiet des südchinesischen Meeres gemessen und sollen zur Identifikation und Quantifikation von CO_2- und O_2-Quellen und -Senken, und zur Separation physikalischer und biologischer Faktoren für beobachtete Quellen/Senken beitragen. Die Messungen ergänzen die wenigen Messungen dieser Gase im Bereich des tropischen West-Pazifik in Küstennähe und auf Schelfen. Aufgrund der Dynamik der biogeochemischen Prozesse auf den Kontinentalschelfen, der tropischen Lage und den terrestrischen Einflüssen war die Region durch Disäquilibriums in CO_2 und O_2 gekennzeichnet, was bisher nicht untersucht und dokumentiert wurde. Generell ist die Meeresregion eine CO_2-Quelle für die Atmosphäre, während der Oberflächenozean häufiger leichte Sauerstoffuntersättigungen aufweist (**Anhang Report 4**).

Es wurden intensive **Radiosondierungen (Prof. Dr. Kirstin Krüger)** und sieben Ozonsondierungen während der Seereise von Singapur nach Manila (Philippinen) durchgeführt. Die so gewonnenen meteorologischen Daten ergaben Aufschluss über den vertikalen Aufbau der Troposphäre und wurden für die Modellierung des Transports von Spurengasen vor allem in der tropischen freien Troposphäre und der Tropopausenschicht verwendet. Weiterhin lieferten diese Messungen notwendige Beiträge zu Strahlungstransportrechnungen und für die Bestimmung der Mischungsschichthöhe. Damit wurden

Spurengasprofile von den Messinstrumenten (z.B. MAX-DOAS) während der Kampagne erstellt und der Transport von Spurengasen aus der marinen atmosphärischen Grenzschicht berechnet (**Anhang Report 5**)

Ein bis dreistündig gewonnene Kanisterluftproben zur **Bestimmung der Spurengaskonzentration in der marinen Grenzschicht (Prof. Dr. Elliot Atlas)** wurden in Miami analysiert. Die Probenahmehäufigkeit wurde an den beiden Tagesstationen und an der Nordostküste Borneos erhöht. In den Kanistern werden 70 verschiedene, meist anthropogene aber auch natürliche atmosphärische Spurengase (z.B.: Fluorchlorkohlenwasserstoffe, Alkane, Alkylnitrate, Brom, Chlor und Jodverbindungen) analysiert, um ihre Quellen, den Transport und die Umwandlungen in der globalen Atmosphäre zu charakterisieren. Die Spurengasgehalte in der Atmosphäre waren niedrig, wobei erwartungsgemäß in Landnähe und in der Nähe von Bohrinseln kleinräumige Kontaminationsquellen für Kohlenwasserstoffe gefunden wurden und die halogenierten Spurengase eher kontinuierlich und variabel in der Atmosphäre vorhanden waren (**Anhang Report 6**).

Mittels spektroskopischer Multi-Axis-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) Messung wurde die Konzentration **anorganischer Spurengase (Prof. Dr. Ulrich Platt, Prof. Dr. Klaus Pfeilsticker, Dr. Folkard Wittrock)** darunter freie Halogenradikale (BrO, IO) innerhalb der tropischen marinen Grenzschicht bestimmt, sowie Aussagen über deren Höhenverteilung getroffen. BrO und IO, die eine wichtige Rolle in der Photochemie von Ozon spielen und die troposphärische Oxidationskapazität beeinflussen wurden gemessen. Das zum Vergleich mitgeführte neuartige „Cavity- Ring Down“ Spektrometer zur Messung von IO mitgeführt, zeigte Werte zwischen 0.5 and 2 ppt und leicht höhere Werte in der Sulu See, während BrO unterhalb der Detektionsgrenze lag (**Anhang Report 7**).

Zur Analyse der Herkunft und zur Charakterisierung der chemischen Zusammensetzung der Luftmassen, fanden in situ Messungen ausgewählter **atmosphärischer Spurengase CO, CH_4, CO, O_3 (Dr. Hans Schlager, Dr. Tina Jurkat, Dr. Dominik Schäuble, Dr. Christiane Voigt (DLR)** statt. Diese Messungen zeigten eine leicht verschmutzte atmosphärische Mischungsschicht mit Verschmutzungsherden in der Nähe der größeren Städte, in denen auch Halogenfreisetzung durch Säureaustauschreaktionen beobachtet werden konnten (**Anhang Report 10a**). Mit Hilfe der Tracermessungen wurde die Zusammensetzung der Grenzschicht im Südchinesischen Meer charakterisiert und diese Daten zusammen mit entsprechenden Messungen an Bord des Forschungsflugzeuges Falcon im Ausströmgebiet von Konvektionszellen analysiert (**Anhang Report 10b**).

Messungen von anorganischen Iodspezies **IO, I_2 und HOI+ICl (Dr. Hannah Walker, Dr. Dwayne Heard**) zeigten Maxima der reaktiven Iodspezies IO im Nordosten von Borneo, die nicht mit einer physikalischen Messgröße oder Chlorophyll korrelierten, jedoch negativ mit molekularem Iod I_2 und ozeanischem Methyliodid und Chloriodmethan korreliert waren. Die atmosphärischen Gehalte von HOI und ICL wurden erstmalig über dem Ozean gemessen (**Anhang Report 10a und 10b**)

Während der Fahrt wurden tägliche Proben atmosphärischer **Aerosole (Dr. Alex Baker)** gewonnen, die auf Trockeneis nach Norwich transportiert und dort auf ihre Hauptbestandteile sowie Chlor, Brom und Iod-Spezifikationen analysiert wurden. Es bestätigte sich, dass die Aerosole in der marinen Atmosphäre beim Halogenkreislauf eine Schlüsselrolle spielen, indem Brom durch die Reaktion mit Ozon an Meersalzpartikeln in die Gasphase überführt wurde (Aerosole waren abgereichert). Letztendlich scheinen Aerosole eine Quelle für atmosphärisches Chlor und Brom und eine Senke für Jod zu sein, dass sich in den Aerosolen stark anreicherte (**Anhang Report 11**).

In der Sulu See wurden an vier tiefen Stationen anthropogenen Fluorchlorkohlenwasserstoffe als **transiente Tracer (Dr. Toste Tanhua)** analysiert, um das Alter der Wassermassen und den Gehalt

von anthropogenem Kohlenstoff in der Sulusee zu analysieren. Die Ergebnisse zeigen, dass das Bodenwasser (400 bis 600 Jahre) in der Sulusee sehr alt ist und dass sie nur geringe Menge anthropogenen Kohlenstoff enthält (**Anhang Report 12**).

Es wurde in Kooperation mit mehreren malaysischen Universitäten drei **lokale Küstenbootseinsätze** durchgeführt auf denen auch **Untersuchungen zur schädlichen Algenblüten (SAB) und Vergleich der Wasserqualität der Westküste Sabahs und der Küstengewässer (Dr. Moritz Müller, Dr. Aazani Mujahid, Felicity W.I. Kuek, Hong-Chang Lim' Sing-Tung Teng, Chui-Pin Leaw, Dr. Lim Po Teen, Prof. Dr. Ann Anton)** stattfanden. Als Teil der komplementären dreiteiligen Reihe von lokalen Ausfahrten in Kuching, in Kota Kinabalu und in Semporna wurden zwei Transekte in Kuching am 16. und 19. November 2011 unternommen. Luft-und Wasserproben wurden an 5 Stationen mit Abständen von 5 km gesammelt, entlang von Transekten bis zu 20 km von der Küste (siehe Abbildung 1).

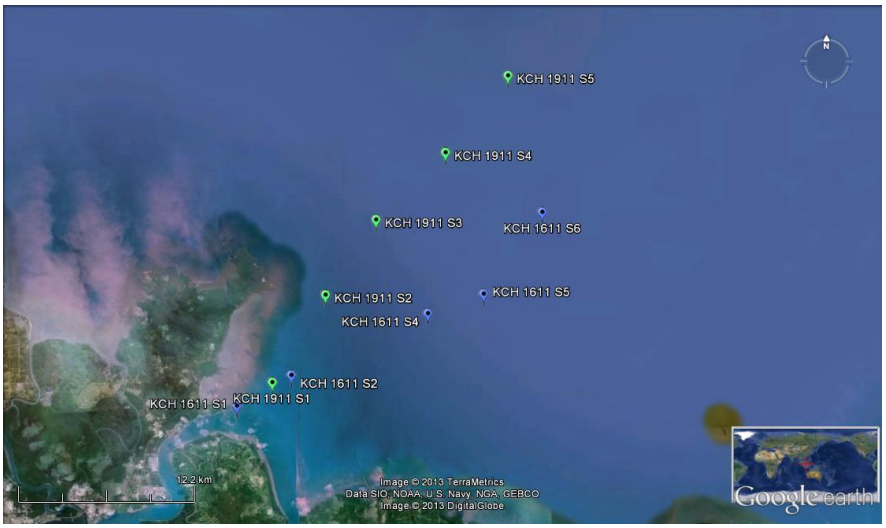


Abbildung 1: Übersicht der Messstationen in Kuching, Sarawak .

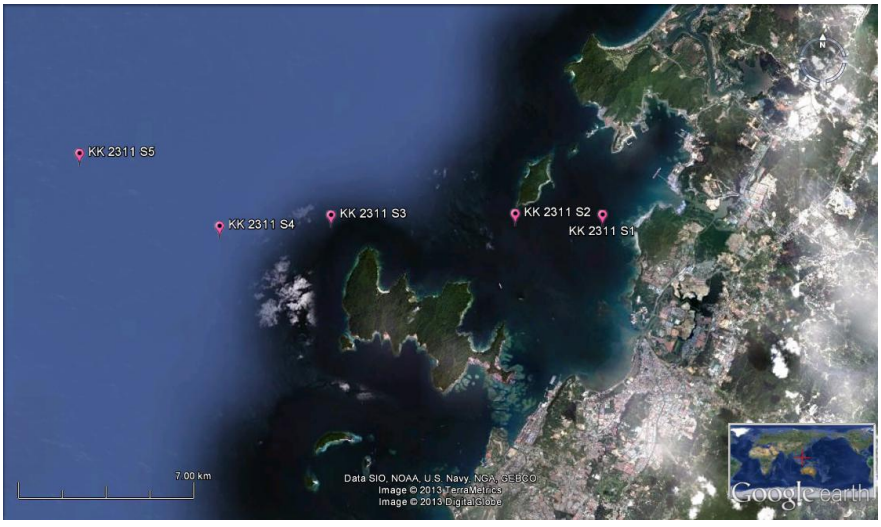


Abbildung 3: Übersicht der Messstationen in Kota Kinabalu, Sabah.

Abbildung 4: Übersicht der Messstationen in Semporna, Sabah.

Die Hauptziele der lokalen Ausfahrten waren: (i) küstennahe Proben zur Ergänzung der offenen Ozean Proben von der FS Sonne, der Falcon Flugzeug Daten und der Satelliten Daten zu erhalten (ii) Proben, die an der Küste gesammelt waren, auf die Sonne für weitere Analysen (z.B. VSLS und Nährstoffe) weiterzugeben und Proben von der FS Sonne (sensible biologische Proben) an das Küstenboot für weitere Analysen in den UNIMAS und Swinburne Laboren weiterzugeben. Die FS Sonne und das Küstenboot von Kuching trafen sich am 19ten November 2011. Zu den gemessenen Parametern gehören VSLS in Meerwasser und Luft (UEA, UM), Plankton (UNIMAS, UMS) und ausgewählten Oberflächen Wasser-Parameter (UNIMAS, SUTS). Des Weiteren wurden Proben gesammelt, um Informationen über die bakteriellen Gemeinschaften in Kuching zu erhalten. All diese Daten können mit den Daten aus den anderen lokalen Booten (Kota Kinabalu und Semporna) verglichen werden, zum Beispiel die bakteriellen Gemeinschaften im Hinblick auf *in-situ* physikalisch-chemische Wasserparameter. Die erste Station in Kuching war in der Nähe der Flussmündung des 'Sarawak-river' und zeigte einen sichtbaren Einfluss von Flusswasser wie zum Beispiel einen Salzgehalt von 28,48 ppt und einen pH-Wert von 7,90 an der Oberfläche. Der Einfluss des Flusses war auch sichtbar an deutlich höheren Nitrat, Phosphat, Nitrit, und Silikat Werten in der Nähe der Flussmündung (**Anhang Report 12**). Nährstoffgehalte in Kuching waren in der Regel höher als in Kota Kinabalu. Um Unterschiede in der Verteilung in der oberen Deckschicht zu beurteilen, wurden auch Proben in 5 m Tiefe genommen. Aus Kuchings' Gewässern wurden 89 bakterielle Isolate während der beiden Ausfahrten (16. November und 19, 2011) gewonnen. Die bakterielle Gemeinschaft hatte Vertreter der Alpha-, Beta- und Gamma-proteobacteria sowie der Firmicutes; die Vielfalt war jedoch eng mit der Tiefe der Proben verbunden (**Anhang Report 2c**). Bakterien aus Kuching zeigten die höchste Fülle von den beiden untersuchten DMSP-degradierenden Genen (36%) im Vergleich zu bakteriellen Gemeinden von Kota Kinabalu und Semporna (13 und 19%). Unsere Ergebnisse zeigen, dass die Gemeinschaftsstruktur der Gammaproteobacteria in Kuching's Gewässern eng mit dem lokalen Schwefel und möglicherweise auch dem Stickstoffkreislauf verknüpft sind (**Anhang Report 2d**). Zur Analyse der Gemeinschaftsstruktur der Pseudo-nitzschia entlang der östlichen SCS wurden Amplifikation an insgesamt 75 Oberflächen-Wasserproben (gesammelt während der lokalen und SHIVA Ausfahrten) durchgeführt und die Amplifikate wurden durch Fragment-Analyse der DNA analysiert. Insgesamt 50 Ribotypen wurden nachgewiesen und so die Gemeinschaftsstruktur mit Hilfe genetischer Information (automated ribosomal intergenic spacer analysis, ARISA) identifiziert (**Anhang Report 2b**). Die Ergebnisse einer Cluster-Analyse zeigten ein Cluster mit Standorten in denen P. caciantha Ribotyp 2 dominierte, und ein Cluster mit Standorten an denen P. caciantha fehlte. Es konnte jedoch kein

signifikanter Unterschied zwischen Proben aus Küstengewässern oder dem offenen Ozean festgestellt werden.

Die Abteilung für schädliche Algenblüten (SABs) innerhalb des UMS Borneo marinen Forschungsinstituts (BMRI), führte Studien im Küstengewässer von Sabah durch, wo häufig und wiederholt „rote Tiden“ vorkommen. Im Bezug auf dieses Thema sind die biogeographischen Ursprünge und phylogenetischen Beziehungen der „Cochlodinium polikrikoides“, aktuell die verursachende Art der SAB in Sabah und zudem jüngst in vielen anderen Regionen beschrieben von Interesse Die Wasserqualität im offshore Bereich Sabahs wurde mit den küstennahen Resultaten verglichen. Die gewonnenen physikalischen Daten unterstützen die Ergebnisse vorangegangener Wassermassenanalysen zur Identifizierung der Herkunft der Wassermassen von der Westküste Sabahs und damit die laufende Forschung der Malaysia Sabah Universität und im Besonderen die des marinen Forschungsinstituts Borneo **(Anhang Report 13).**

Da es ein Ziel der Untersuchungen war, die Bedeutung der ozeanischen Emissionen leichtflüchtiger Brom- und Jodverbindungen aus der untersuchten tropischen Region für die stratosphärische Halogenbelastung abzuschätzen wurde der **Transport der** Emissionen im tropischen Atlantik und West Pazifik **in die Stratosphäre** mit Hilfe des Trajektorienmodells FLEXPART untersucht **(Dr. Susann Tegtmeier, Prof. Dr. Kirstin Krüger, Dr. Birgit Quack).** Die Transportsimulationen, die das Auswaschen und den chemischer Zerfall der sehr kurzlebigen Halogenverbindungen berücksichtigen, basieren auf den Messungen der Brom- und Jod-Emissionen während der SHIVA SONNE SO218-Kampagne. Im Vergleich dazu wurden außerdem Messungen im tropischen Ostatlantik im Mai/Juni 2010 (DRIVE P399-Kampagne), und im tropischen Westpazifik im Oktober 2009 (TransBrom Sonne Kampagne) ausgewertet. Während in allen Regionen, einschließlich der mauretanischen Auftriebsregion im Ostatlantik, erhebliche VSLS Emissionen vom Ozean in die Atmosphäre beobachtet wurden, so ist der anschließende Transport von der Meeresoberfläche bis in die tropische Tropopausen-Schicht und die darüber liegende Stratosphäre im küstennahen West Pazifik am intensivsten. Die Evaluierung der drei tropischen Kampagnen zeigt, dass maximale Emissionen bromierter VSLS zusammen mit starken konvektivem Transport zu signifikanten VSLS Vorkommen in der Tropopausenregion führt, welches mit atmosphärischen Messungen gut übereinstimmt. Für Methyliodid allerdings sind die basierend auf den Emissionen berechneten atmosphärischen Vorkommen größer als Beobachtungen basierend auf Flugzeug- und Ballonmessungen. Dieser Vergleich deutet an, dass existierende Messungen möglicherweise nicht repräsentativ sind und Methyliodid einen größeren Einfluss auf die atmosphärische Ozonchemie haben könnte als bisher angenommen **(Anhang Report 14).**

II.2. POSITIONEN DES ZAHLENMÄßIGEN NACHWEISES

Im EU-geförderten Projekt SHIVA war ein Großteil der Mittel für die Durchführung der Seereise beantragt worden. Die in diesem BMBF SHIVA-Sonne SO218 Antrag veranschlagten Kosten waren zusätzliche Ausgaben, die in dem SHIVA-Vorhaben nicht berücksichtigt waren, und die durch die enge Zusammenarbeit mit Malaysia und den Philippinen entstanden. In stattfindenden Vorbesprechungen bekundeten Malaysier aller Provinzen deutlich ihr Interesse an der Kampagne und auch der Datenauswertung aktiv beteiligt zu sein. Es wurden daraufhin Bordplätze für 4 malaysische und 1 philippinischen Wissenschaftler angeboten, die zum Gelingen des Programmes beitrugen. Zusätzlich entstanden Reisekosten für einen malaysischen und einen philippinischen Militärbeobachter. Darüber hinaus wurde mit der Universität Kuala-Lumpur als ein malaysisches Kooperationsprojekt der Einsatz ihres 75khZ-ADCP zur Messung der Oberflächenmeeresströmungen verabredet. Das Gerät wurde von einem malaysischen Techniker an Bord der Sonne in Singapur installiert und in Manila wieder

deinstalliert. Die beteiligten Gruppen der vier malaysischen Universitäten benötigten insbesondere Reisegelder und Transportkosten, sowie einen kleinen Bedarf an Verbrauchsmaterial und Chemikalien. Einen weiteren großen Kostenpunkt stellten die im Arbeitsplan vorgesehenen Einsätze lokaler Boote zur küstennahen Probenahme und zum Probentransport zu FS Sonne dar, da gerade an der Küste hohe Spurengaskonzentrationen und -emissionen erwartet und bestätigt wurden und FS Sonne nicht so nah an die Küste heranfahren kann. Zur Vor- und Nachbereitung der Seereise wurde insgesamt drei Reisen nach Malaysia durchgeführt. Die im Projekt beantragten internationalen Reisegelder für die malaysischen Wissenschaftler mussten für eine Erhöhung der Transportkosten sowie einer weiteren Vortragsreise nach Malaysia verwendet werden, da die Partner trotz Einladung keine Zeit fanden zu der im Mai 2012 stattfindenden Seereisenachbesprechung zu kommen. Die entsprechenden Voranfragen beim Mittelgeber wurden durchgeführt. Durch den unerwartet hohen Einsatz vieler Gerätschaften, mussten drei Container (darunter ein 10“ Spezialcontainer) nach Malaysia transportiert werden, wovon zwei Transporte über diesen BMBF-Antrag finanziert wurden.

Arbeits-, Zeit- und Ausgabenplanung wurden daher im Wesentlichen eingehalten. Die vom BMBF zur Verfügung gestellten Mittel für die Kooperation mit den malaysischen und philippinischen Wissenschaftlern, darunter im wesentlichen Reisekosten der sieben auf FS Sonne beteiligten malaysischen und philippinischen Wissenschaftler und Beobachter, sowie einiger Aufbauhelfer, Einsatzkosten für drei örtliche Bootseinsätze (Kuching, Kota Kinabalu, Semporna - hier kein direkter Kontakt mit FS Sonne), sowie Transportkosten der an Bord gesammelten Proben und Geräterücktransporte zu den Heimatinstituten wurden bestimmungsgemäß und erfolgreich verwendet.

II.3. NOTWENDIGKEIT UND ANGEMESSENHEIT DER GELEISTETEN ARBEIT

Im Rahmen der Schiffreise und der gesamten SHIVA-Kampagne wurde zur Zusammenarbeit von verschiedenen Gruppen und Disziplinen aufgerufen, um zum einen die Einmaligkeit der logistisch und administrativ aufwendigen Forschungsreise für die Spurengasfragestellungen zu nutzen und zum anderen die Zusammenarbeit mit den im EU-Projekt SHIVA beteiligten wissenschaftlichen Disziplinen zu verwirklichen. Dadurch wurde eine zusätzliche Ressource für die wissenschaftliche Gemeinschaft generiert, die es ermöglicht Werkzeuge zu entwickeln, um die Ozean- und Atmosphärenflüsse der halogenierten Verbindungen zu parametrisieren und dadurch eventuell vorhersagbar zu machen. Diese wissenschaftlichen Produkte sind notwendig um den stratosphärischen Halogengehalt besser abschätzen zu können und damit die Ozonentwicklung im Rahmen zukünftiger Klimaänderungen und atmosphärischer Verschmutzung besser vorhersagen zu können.

Die Arbeiten, besonders die in diesem Forschungsvorhaben beantragen biologischen Arbeiten der malaysischen und philippinischen Wissenschaftler stellten eine hervorragende Ergänzung zu dem SHIVA-Projekt dar. Es wurden aus einem Gebiet, aus dem es bisher kaum Messungen gab, eine Vielzahl klimarelevanter Spurengase in Ozean und Atmosphäre gemessen und eine intensive Analyse der ozeanischen Biologie führe zur weiteren Aufdeckung von Quellen und ihre Einträge aus dem Ozean bis in die Troposphäre und Stratosphäre konnte berechnet werden.

Da die meisten Arbeiten erfolgreich verliefen und die meisten Daten ausgewertet sind und ein einmaliger Datensatz erhalten wurde, kann die geleistete Arbeit als notwendig und angemessen gelten.

II.4. Der voraussichtliche Nutzen, insbesondere der Verwertbarkeit des Ergebnisses im Sinne des fortgeschriebenen Verwertungsplans

Das erreichte Ziel des Projektes war es, wissenschaftliche Informationen und Fachwissen zu globalen Umweltfragestellungen und Anpassungsmechanismen an den globalen Klimawandel zu liefern. Dies beinhaltete die Bereitstellung wissenschaftlicher Beiträge von öffentlichem Interesse zum internationalen SOLAS (Surface Ocean Lower Atmosphere Study)-Programm, an dem sich das BMBF mit der Förderung des Verbundprojektes SOPRAN (Surface Ocean Processes in the Anthropocene) beteiligt, in dem auch die Thematik der Ozeanemissionen halogenierter Verbindungen integriert ist.

Die Ergebnisse dienen der Stärkung der wissenschaftlichen Basis gesellschaftspolitisch relevanter Bewertungen und liefern Beiträge zum „WMO Ozone-Assessment“ und zu Fragen und Studien des IPCC (Intergovernmental Panel on Climate Change). Die internationalen Vereinbarungen zum Klimaschutz von Montreal (1989) über die Produktion ozonzerstörender Verbindungen und Kyoto (1997) zur Emissionsbegrenzung von Treibhausgasen, haben gezeigt, wie wichtig die Kenntnisse über die Emissionen von Spurengasen bei politischen Entscheidungen sind. Es könnte sich zukünftig herausstellen, dass die globale Erwärmung und die dadurch zunehmende Temperatur des Ozeans und verstärkte Windgeschwindigkeiten zu einer verstärkten Emission ozeanischer Spurengase führt. Eine mögliche Zunahme von Konvektionsgebieten könnte einen bisher unterschätzten Beitrag zur Bromchemie der Stratosphäre und damit zum Ozonabbau in Synergie mit den anthropogenen Chlorverbindungen leisten, was weitere Überlegungen beeinflussen würde.

In dem Projekt fand eine Vernetzung bisher getrennter wissenschaftlicher Disziplinen statt, die zu einer Synergie der vorhandenen Expertisen führten, wie es in den internationalen Initiativen und Projekten SOLAS, SOPRAN, SPARC (Stratospheric Processes And their Role in Climate) und CCMVal (coupled Chemistry Climate Model Validating) angedacht ist. Dies beinhaltet zusätzliches Fachwissen für eine Anpassung an den globalen Klimawandel, der zentral für die Aufgabenstellung des BMBF ist.

Um Effekte des globalen Wandels auf das empfindliche marine Ökosystem besser beschreiben zu können, müssen zunächst die existierenden Systeme besser verstanden werden. Ein solches Verständnis ist eine Grundvoraussetzung, um die Folgen anthropogener Einflüsse, einschließlich des Klimaschutzes, sowie Schutzes globaler Ökosysteme und mariner Ressourcen, vorhersagen und bewerten zu können. Es ermöglicht die Empfindlichkeit dieser entscheidenden Beziehungen des globalen Systems gegenüber veränderlichen Klimaeinflüssen beurteilen zu können, die für zahlreiche Aspekte der Klimaschutzbemühungen von Bedeutung sind.

Als ein Projektergebnis stehen unter anderem die ersten Daten einer Vielzahl von Spurengasen und weiterer Parameter aus einer wenig untersuchten Ozeanregion zur Verfügung. Die wissenschaftlichen Erfolge dieses Projektes schlagen sich im Wesentlichen in Veröffentlichungen in anerkannten und begutachteten wissenschaftlichen Zeitschriften nieder. Dieser einmalig kombinierte Datensatz, auch von verschiedenen Messplattformen aus, liefert die Grundlage für interdisziplinäre Veröffentlichungen, die zum Wissenschaftstransfer führen werden.

In den folgenden Jahren wird weiterhin an der Auswertung der Feldkampagnen gearbeitet, und die Themen und Partner während SO218 sind weiterhin ein integrativer Bestandteil neuer Projekte und werden weiterhin Grundlagen für zukünftige und innovative Projekte im Hinblick auf die schützende Ozonschicht und den Klimawandel liefern.

Während SO218 wurden aus dem südchinesischen Meer und der Sulu-See wertvolle Erkenntnisse und erstmalige Daten für die Extrapolation lokaler Datensätze auf großräumige und globale Skalen erhalten. Die regional neuartigen Daten fließen in die Datenbank HalOcAt ein, die im Rahmen der

EU-COST (European Cooperation in the field of Scientific and Technical Research) ACTION 735: "Tools for Assessing Global Air–Sea Fluxes of Climate and Air Pollution Relevant Gases" als Teil des internationalen SOLAS (Surface Ocean - Lower Atmosphere Study) initiiert wurde (htttp://www.halocat.geomar.de). Die während der Schiffskampagne gewonnenen Daten werden unter der Anwendung neuer wissenschaftlicher Erkenntnisse von Atmosphärendynamikern ausgewertet und stehen nach der Auswertung durch die SHIVA-Community der internationalen Gemeinschaft der Klimachemiemodellierer „coupled Chemistry-Climate Model Validation/ Stratospheric Processes And their Role in Climate" (CCMVal/ SPARC-Initiative) zur Verfügung. Ebenso sind Atmosphärenchemiker auf die Erweiterung des begrenzten Datensatzes der Ozeanemissionen halogenierter Spurenstoffe angewiesen. Somit wird die Datengrundlage für Modellexperimente verbessert, die dadurch korrektere Ergebnisse liefern können. Die Daten werden letztendlich in die vom AWI World Data Center for Marine Environmental Sciences (WDC-MARE) geführte internationale Datenbank Publishing Network for Geoscientific & Environmental Data PANGAEA eingetragen und stehen so der gesamten wissenschaftlichen Gemeinschaft zur Verfügung.

Mit Hilfe des erweiterten Datensatzes wird zum Beispiel im vom BMBF geförderten Projekt „Quellen und Senken bromierter und jodierter Verbindungen im tropischen Ozean" innerhalb SOPRANs (Surface Ocean Processes in the Anthropocene) in den kommenden zwei Jahren der Luft-Wassergasaustausch von bromierten und jodierten Verbindungen regional und global synthetisiert und simuliert. Mit der nationalen und internationalen atmosphärischen Wissenschaftsgemeinschaft ergaben sich neue Projekte, wie zum Beispiel das vom BMBF im Rahmen von ROMIC (Role Of the MIddle atmosphere in Climate) kürzlich bewilligte Projekt „THREAT: The role of oceanic halogen and sulfur compounds for the middle atmosphere in a changing climate", in dem bis 2016 gegenwärtige und zukünftige Ozeanemissionen und ihre atmosphärischen Transportwege und Eintragswege in die Stratosphäre eine bedeutende Rolle spielen. Die Erkenntnisse über Probenschema und Ergebnisse der Forschungsreise SHIVA-SONNE wurden für eine Seereise in das peruanische Auftriebsgebiet im Dezember 2012 in den östlichen Pazifik genutzt, aus dem nun auch zum ersten Mal Daten über Emissionen und Quellen kurzlebiger Halogenkohlenwasserstoffe vorliegen. In einem neuen Projekt – eine Seereise mit FS Sonne in den indischen Ozean (OASIS) werden erstmalige Messungen dieser und weiterer Spurengase im zentralen indischen Ozean mit FS Sonne im Jahr 2014 durchgeführt. Die Erfahrungen mit den Projektpartnern der DLR und der malaysischen Institutionen können in den kommenden Jahren für weitere Projektplanungen genutzt werden.

II.5. WÄHREND DER DURCHFÜHRUNG DES VORHABENS BEKANNT GEWORDENER FORTSCHRITT AUF DEM GEBIET DES VORHABENS BEI ANDEREN STELLEN

Da es sich bei der Forschung auf dem Gebiet der halogenierten Spurengase, ihren Quellen und ihrem Transport in die Stratosphäre um ein aktives Forschungsgebiet handelt, auf dem weltweit jedoch nur relativ wenige Wissenschaftler arbeiten, sind während der Projektjahre natürlich und glücklicherweise weitere Publikationen über ozeanische Quellen der halogenierten Spurengase vorwiegend aus anderen Meeresregionen bekannt geworden. Ebenso wurden neue globale Modellansätze getestet, um Quellen, Transport und Eintrag der Spurengase in die Stratosphäre zu untersuchen. Einige der Arbeiten wurden von SHIVA-beteiligten Wissenschaftlern initiiert. Es werden einige Literaturbeispiele angehängt.

Da die chlorierten, bromierten und iodierten Verbindungen, die aus dem Ozean in die Atmosphäre gelangen sehr heterogen verteilt sind und ihr Eintrag in die Atmosphäre von vielerlei Faktoren abhängt, die bisher nur sehr unzureichend untersucht und verstanden sind, sind weitere Untersuchungen unabdingbar. Die in diesem Projekt gesammelten Daten tragen ein wenig zu dem unzureichenden globalen Datensatz bei, der nur aus einem winzigen Bruchteil der Datenmengen

besteht, die für andere Spurengase gesammelt wurden. Gerade die Heterogenität und Dynamik der Quellen sowie die lokalen über regionalen bis hin zu globalen Bedeutungen dieser Spurenstoffe macht weitere Forschungen und Messkampagnen notwendig. Da ein Teil der Verbindungen, die auch in Spurenkonzentrationen große Auswirkungen in der Atmosphäre haben können, durch anthropogene Aktivitäten beeinflusst wird, müssen die Beobachtung der Entwicklungen der ozeanischen Emissionen, sowie die anthropogenen und natürlichen Einflussfaktoren auch weiterhin im Focus der Wissenschaftler bleiben.

beispielhaft Publikationen von andere Seite

Pyle, J. A., Ashfold, M. J., Harris, N. R. P., et al. Bromoform in the tropical boundary layer of the Maritime Continent during OP3, Atmos. Chem. Phys., 11, 529-542, 2011
Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., et al.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12, 1423-1447, doi:10.5194/acp-12-1423-2012, 2012
Hossaini,R, Chipperfield, M.P., Dhomse, S., et al., Modelling future changes to the stratospheric source gas injection of biogenic bromocarbons, Geophysical Research Letters, 39, 20, 2012
Mattsson, E. Karlsson, A Abrahamsson, K., Regional sinks of bromoform in the Southern Ocean,Geophysical Research Letters, 40, 15, 3991–3996, 2013
Andrews, S. J., Jones, C. E., Carpenter, L. J., Aircraft measurements of very short-lived halocarbons over the tropical Atlantic Ocean, Geophysical Research Letters. 40, 5, p 1005–1010, 2013

II. 6. Die erfolgten und geplanten Veröffentlichungen des Ergebnisses

Im Laufe der letzten Jahre wurden schon Veröffentlichungen zur Seereise und zur Shiva- Kampagne publiziert und weitere sind in Planung. Ebenso wurden die Daten und Ergebnisse bei nationalen und internationalen Konferenzen auf Postern und in Vorträgen präsentiert.

Publikationen in begutachteten Zeitschriften (Veröffentlicht und Geplant)

1. Bracher, A., Cheah, W., Dinter ,T., Steinmetz, F. Deriving phytoplankton characteristics from optical properties in the South China Sea and Sulu Sea, in prep for Ocean Sciences.
2. Cheah W., et al., Photophysiological state of natural phytoplankton communities in the South China Sea and Sulu Sea, Biogeosciences Discussion 10:12115-12153, 2013.
3. Fuhlbrügge et al., Exchange of VSLS in the marine boundary layer with the free troposphere during SHIVA-SONNE, in prep. for ACPD, 2013.
4. Hamer, P. D., Marécal, V., Hossaini, R., Pirre, M., Warwick, N., Chipperfield, M., Samah, A. A., Harris, N., Robinson, A., Quack, B., Engel, A., Krüger, K., Atlas, E., Subramaniam, K., Oram, D., Leedham, E., Mills, G., Pfeilsticker, K., Sala, S., Keber, T., Bönisch, H., Peng, L. K., Nadzir, M. S. M., Lim, P. T., Mujahid, A., Anton, A., Schlager, H., Catoire, V., Krysztofiak, G., Fühlbrügge, S., Dorf, M., and Sturges, W. T.: Modelling the chemistry and transport of bromoform within a sea breeze driven convective system during the SHIVA Campaign, Atmos. Chem. Phys. Discuss., 13, 20611-20676, doi:10.5194/acpd-13-20611-2013, 2013.
5. Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys. Discuss., 13, 12485-12539, doi:10.5194/acpd-13-12485-2013, 2013.
6. Keng, F. S.L., S.M. Phang, N. A. Rahman, E. C. Leedham, C. Hughes, A. D. Robinson, N. R. P. Harris, J. A. Pyle, W. T. Sturges, Volatile halocarbon emissions by three tropical brown seaweeds

under different irradiances, Journal of Applied Phycology., 25, 5, 1377-1383, 1386, DOI 10.1007/s10811-013-9990-x, 2013.
7. Kuek, F.W.J., Mujahid. A, Po Teen, L., Chui Pin, L., Müller, M.; Bacterial communities from the eastern South China Sea and the Celebes Sea, and their potential role in the DMS(P) cycle, in prep. for Biogeosciences.
8. Leedham, E., Hughes, C., Keng, F., Phang, S., Malin, G., Sturges, W., Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, Biogeosciences, 10, 3615-3633, doi:10.5194/bg-10-3615-2013, 2013.
9. Marécal et al.: What do we learn on bromoform transport and chemistry in deep convection from fine scale modelling?, Atmospheric Chemistry and Physics, 12, 6073-6093, 2012.
10. Huang, Peng,, Tanhua, T., Ventilation and anthropogenic carbon in the Sulu Sea. in prep for Water
11. Ooi, S. H., Samah, A. A., and Braesicke, P.: Primary productivity and its variability in the equatorial South China Sea during the northeast monsoon, Atmos. Chem. Phys. Discuss., 13, 21573-21608, doi:10.5194/acpd-13-21573-2013, 2013.
12. Raimund, S., Quack, B., et al., Oceanic sources of VSLS in the South China and Sulu Seas, in preparation.
13. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A., Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F.: The contribution of oceanic methyl iodide to stratospheric iodine, Atmos. Chem. Phys. Discuss., 13, 11427-11471, doi:10.5194/acpd-13-11427-2013, 2013.
14. Tegtmeier, S., K. Krüger, B. Quack, I. Pisso, F. Ziska et al.: ODP weighted VSLS emissions for present and future scenarios
15. Walker, H., Folkard Wittrock, Johannes Lampel, Martin Horbanski, Justin Sentian, Enno Peters, Anja Schönhardt, Tilman Dinter, Astrid Bracher, Mihalis Vrekoussis, Ru-Jin, Katja Großmann, Karin Kreher et al., Measurements of reactive iodine species during and related to the SHIVA campaign, in prep.
16. Yang, X., Pyle, J. A., and others, Response of atmospheric ozone to the perturbation of VSLS emissions under different chlorine and bromine backgrounds, (in prep), 2013a.
17. Yang, X., Pyle, J. A., Hossaini R, Chipperfield M.P., and others, Modelling future changes of the stratospheric ozone due to biogenic bromocarbons, (in prep), 2013b.
18. Ziska, F., Quack, B., et al., Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmos. Chem. Phys. Discuss., 13, 5601-5648, doi:10.5194/acpd-13-5601-2013, 2013.
19. Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., et al., Future trend in oceanic halocarbon emissions
20. Ziska F., Bracher A., Cheah W., Dinter T., Quack B. Inferring oceanic concentration of VSLS from oceanic biological and physical parameters over the maritime continent, in prep for Biogeosciences

PRÄSENTATIONEN (POSTER UND VORTRÄGE)

1. Cheah, W., Taylor, B., Dinter, T., Wiegmann,S., Altenburg-Soppa, M.,Palermo, J., Bracher, A., Composition and optical features of phytoplankton during SHIVA-SONNE (SO218) expedition, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
2. Fuhlbrügge, S., Krüger, K., Quack, B., und das SHIVA-SONNE Team; SHIVA SONNE SO-218: Meteorologie- und Luftmassenanalyse, SONNE Statusseminar, Kiel, Feb. 2013,
3. Fuhlbrügge, S., Quack, B., Tegtmeier, S., Atlas, E., Sala, S., Boenisch H., Hepach, H., Raimund S., Shi Q., Krüger, K.; Exchange of VSLS in the marine boundary layer with the free troposphere during SHIVA-SONNE, EGU General Assembly, Vienna, Poster, 2013
4. Jurkat, T., Voigt, C., Schäuble D. , Investigation of anthropogenic pollution in the marine boundary layer of the South China Sea and Sulu Sea (SO218), BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
5. Krüger Kirstin, "Ocean-stratosphere interactions in a changing climate", UiO, Oslo, 22. November 2012, (invited) Talk, 2012.

6. Krüger, K., B. Quack, S. Fuhlbrügge, S. Tegtmeier, First results from the SHIVA SONNE expedition to the tropical Western Pacific during November 2011, EGU, General Assembly, Vienna, Poster, 2012.
7. Krüger, K., B. Quack , E. Atlas, S.Tegtmeier, and F. Wittke, Towards bridging the gap between oceanic and upper air VSLS measurements: The SHIVA-SONNE campaign, CCMVAL workshop, Davos, 21.-24. May, 2012, Poster, 2012.
8. Kuek, F.W.I., Ngu, E.S.L., Lee, S.T.H., Mujahid, A., Lim, P-T., Leaw,C-P., Müller, M. , Microbial communities of the Eastern South China Sea and Sulu Sea and their possible roles in the DMS(P) cycle, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
9. Lampel, J., Wittrock, F., Großmann, K., Peters, E., Horbanski, M., Pöhler, D., Frieß, U., Pfeilsticker, K., Platt, U., DOAS measurements from space, ship and plane: trace gas distributions over the South China and Sulu Sea, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. February 2013, Kiel, Poster
10. Leedham, E., W Sturges, G Malin, C Hughes, D Oram, F Keng & S-M Phang, Halocarbon Production in the Tropical Coastal Zone, SOLAS Open Science Conference, poster, May 2012.
11. Mohr, V., K. Krüger, S.Tegtmeier, M. Neish, T. Shepherd,and D. Smale, Towards analysing transport pathways of VSLS in CCMs, WAVACS summer school, Corsica, France, poster, 14.-26.09.2009.
12. Mohr, V., Tegtmeier, S., Schofield, R., Rex, M., Neish, M., Smale, D., Gettelman, A., Garny, H. und Krüger, K., Analysing the tropical widening of the TTL with a Lagrangian approach using CCM and ERA-Interim data, AGU Fall meeting San Francisco, CA, USA., poster, 15.12.2010.
13. Mujahid, A, Müller, M, Emily S.L. Ngu, E.S.L., T.H., Samson, L., Yao-Long, L., Y.2, Felicity W.I. Kuek, F.W.I., Hong-Chang, L., Sing-Tung, T., Chui-Pin, Leaw, Po-Teen, L., Shiva Local boat deployment in Kuching and major findings from Sarawak, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
14. Peters, E., Lampel, J., Wittrock, F., Vrekoussis, M., Richter , A., Burrows, J.P., Tschritter, J., Dorf , M., Quack, B., Sentian, J., Pfeilsticker, K., MAX-DOAS measurements of atmospheric trace gases during the SHIVA-Campaign, EGU, General Assembly , Vienna, Poster, 2012.
15. Qiang Shi, Gert Petrick, Birgit Quack, Douglas Wallace, Production in variability of methyl iodide (CH_3I) in the surface Ocean, SOLAS OPEN Science Conference, 7.-10.5.2012, Poster, 2012.
16. Quack, B. and Krüger, K., Die SHIVA-SONNE SO218 Kampagne, SONNE-Statusseminar, Kiel, Germany, Talk, 15.02.2013, 2013.
17. Quack, B. and Krüger, K., From the ocean to the stratosphere: The SHIVA SONNE cruise Marine Science Institute, 01.12.2011, Quezon City, Manila, Philippines, Talk, 2011.
18. Quack, B., Atlas, E., Hepach, H., Raimund, S., Tegtmeier, S., Shi, Q., Kinzel, J., Leedham, E., Fuhlbrügge, S., Taylor, B., , Chea, W., , Wittke, F., Robinson, A., Harris, N., Kreher, K., Sturges, B., Bracher, A., Wallace, D., Krueger, K., Halocarbon distributions and emissions in the South China and Sulu Sea during the SHIVA SONNE expedition in November 2011, South China Sea Conference, 22.-26. October 2012, Kuala Lumpur, talk
19. Quack, B., Elliot Atlas, Qiang Shi, Helmke Hepach, Stefan Raimund , Julian Kinzel , Emma Leedham , Steffen Fuhlbrügge , Sonja Wiegmann , Wee Chea, Franziska Wittke , Andrew Robinson, Neil Harris , Karin Kreher , Bill Sturges , Astrid Bracher , Doug Wallace and Kirstin Krüger, Halocarbon distributions and emissions in the western tropical Pacific during the SHIVA SONNE expedition in November 2011, EGU General Assembly, Vienna, Talk, 2012.
20. Quack, B., Krüger, K. Ziska, F. Hepach, H. Raimund, S. Tegtmeier, S. Shi Q., Atlas, E. S. Fuhlbrügge, S., Wallace, D. Halogenated trace gases from the ocean to the atmosphere, 17. January, 2013, Technische Universität Braunschweig, Geoökologisches Kolloquium, talk
21. Quack, B., Krüger, K., Hepach, H., Raimund, S., Ziska, F., Tegtmeier, S., Shi, Q., Atlas, E., Fuhlbrügge, S., Flöter, S., Petrick, G., Wallace D., Marine halogenated trace gases for the atmosphere, Physical Chemistry, University of Kiel, 22. May, 2013,talk.
22. Quack, B., Krüger, K., Hepach, H., Wittke, F., Raimund, S., Tegtmeier, S., Petrick, G.. Fuhlbrügge, S., Wallace, D., Atlas, E., The oceans as source of brominated halocarbons for the atmosphere, Johann Wolfgang University, 9. Februar, 2012, Frankfurt, talk

23. Quack, B., Krüger, K., Hepach, H., Wittke, F., Raimund, S., Tegtmeier, S., Petrick, G.. Fuhlbrügge, S., Wallace, D., Atlas, E., Marine halogenated trace gases for the atmosphere, Miami Haloproc, Annual meeting, Oberjoch, 22. März, 2012, talk
24. Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., und das SHIVA-Sonne Team, SO218 – Die SHIVA-SONNE (SO218) Kampagne: Die Bedeutung mariner Spurengasquellen im tropischen West Pazifik für stratosphärisches Ozon (Singapur-Manila: 15.-29. November 2011), BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, talk
25. Quack, Birgit, Kirstin Krüger, Stefan Raimund, Helmke Hepach, Elliot Atlas, From the ocean to the stratosphere: First results from a large-scale tropical western Pacific campaign, Helmholtz-Centre for Ocean Research Kiel (GEOMAR), Kiel, Germany , Scientific advisory board evaluation, 9.5.2012, Poster, 2012.
26. Raimund, S., Hepach, H., Shi, Q., Atlas, E., Chea, W., Bracher, A., Quack, B., Quellen und Emissionen kurzlebiger halogenierter Verbindungen im westlichen tropischen Pazifik, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
27. Schlager, H., and SHIVA Science Team SHIVA Experiment in Malaysia in Nov/Dec 2011 DC3 - SEAC4RS Science Team Meeting, Boulder, USA, Oral, 21-23 Feb 2012.
28. Steinhoff, T., Bange, H.W., Fiedler, B., Fietzek, P., Ihnenfeld, V., Kock, A., Körtzinger, A., Schneider, A., Methane-, N2O-, O2 and pCO2- measurements in the surface layer of the South China Sea, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
29. Tegtmeier, S.: SPARC Data Initiative - stratospheric satellite observations for model evaluation, invited presentation, IGAC-SPARC-CCMVal workshop, Oral, Davos, Switzerland, 21–25 May, 2012.
30. Tegtmeier, S., and Hegglin, M.I.: SPARC Data Initiative - Intercomparison of vertically resolved chemical trace gas and aerosol climatologies, SPARC SSG meeting, Oral, Zürich, Switzerland, 7-10 February 2012.
31. Tegtmeier, S., Bieligk, H., Krüger, K., Atlas, E., Fuhlbrügge, S., Hepach, H., Hossaini, R., Wittke, F., Quack, B.: Oceanic VSLS contribution to the stratosphere: Comparing tropical East Atlantic with tropical West Pacific emissions, EGU 2012, Poster, Vienna, Austria, April 2012.
32. Tegtmeier, S., Chemical Composition of the Tropical Tropopause Layer, invited presentation, School of GeoSciences, Oral, University of Edinburgh, UK, 21.5.2013.
33. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Bieligk, H., Wittke, F.: Oceanic VSLS contribution to stratospheric ozone, EGU 2012, IGAC-SPARC-CCMVal workshop, Poster, Davos, Switzerland, 21–25 May, 2012.
34. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Hepach, H., S. Raimund, S., Shi, Q., and Ziska, F.: Transport of VSLS from the ocean to the stratosphere, Sonne Statusseminar, Poster, Kiel, 2012.
35. Tegtmeier, S., Krüger, K., Quack, B., Wittke, F., Atlas, E., Bieligk, H., Hepach, H., Hossaini, R., Raimund, S., Shi, Q.: Oceanic VSLS contribution to stratospheric ozone, Quadrennial Ozone Symposium, Oral, Toronto, Canada, 27-31 August 2012.
36. Tegtmeier, S., M. I. Hegglin, J. Anderson, S. Brohede, L. Froidevaux, R. Fuller, B. Funke, J. Gille, A. Jones, Y. Kasai, E. Kyröla, G. Lingenfelser, C. McLinden, J. Neu, E. Remsberg, A. Rozanov, L. Smith, M. Toohey, J. Urban, T. von Clarmann, K. A. Walker, and R.Wang, SPARC Data Initiative – Climatology comparisons for O3, N2O, NOy, NOx, ClO, and BrO WCRP Open Science Conference, Denver, USA, Poster, 2011.
37. Tegtmeier, S.: Meridional structure of the downwelling branch of the BDC, invited presentation, SPARC Brewer-Dobson Circulation Workshop, Oral, Grindelwald, Switzerland, 25-29 June 2012.
38. Walker, H., Ingham, T., Lampel, J., Wittrock, F., Heard, D., Huang, R.-J, Hoffman,T. ,Reactive iodine species in the western Pacific atmosphere during SHIVA, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
39. Wittke, Franziska, Birgit Quack, Kirstin Krüger and HalOcAt contributors, Global VSLS emission estimates based on in-situ measurements for the past and future, CCMVAL work-shop, Davos, 21.-24. May, 2012, Poster, 2012.
40. Ziska F., Quack B. und HalOcAt Beitragende, Emissions of halogenated trace gases from the South China and Sulu Sea in a global context (Comparison of the SO218 emissions with climatological values), BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster

RV SONNE - Cruise

SO218- SHIVA

Singapore to Manila, Philippines

15 to 29 November 2011

(In the frame work of the SHIVA Western Pacific campaign in November and December 2011.)

Appendix to BMBF_FKZ 03G0218a_ Final Report

English reports of participating groups

Chief Scientists on board RV Sonne: Dr. Birgit Quack
Dr. Kirstin Krüger
GEOMAR Helmholtz Centre for Ocean Research Kiel
Düsternbrooker Weg 20
24105 Kiel
Tel : +431 6004206
Email: bquack@geomar.de

Responsible institution: GEOMAR Helmholtz Centre for Ocean Research Kiel

Projects: SHIVA (EU-Project 226224), SHIVA-SONNE (BMBF 03G218A, 03SO480), TransBrom (Leibniz Association), SOPRAN (BMBF 03F0462A)

GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung
Projektträger Jülich Forschungszentrum Jülich
GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel
SHIVA

GEOMAR Helmholtz—Centre for Ocean Research Kiel
Düsternbrooker Weg 20
D-24105 Kiel
Tel: +431 6004206
Fax: +431 6004205
email: bquack@geomar.de

RV Sonne cruise SO218: Singapore-Manila, 15-29 November 2011

Scientific background 6

Objectives, participating institutions and measurements 6

Work Program during the cruise 11

Report 1: Halocarbons in the South China and Sulu Sea: distributions emissions and sources 21

Report 2a: Natural phytoplankton communities and optical properties of phytoplankton during SHIVA-Sonne expedition in November 2011 in the South China Sea and Sulu Sea, Infinity ME 26

Report 2b: Community structure of *Pseudo-nitzschia* (Bacillariophyceae) from the SHIVA expedition 29

Report 2c: Microbial communities of the eastern South China Sea and the Celebes Sea and their possible roles in the DMS(P) Cycle 30

Report 2d: Culturable bacteria from Talang-Talang Reef and its surrounding waters 36

Report 3: Interaction of climate active gases during the SHIVA-Sonne SO218 campaign: Dimethylsulfide, oxygenated volatile organic compounds, nitrous oxide (N_2O), and methane (CH_4) 39

Report 4: Underway measurements of pCO_2, oxygen and total gas pressure 45

Report 5: SHIVA SONNE SO218: Radio- and Ozonesounding 48

Report 6: Determination of trace gas concentrations in the marine boundary layer 52

Report 7: Trace Gas Measurements using MAX-DOAS and CE-DOAS instruments 54

Report 8: µ-Dirac – continuous measurements of halogenated trace gases 57

Report 9: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH_4, O_3, CO_2) 62

Report 10a: DLR- CIMS measurements: Investigation of anthropogenic emissions affecting air quality in the marine boundary layer of the South China and Sulu Sea 63

Report 10b: Sonne- Falcon Lagrangian tracer experiment and continuos carbon monoxide and ozone measurements 66

Report 10c: *In situ* measurements of IO by Laser-Induced Fluorescence Spectroscopy 68

Report 10d: Measurements of I_2 and the sum of HOI + ICl during SHIVA 70

Report 11: Aerosol chemistry of halogens during SHIVA 73

Report 12: Oceanic Circulation -Transient tracer measurements during cruise Sonne-218 76

Report 13a: Results of the local boat deployments in Kuching, Kota Kina Balu, and Semporna 78

Report 13 b: Results of the local boat deployment Kuching 82

Report 13 c: Results of the local boat deployment Kota Kinabalu, 84

Report 14: The contribution of oceanic halocarbons to the stratospheric halogen loading 86

Acknowledgements 90

RV SONNE CRUISE SO218: SINGAPORE-MANILA, 15-29 NOVEMBER 2011

Within the frame work of the EU-project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) the research cruise SO218 of the German research vessel SONNE was organized and conducted by the Leibniz-Institute of Marine Sciences (IFM-GEOMAR, http://www.ifm-geomar.de/, now GEOMAR Helmholtz-Zentrum für Ozeanforschung, Kiel http://www. geomar.de/) from 15 to 29 November 2011 in the South China and Sulu Sea. The RV Sonne (cruise SO218) sailed from Singapore to the Philippines (15-29 Nov), following a track along the coast of Borneo and through the Sulu Sea (Figure 1). The route incorporated 2 diurnal stations off the western coast of Borneo, 2 contacts with local boats from the universities in Kuching and Kota Kinabalu, and was overflown by the GERMAN research air craft Falcon from the DLR German Aerospace Center on 3 occasions. The cruise was mainly bound to investigate tropical trace gas emissions in Malaysian and Philippine waters of various biogeochemical regimes between Singapore and Manila (Philippines) and their contribution to stratospheric halogens. Partners on board were from the European project SHIVA - Stratospheric halogens in a varying atmosphere - (http://shiva.iup.uni-heidelberg.de/) and from Malaysia, the University of Malaya, Kuala-Lumpur (IOES) Universiti of Malaya, Sarawak (UNIMAS), Universiti of Malaya, Sabah) and the University of the Philippines Diliman, Quezon. During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed. Halocarbon concentrations were determined in water and air, and sea-to-air fluxes were calculated. Many other atmospheric trace gases, transport processes and various oceanic chemical, physical and biological parameters were also determined.

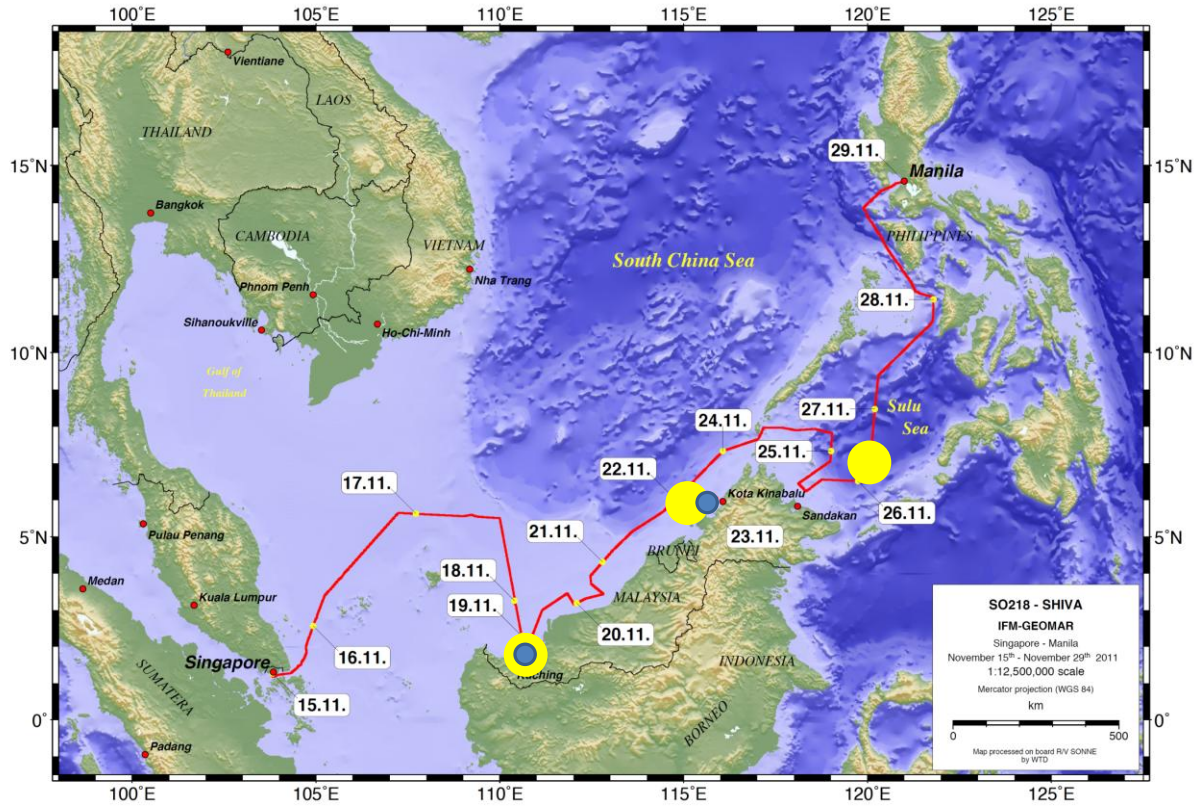


Figure 1: Cruise track of *RV Sonne*: Singapore-Manila (15-29 November 2011), including the local boat meetings at Kuching and Kota Kinabalu (blue circles) and overflights by the DLR air craft Falcon (yellow circles).


Coastal team at Kuching, Sarawak, 2011


Coastal team at UMS Jetty, Kota Kinabalu, Sabah 21th November 2011


Field equipment testing at UMS Jetty, Kota Kinabalu, Sabah 21th November 2011


Coastal team at UMS Jetty, Kota Kinabalu, Sabah 21th November 2011

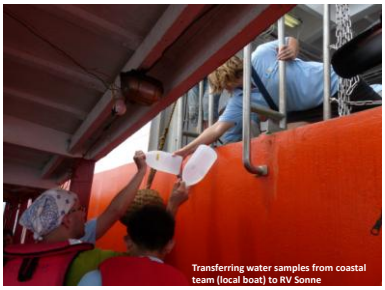


Figure 2: Impressions from the local boat deployments at Kuching, with additional deployment of deployment of Falcon and local cruise at Kota Kinabalu.

SCIENTIFIC BACKGROUND

Trace gases, containing halogens as chlorine and bromine are broken down by solar radiation in the stratosphere, where the halogens are highly efficient at destroying ozone. Increasing emissions from human activities have led to depletion of global stratospheric ozone over the last three decades. Whereas the chlorine supply is dominated by anthropogenic compounds, a major part of the bromine is supplied by natural, short-lived species, with oceanic sources. The tropical oceans are a known source of reactive bromine and iodine to the atmosphere in the form of short-lived brominated and iodinated methanes as e.g. bromoform ($CHBr_3$). Elevated atmospheric concentrations above the oceans are related to oceanic supersaturations of the compounds, and to natural photochemical and biological production. Macro algae in coastal regions, as well as regionally enhanced phytoplankton, river outflow, photochemical reactions and local anthropogenic sources all contribute to marine and atmospheric concentrations.

Trace gases enter the stratosphere principally in the tropics, where ascending warm air carries them upwards. The intense vertical transport of the tropical atmosphere implies that the oceanic sources could supply significant amounts of halogens to the upper troposphere/ lower stratosphere where they may contribute to the observed ozone amounts and trends. The tropical western Pacific is a largely uncharacterized region for the oceanic compounds and a projected hot spot, especially in coastal regions for their emissions and transport pathways into the stratosphere.

Spatial and temporal variability in production and sea-to-air flux of the short-lived halogenated trace gases create strong varying marine and atmospheric distributions and thus also varying stratospheric contributions. The current impact of the natural ozone depleting substances is still highly uncertain and future changes in the mechanisms, that regulate their emissions to the atmosphere, their transport, and their chemical processing are largely unknown. Therefore the oceanic emissions have the potential to cause surprises in the future evolution of the ozone layer in a changing climate, unless they are better understood. The measurements were thus needed to improve the understanding of future stratospheric halogen loading and therewith ozone depletion. The results of the SHIVA-SONNE campaign contribute to the scientific underpinning of the United Nations Montreal Protocol on Substances that Deplete the Ozone Layer, to the United Nations Framework Convention on Climate Change, and to global climate change research.

OBJECTIVES, PARTICIPATING INSTITUTIONS AND MEASUREMENTS

Of particular relevance during SO218 were oceanic and atmospheric measurements of a suite of short-lived trace gases containing the halogens chlorine, bromine and iodine in various marine biogeo-chemical regimes, as close to the coasts, in regions of high chlorophyll, close to coral reefs, in oceanic upwelling regions and in river outflow, compared to more open oceanic conditions and under differing meteorological conditions. From these measurements the climate-sensitive oceanic emission strengths and real contributions of the emissions to stratospheric halogens are characterized by modeling.

The atmospheric structure was determined by intense radio and ozone sounding during the cruise. Other marine trace gases as i.e. nitrous oxide (N_2O), dimethylsulfide (DMS), oxygen (O_2) and carbon dioxide (CO_2), were investigated as well. In situ and satellite measurements of phytoplankton groups, obtained by special retrieval methods from the SCIAMACHY and GOME-2 instruments gave further information about biogeochemical conditions during the ship expedition. Atmospheric concentrations of a variety of long-lived anthropogenic and natural trace gases were also determined. These measurements help to identify transport pathways of the tropospheric trace gases towards and away from the ship. The measurements on RV SONNE in the South China Sea and along the coastline of Peninsula Malaysia and Borneo in conjunction with Malaysian research partners were accompanied by

parallel measurements with the DLR Falcon and land-based investigation teams (see: The SHIVA Western Pacific campaign in November and December 2011, Post-campaign Activity Report by Pfeilsticker, 2012 and the SHIVA final report).

The instruments on board of the ship made quasi-continuous measurements of VSLS and related species in both seawater and air to determine actual sea to air fluxes, whilst the aircraft carried out surveys of the larger scale concentrations in the marine boundary layer and in the convective outflow at altitudes up to ~13 km.

Together with the main scientific objective of the cruise to characterize the oceanic emissions of natural halogenated gases in the western Pacific, the participating groups followed additional research questions. Thus, more specifically, the overall scientific program of SO218 included the following themes, which could roughly be assorted to individual working groups (Table 1):

1.) HALOCARBONS: Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons, in order to derive their sea to air fluxes.

2.) PHYTO-OPTICS and PLANKTON: Phytoplankton pigments, species and size distribution, radiation and absorption spectra of seawater and plankton content in order to characterize the phytoplankton and zooplankton composition and to validate satellite data from the western Pacific.

3.) OCEANIC TRACE GASES: Oceanic concentrations of dimethyl sulfide and related compounds (DMS, DMSO, DMSP), nitrous oxide and methane, in order to understand their distribution in the different biogeochemical regimes of the western Pacific and to gain new insights into halocarbon sources.

4.) OCEANSENSORS: Identification of carbon dioxide and oxygen sources and sinks; separation of physical and biological factors for observed sources and sinks, temperature and salinity.

5.) RADIOSOUNDING: Identification of meteorological vertical and ozone profiles in order to evaluate the mixing layer and tropopause height and to calculate air mass back trajectories to identify origin of sampled air masses. Finally, to validate chemical transport model results and the distribution of ozone in the western Pacific atmosphere.

6.) AIRSAMPLING: Determination of anthropogenic and natural trace gas concentrations by flask sampling, to identify regional and diurnal gradients of some compounds and for intercalibration of different instruments.

7.) SPECTROSCOPY: Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy (MAX DOAS) in a three dimensional field and Cavity Ring Down Spectroscopy as possible decomposition products of organic trace gases and for validation of satellite-data.

8.) µ-DIRAC: Quasi-continuous measurements of some VSLS in the marine atmospheric boundary layer (15 m altitude) for real time concentrations.

9.) ATMOSPHERIC TRACE GASES: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH_4, O_3, CO_2) in order to investigate their spatial and temporal variability in the lower tropical marine boundary layer.

10.) CIMS-REACTIVE COMPOUNDS; Continuous measurements of Br_2, BrCl, HOBr, BrO, and $ClNO_2$ and HNO_3, HCl, SO_2, and HBr in the marine boundary layer with two Atmospheric Chemical Ionization Mass Spectrometers, a LIF Instrument for IO and a NOx detector, which were deployed inside a specifically designed 10 ft container on the forecastle deck of the ship.

11.) ATMOSPHERIC AEROSOL: Major ions and halogens in aerosol samples, in order to identify their sources and quantify the halogen budget in the western Pacific atmosphere.

12) OCEAN CIRCULATION: Ocean surface currents and transient tracers for age determination.

13) LOCAL BOAT DEPLOYMENTS: Local boats visited the RV Sonne from our Malaysian partners (University of Malaysia-Sarawak) at Kuching on 19th November at noon and the University of Malaysia, Sabah at Kota-Kinabalu on 22nd November.

14) TRANSPORT INTO THE STRATOSPHERE: The halogen contribution of the local oceanic emissions to the upper tropospheric and lower stratospheric halogen content were calculated with the Lagrangian transport model FLEXPART.

Table 1: **SCIENTIFIC GROUPS. PARTICIPATING INSTITUTIONS AND CONTACTS:**

	Principal Investigator (PI)	groupno.+ name	Last Name	Fore Name	Function	University
	Ship					
			Quack	Birgit	chief scientist	IFM-GEOMAR
			Sapii	Mohamad Zaid bin	observer	NHD-Malaysia
			Magura	Benjamin Z. Magura	observer	Navy-Philippines
in water	Quack	1a: Halocarbons MS	Hepach	Helmke	student	IFM-GEOMAR
			Raimund	Stefan	technician	IFM-GEOMAR
	Wallace	1b: Halocarbons ED	Qiang	Shi	student	IFM-GEOMAR
	Bracher	2a: Biology; Pigments	Altenburg Soppa	Mariana	scientist	AWI- BREMERHAVEN
			Wiegmann	Sonja	technician	AWI- BREMERHAVEN
			Cheah	Wee	scientist	AWI- BREMERHAVEN
	UM/UNIMAS	2b: Biology, speciation	Idid	Rizman	scientist	Universiti Malaya Kuala Lumpur
			Muhajid	Aazani	scientist	University Malaysia Sarawak
	Palermo		Palermo	Joseph	scientist	University of the Philippines Dilimar
	Marandino	3a: OVO, C	Zindler	Cathleen	student	IFM-GEOMAR
	Quack	3b: Ox, Nuts	Marandino	Christa	student	IFM-GEOMAR
	Bange	3c: N_20, CH_4, DMS				
	Körtzinger/Tanhu	4: P_{CO2}, P_{O2}, S,T	Schneider	Anke	scientist	IFM-GEOMAR
in air	Krüger	5: radiosonding	Krüger	Kirstin	scientist	IFM-GEOMAR
			Bieligk	Henner	scientist	IFM-GEOMAR
			Fuhlbrügge	Steffen	student	IFM-GEOMAR
	Atlas	6: air sampling	Wittke	Franziska	scientist	IFM-GEOMAR
	Pfeilsticker	7: CE- DOAS	Lampel	Johannes	student	Uni Heidelberg
	Harris/ Kreher	8: µ- DIRAC	Kinzel	Julian	scientist	Cambridge/IFM-GEOMAR
	Schlager	9: CO, CO_2, CH_4, O_3	Sentian	Justin	scientist	University Malaysia Sabah
			Abdullah	Nur Aleesha	scientist	Malaysian Meteorological Dep.
	Voigt	10a: CIMS, Br	Jurkat	Tina	student	DLR
			Schäuble	Dominik	scietist	DLR
	Heard	10b: IO, OH, Hox	Ingham	Trevor	scientist	Uni Leeds
	Hofmann		Bunyan	Hannah	student	Uni Leeds
	Baker	11: Aerosol				UEA-Norwich

AWI BREMERHAVEN — Alfred-Wegener-Institute für Polar und Meeresforschung, Fachbereich. Klima. Bussestraße 24, D- 27570 Bremerhaven.de, email: Astrid.Bracher@awi.de

DLR — Deutsches Zentrum fuer Luft-und Raumfahrt (DLR), Oberpfaffenhofen, D-82234 Wessling, email: tina.jurkat@dlr.de, hans.schlager@dlr.de

IFM-GEOMAR — Leibniz-Institut für Meereswissenschaften, Düsternbrooker Weg 20, D-24105 Kiel, Tel: +431 6004206, Fax: +431 6004205, email: bquack@ifm-geomar.de; New name since 1. January 2012: GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel, bquack@geomar.de

IUP BREMEN — Institut für Umweltphysik, Universität Bremen, Otto-Hahn-Allee 1, D-28359 Bremen, Deutschland, folkard@iup.physik.uni-bremen.de

IUP HEIDELBERG	Institut für Umweltphysik, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, email: johannes.lampel@iup.uni-heidelberg.de
MMD	Malaysian Meteorological Department, Jabatan Meteorologi Malaysia, Kementerian Sains, Teknologi dan Inovasi, Nur Aleesha Abdullah, email: aleesha@met.gov.my
NHD-Malaysia	National Hydrographic Centre-Malaysia, Comannder Zaid Sapii, email: zaidsapii@gmail.com
NIWA	Lauder, Central Otago, New Zealand, Karin Kreher, email: k.kreher@niwa.co.nz
Philippine-Navy	ENS Benjamin Zambrano Magura, email: mantarayz12@yahoo.com
RSMAS MIAMI	Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, email: eatlas@rsmas.miami.edu
UEA	University of East Anglia, Norwich, NR4 7TJ, UK, email: alex.baker@uea.ac.uk
UM	Institute of Biological Sciences, Faculty of Science, 50603 Kuala Lumpur, Dr.Mohammed Rizman Idid, email: rizman@um.edu.my
UM SABAH	Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu, Sabah, email: aanton@ums.edu.my
UNI LEEDS	School of Chemistry, University of Leeds, LS2 9JT, UK, email: t.ingham@leeds.ac.uk
UCAM	University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, neil@atm.ch.cam.ac.uk
UNIMAS	Department of Aquatic Science, Faculty of Resource Science & Technology, University Malaysia Sarawak, 94300 Kota Samarahan, Sarawak Malaysia, Aazani Mujahid, email: maazani@frst.unimas.my
UNI MAINZ	Institute for Analytical Chemistry, D-55128 Mainz, Thorsten Hoffmann, Ru-Jin, Huang, email: rujin@uni-mainz.de
UPHI	Biological Oceanography and Modeling of Ecosystem Lab., The Marine Science Institute, University of the Philippines, Diliman, Quezon City, 1101 Philippines, email: jaydeepalermo@gmail.com

WORK PROGRAM DURING THE CRUISE

During the SO218 cruise of 'RV Sonne' from 15 to 29 November 2011 in the South China and Sulu Sea between Singapore and Manila (Philippines) a variety of chemical and physical parameters within the surface waters as well as between the atmospheric boundary layer and the stratosphere have been examined with different measurement frequencies. Data and samples were obtained using a variety of analytical instruments and sampling devices (Tables 1 and 2).

Table 2: Installed and operating instruments on board (Singapore-Manila; 15.-29. November 2011)

	Group	Instrument	Parameter
1	Halocarbons	Agilent GC/MS	iodinated, brominated and chlorinated VSLS
2	Halocarbons	Fisons GC 8000	iodinated, brominated and chlorinated VSLS
3	Phytoplankton/AWI	Pigments/Filtration	phytoplankton pigments, chlc3, chlc1+2,
4		Flowcytometry	phytoplankton size classes
5		Remote sensing (chla maps)	phytoplankton speciation
6		FRRF_Fluorometer	chla
7		Peristaltik/Pump	water supply
8		Microscopy	phytoplankton species
9	Radiation	RAMSES/ Container top	Radiane/Irradiance
10		RAMSES/ Monkey deck	Radiane/Irradiance
11		Fasttracka/ CTD	Radiane/Irradiance
12	Phytoplankton/Malaysia	UW Phyt. + Bacteria / Filter (150L water)	molecular characterization
13		CTD Phyt. + Bacteria / Filter (150L water)	zooplankton
14		Bongo Net/Plankton Net	zooplankton
15	Phytoplankton/Philippines	Infinity ME/ station/ fluorescence	phytoplankton
16	OVOC	GC/ MS	acetone, acetaldehyde, propanal, butanal, butanon
17		CDOM	humic acdis
18	DMS	GC	DMSP, DMSO, DMS
19	Ox/Nuts	Oxygen	CTD- discrete Winkler Oxygen
20		Nutrients	NO^{3-}, PO_4^{3-},
21		N2O; CH4	nitrous oxide, methane
22	Tracer	Freon samples	CFC water age
23	PCO2	PCo_2	CO_2 pressure in seawater
24		PO_2 (Oxygen optode)	Oxygen in Seawater
25		T	SST from Optode
26		Gas tension device	Total gas pressure in water
27	CTD	CTD	Temperature and Salinity profiles
28		Rosette sampler	water depth samples
29		Fluorometer	chlorophyll
30	Thermosalinograph	T/S	Temperature and Salinity continuous
31		meteorology	air temp, humidity, wind speed and direction,
32	Hydrographic shaft	CTD	temperature and salinity continuous
33		ADCP	ocean surface currents
34		sun-Pump	water samples from 4m depth
35		lowara	water samples from 4m depth
36	Radiosounding	Radiosondes	air temp, humidity, wind speed and direction profiles
37		Disdrometer	rain dropsizes
38		Rainsensor (Rudolph IRSS88)	rain
39		Ozon- sondes	ozone profiles
40	Air- sampling	Atlas flasks	> 50 trace gases, hydro-, halocarbons, freons, alkylnitra
41		Baker Aerosol	aerosol bromine, iodine speciation
42	Max Doas	Max Doas HD /Spectrometer (Acton)	BrO, IO
43		Max Doas HB/Spektrometer Shamrock 303i	BrO, IO,
44		Cavity HD	IO
45	µ-dirac	GC	$CHBr_3$, CH_2Br_2, and chlorinated compounds
46	DLR	cavity ring down (CO2, CH4,H2O)	CH_4, CO_2; O_3; CO
47		UV-absorp., VUV-fluoresc. (CO/O3)	carbon monoxide, ozone
48		CIMS1(BrO, Br_2, HOBr)	Br, HBr, BrO
49		CIMS2 (SO_2,HCl, HBr)	SO2,HCl, HBr, nitril chloride
50	Leeds	LIF (IO)	IO
51		Nox-Box (NO_2)	nitrous oxide
52		Denuder-Hofmann (I_2)	I_2

Regular water samples were collected from pump supplies submersed in the hydrographic shaft of the ship. Depth profiles were undertaken at selected locations to investigate the vertical hydrographic structure of the water column and to obtain trace gas profiles. Deep profiles of anthropogenic tracers were determined in the Sulu Sea to determine the water mass age. Several VSLS from sea water and air were analyzed directly on board the ship.

Table 3: Underway work plan and sampling strategy on board FS Sonne during SO218- SHIVA.

Zeit	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Group pe																								
1	w/a	w	w	s	w	w	w/a	w	w	s	w	w	w/a	w	w	s	w	w	w/a	w	w	s	w	w
2	w	c	c	c	c	c	c	w	c	c	c	c	c	w	c	c	c	c	c	w	c	c	c	w
3		w			w			w			w			w			w			w				w
4	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c
5	r						r						r/w/o						r					
6	(a)	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	2a	(a)	(a)	(a)	(a)	(a)
7	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c
8	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c
9	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c
10	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c

w: water sample
a: air sample (occasional)
c: continuous
r: radio sonde
o:ozone sonde
st: standard

The working schedule during transit included continuous sampling of seawater, a collection of discrete air samples, the installation of optical measuring techniques and the uplift of research balloons. During the cruise samples have been obtained with 52 instruments and sampling devices (Table 2). Routinely hourly to three hourly water and - air samples have been taken from pump supplies submersed in the hydrographic shaft, respectively installed on the monkey deck (Work Groups 1,2,3,4,6). Meteorologists sent weather balloons with trace gas instruments to the stratosphere (up to 30 km height) every six hours (Work Group 5), with an increased frequency of two hours on the two diurnal stations on 18./19th and 21./22nd November , which were conducted in open waters each roughly 60 nm off-coast from Kuching and Kota-Kinabalu.

After these stations, boats from our Malaysian partners at Kuching from the University of Malaysia-Sarawak on 19th November at noon, at Kota-Kinabalu from the University of Malaysia, Sabah visited the RV Sonne. During these local ship cruises, water samples were taken (at 1 km, 5 km, 10 km, 15 km, and 20 km off-coast) and exchanged with samples taken in the open ocean by the RV Sonne team. The local boat water samples were analyzed for their content of trace gases and phytoplankton on board RV Sonne. Open ocean measurements were thus complemented by near shore and coastal

gradients from the local ships and atmospheric measurements through the troposphere by the aircraft Falcon, starting at the same height of 15m above sea level as air samples were taken on board the Rv Sonne.

Figure 3: Meetings and simultaneous measurements of RV SONNE and DLR aircraft Falcon – stationed in Miri on Borneo during the SHIVA campaign- were and performed on 19th November, 12 o'clock local time and on 21st November, 11o' clock local time (Photo: Torsten Bierstedt).

The optical sensors and continuous instruments have been installed in the beginning of the cruise on the monkey deck, the bow and in a research container (Work Groups 3, 7, 8, 9, 10).

Various halogenated hydrocarbons have been analyzed directly on board using a gaschromatography/ mass spectrometry system (Work Group 1). Oxygenated trace gases and dimethyl sulfide were also analyzed directly with a gas chromatograph/mass-spectrometric system from sea water (Work Group 3), while carbon dioxide and oxygen were measured immediately with sensors within the upper oceanic layer (Work group 4). More trace gases in sea water (N_2O, CH_4) where analyzed by gas chromatography post-cruise in the laboratory (Work group 3). Biological sampling included parameters of organic carbon and nitrogen as well as pigments, the amount and sizes of cells and the composition and activity of the phytoplankton and zooplankton (Work Group 2). The optical properties of seawater and its ingredients were measured as reference spectra for the validation of satellite data analysis and models, in order to detect the composition, distribution and productivity of phytoplankton (Work Group 2).

Figure 4: Local boats visited the RV Sonne from our Malaysian partners (University of Malaysia-Sarawak) at Kuching on 19th November at noon and the University of Malaysia, Sabah.at Kota-Kinabalu on 22nd November.

Discrete air samples were taken for partners of the Universities Norwich (15 samples) as well as the 'Rosenstiel School of Marine and Atmospheric Sciences' in Miami (200 samples) (Work Groups 6, 11). In the respective home laboratories more than 70 anthropogenic and natural trace gases, and elements in aerosols within the marine boundary layer where analyzed following the cruise. Atmospheric profiles of temperature, humidity and different kinds of trace gases (e.g. ozone, nitric oxide, bromine oxide, carbon monoxide) were examined on the basis of optical measurements, by rises of research balloons and mass spectrometers (Work Groups 5, 6, 8, 9, 10).

The analysis of the extensive dataset from the ocean and the atmosphere collected during SO218 brought new insights into the interaction of ocean and atmosphere, were presented at international conferences (SOLAS, EGU and AGU conferences) and first publications are already published in peer reviewed scientific journals and further will follow (Table 4).

Figure 5: Release of an ozone-sonde at night (photos: Johannes Lampel).

Table 4: **PUBLISHED ARTICLES, PUBLICATIONS IN PROGRESS AND PRESENTATIONS AT NATIONAL AND INTERNATIONAL CONFERENCES**

Articles

1. Bracher, A., Cheah, W., Dinter ,T., Steinmetz, F. Deriving phytoplankton characteristics from optical properties in the South China Sea and Sulu Sea, in prep for Ocean Sciences.
2. Cheah W., et al., Photophysiological state of natural phytoplankton communities in the South China Sea and Sulu Sea, Biogeosciences Discussion 10:12115-12153, 2013.
3. Fuhlbrügge et al., Exchange of VSLS in the marine boundary layer with the free troposphere during SHIVA-SONNE, ACPD (in prep.), 2013.
4. Hamer, P. D., Marécal, V., Hossaini, R., Pirre, M., Warwick, N., Chipperfield, M., Samah, A. A., Harris, N., Robinson, A., Quack, B., Engel, A., Krüger, K., Atlas, E., Subramaniam, K., Oram, D., Leedham, E., Mills, G., Pfeilsticker, K., Sala, S., Keber, T., Bönisch, H., Peng, L. K., Nadzir, M. S. M., Lim, P. T., Mujahid, A., Anton, A., Schlager, H., Catoire, V., Krysztofiak, G., Fühlbrügge, S., Dorf, M., and Sturges, W. T.: Modelling the chemistry and transport of bromoform within a sea breeze driven convective system during the SHIVA Campaign, Atmos. Chem. Phys. Discuss., 13, 20611-20676, doi:10.5194/acpd-13-20611-2013, 2013.
5. Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys. Discuss., 13, 12485-12539, doi:10.5194/acpd-13-12485-2013, 2013.
6. Keng, F. S.L., S.M. Phang, N. A. Rahman, E. C. Leedham, C. Hughes, A. D. Robinson, N. R. P. Harris, J. A. Pyle, W. T. Sturges, Volatile halocarbon emissions by three tropical brown seaweeds under different irradiances, Journal of Applied Phycology., 25, 5, 1377-1383, 1386, DOI 10.1007/s10811-013-9990-x, 2013.
7. Kuek, F.W.J., Mujahid. A, Po Teen, L., Chui Pin, L., Müller, M.; Bacterial communities from the eastern South China Sea and the Celebes Sea, and their potential role in the DMS(P) cycle, in prep. for Biogeosciences.
8. Leedham, E., Hughes, C., Keng, F., Phang, S., Malin, G., Sturges, W., Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, Biogeosciences, 10, 3615-3633, doi:10.5194/bg-10-3615-2013, 2013.
9. Marécal et al.: What do we learn on bromoform transport and chemistry in deep convection from fine scale modelling?, Atmospheric Chemistry and Physics, 12, 6073-6093, 2012.
10. Huang, Peng, Tanhua, T., Ventilation and anthropogenic carbon in the Sulu Sea. in prep for Water
11. Ooi, S. H., Samah, A. A., and Braesicke, P.: Primary productivity and its variability in the equatorial South China Sea during the northeast monsoon, Atmos. Chem. Phys. Discuss., 13, 21573-21608, doi:10.5194/acpd-13-21573-2013, 2013.
12. Raimund, S. et al., Oceanic sources of VSLS in the South China and Sulu Seas, in preparation.
13. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A., Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F.: The contribution of oceanic methyl iodide to stratospheric iodine, Atmos. Chem. Phys. Discuss., 13, 11427-11471, doi:10.5194/acpd-13-11427-2013, 2013.
14. Tegtmeier, S., K. Krüger, B. Quack, I. Pisso, F. Ziska et al.: ODP weighted VSLS emissions for present and future scenarios
15. Walker, H., Folkard Wittrock, Johannes Lampel, Martin Horbanski, Justin Sentian, Enno Peters, Anja Schönhardt, Tilman Dinter, Astrid Bracher, Mihalis Vrekoussis, Ru-Jin, Katja Großmann, Karin Kreher et al., Measurements of reactive iodine species during and related to the SHIVA campaign.
16. Yang, X., Pyle, J. A., and others, Response of atmospheric ozone to the perturbation of VSLS emissions under different chlorine and bromine backgrounds, (in prep), 2013a.

17. Yang, X., Pyle, J. A., Hossaini R, Chipperfield M.P., +others, Modelling future changes of the stratospheric ozone due to biogenic bromocarbons, (in prep), 2013b.
18. Ziska, F., Quack, B., Abrahamsson, K., Archer, S., Atlas, E., Bell, T., Butler, J., Carpenter, L., Jones, C., Harris, N., Hepach, H., Heumann, K., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R.M., Orlikowska, A., Raimund, S., Reeves, C., Reifenhaeuser, W., Robinson, A., Schall, C., Tanhua, T., Tegtmeier, S., S. Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., Yokouchi, Y., Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmos. Chem. Phys. Discuss., 13, 5601-5648, doi:10.5194/acpd-13-5601-2013, 2013.
19. Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., et al., Future trend in oceanic halocarbon emissions
20. Ziska F., Bracher A., Cheah W., Dinter T., Quack B. Inferring oceanic concentration of VSLS from oceanic biological and physical parameters over the maritime continent, in prep for Biogeosciences

Presentations (poster and talks)

1. Cheah, W., Taylor, B., Dinter, T., Wiegmann,S., Altenburg-Soppa, M.,Palermo, J., Bracher, A., Composition and optical features of phytoplankton during SHIVA-SONNE (SO218) expedition, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
2. Cheah W., Taylor B., Dinter T., Raimund S., Quack B., Bracher A. (2012) Community structure and optical properties of phytoplankton during SHIVA-Sonne expedition: From in-situ and satellite. South China Sea Conference 2012, 22 - 26 October 2012 Kuala Lumpur, Malaysia, Talk
3. Fuhlbrügge, S., Krüger, K., Quack, B. und das SHIVA SONNE Team, SHIVA SONNE SO218: Analysis of meteorology and air masses, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
4. Fuhlbrügge, S., Quack, B., Tegtmeier, S., Atlas, E., Sala, S., Boenisch H., Hepach, H., Raimund S., Shi Q., Krüger, K.; Exchange of VSLS in the marine boundary layer with the free troposphere during SHIVA-SONNE, EGU General Assembly, Vienna, Poster, 2013
5. Hepach H., Raimund S., Taylor B., Bracher A., Fischer T., Quack B. (2013) "Contributions to tropical VSLS emissions from the equatorial Atlantic upwelling regions". SOPRAN Annual Meeting 2013, 19.-20.03.2013, Leipzig, Poster
6. Jurkat, T., Voigt, C., Schäuble D. , Investigation of anthropogenic pollution in the marine boundary layer of the South China Sea and Sulu Sea (SO218), BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
7. Krüger Kirstin, "Ocean-stratosphere interactions in a changing climate", UiO, Oslo, 22. November 2012, (invited) Talk, 2012.
8. Krüger, K., B. Quack, S. Fuhlbrügge, S. Tegtmeier, First results from the SHIVA SONNE expedition to the tropical Western Pacific during November 2011, EGU, General Assembly , Vienna, Poster, 2012.
9. Krüger, K., B. Quack , E. Atlas, S.Tegtmeier, and F. Wittke, Towards bridging the gap between oceanic and upper air VSLS measurements: The SHIVA-SONNE campaign, CCMVAL work-shop, Davos, 21.-24. May, 2012, Poster, 2012.
10. Kuek, F.W.I., Ngu, E.S.L., Lee, S.T.H., Mujahid, A., Lim, P-T., Leaw,C-P., Müller, M. , Microbial communities of the Eastern South China Sea and Sulu Sea and their possible roles in the DMS(P) cycle, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
11. Lampel, J., Wittrock, F., Großmann, K., Peters, E., Horbanski, M., Pöhler, D., Frieß, U., Pfeilsticker, K., Platt, U., DOAS measurements from space, ship and plane: trace gas distributions over the South China and Sulu Sea, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster

12. Leedham, E., W Sturges, G Malin, C Hughes, D Oram, F Keng & S-M Phang, Halocarbon Production in the Tropical Coastal Zone, SOLAS Open Science Conference, poster, May 2012.
13. Mohr, V., K. Krüger, S.Tegtmeier, M. Neish, T. Shepherd,and D. Smale, Towards analysing transport pathways of VSLS in CCMs, WAVACS summer school, Corsica, France, poster, 14.-26.09.2009.
14. Mohr, V., Tegtmeier, S., Schofield, R., Rex, M., Neish, M., Smale, D., Gettelman, A., Garny, H. und Krüger, K., Analysing the tropical widening of the TTL with a Lagrangian approach using CCM and ERA-Interim data, AGU Fall meeting San Francisco, CA, USA., poster, 15.12.2010.
15. Mujahid, A, Müller, M, Emily S.L. Ngu, E.S.L., T.H., Samson, L., Yao-Long, L., Y.2, Felicity W.I. Kuek, F.W.I., Hong-Chang, L., Sing-Tung, T., Chui-Pin, Leaw, Po-Teen, L., Shiva Local boat deployment in Kuching and major findings from Sarawak, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
16. Peters, E., Lampel, J., Wittrock, F., Vrekoussis, M., Richter , A., Burrows, J.P., Tschritter, J., Dorf , M., Quack, B., Sentian, J., Pfeilsticker, K., MAX-DOAS measurements of atmospheric trace gases during the SHIVA-Campaign, EGU, General Assembly , Vienna, Poster, 2012.
17. Qiang Shi, Gert Petrick, Birgit Quack, Douglas Wallace, Production in variability of methyl iodide (CH3I) in the surface Ocean, SOLAS OPEN Science Conference, 7.-10.5.2012, Poster, 2012.
18. Quack, B. and Krüger, K., Die SHIVA-SONNE SO218 Kampagne, SONNE-Statusseminar, Kiel, Germany, Talk, 15.02.2013, 2013.
19. Quack, B. and Krüger, K., From the ocean to the stratosphere: The SHIVA SONNE cruise Marine Science Institute, 01.12.2011, Quezon City, Manila, Philippines, Talk, 2011.
20. Quack, B., Atlas, E., Hepach, H., Raimund, S., Tegtmeier, S., Shi, Q., Kinzel, J., Leedham, E., Fuhlbrügge, S., Taylor, B., , Chea, W., , Wittke, F., Robinson, A., Harris, N., Kreher, K., Sturges, B., Bracher, A., Wallace, D., Krueger, K., Halocarbon distributions and emissions in the South China and Sulu Sea during the SHIVA SONNE expedition in November 2011, South China Sea Conference, 22.-26. October 2012, Kuala Lumpur, talk
21. Quack, B., Elliot Atlas, Qiang Shi, Helmke Hepach, Stefan Raimund , Julian Kinzel , Emma Leedham, Steffen Fuhlbrügge , Sonja Wiegmann , Wee Chea, Franziska Wittke, Andrew Robinson, Neil Harris, Karin Kreher, Bill Sturges, Astrid Bracher, Doug Wallace and Kirstin Krüger, Halocarbon distributions and emissions in the western tropical Pacific during the SHIVA SONNE expedition in November 2011, EGU General Assembly, Vienna, Talk, 2012.
22. Quack, B., Krüger, K. Ziska, F. Hepach, H. Raimund, S. Tegtmeier, S. Shi Q., Atlas, E. S. Fuhlbrügge, S., Wallace, D. Halogenated trace gases from the ocean to the atmosphere, 17. January, 2013, Technische Universität Braunschweig, Geoökologisches Kolloquium, talk
23. Quack, B., Krüger, K., Hepach, H., Raimund, S., Ziska, F., Tegtmeier, S., Shi, Q., Atlas, E., Fuhlbrügge, S., Flöter, S., Petrick, G., Wallace D., Marine halogenated trace gases for the atmosphere, Physical Chemistry, University of Kiel, 22. May, 2013,talk.
24. Quack, B., Krüger, K., Hepach, H., Wittke, F., Raimund, S., Tegtmeier, S., Petrick, G.. Fuhlbrügge, S., Wallace, D., Atlas, E., The oceans as source of brominated halocarbons for the atmosphere, Johann Wolfgang University, 9. Februar, 2012, Frankfurt, talk
25. Quack, B., Krüger, K., Hepach, H., Wittke, F., Raimund, S., Tegtmeier, S., Petrick, G.. Fuhlbrügge, S., Wallace, D., Atlas, E., Marine halogenated trace gases for the atmosphere, Miami Haloproc, Annual meeting, Oberjoch, 22. März, 2012, talk
26. Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., und das SHIVA-Sonne Team, SO218 – Die SHIVA-SONNE (SO218) Kampagne: Die Bedeutung mariner Spurengasquellen im tropischen West Pazifik für stratosphärisches Ozon (Singapur-Manila: 15.-29. November 2011), BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, talk
27. Quack, Birgit, Kirstin Krüger, Stefan Raimund, Helmke Hepach, Elliot Atlas, From the ocean to the stratosphere: First results from a large-scale tropical western Pacific campaign, Helmholtz-Centre for Ocean Research Kiel (GEOMAR), Kiel, Germany , Scientific advisory board evaluation, 9.5.2012, Poster, 2012.

28. Raimund, S., Hepach, H., Shi, Q., Atlas, E., Chea, W., Bracher, A., Quack, B., Quellen und Emissionen kurzlebiger halogenierter Verbindungen im westlichen tropischen Pazifik, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
29. Schlager, H., and SHIVA Science Team SHIVA Experiment in Malaysia in Nov/Dec 2011 DC3 - SEAC4RS Science Team Meeting, Boulder, USA, Oral, 21-23 Feb 2012.
30. Steinhoff, T., Bange, H.W., Fiedler, B., Fietzek, P., Ihnenfeld, V., Kock, A., Körtzinger, A., Schneider, A., Methane-, N2O-, O2 and pCO2- measurements in the surface layer of the South China Sea, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
31. Tegtmeier, S.: SPARC Data Initiative - stratospheric satellite observations for model evaluation, invited presentation, IGAC-SPARC-CCMVal workshop, Oral, Davos, Switzerland, 21–25 May, 2012.
32. Tegtmeier, S., and Hegglin, M.I.: SPARC Data Initiative - Intercomparison of vertically resolved chemical trace gas and aerosol climatologies, SPARC SSG meeting, Oral, Zürich, Switzerland, 7-10 February 2012.
33. Tegtmeier, S., Bieligk, H., Krüger, K., Atlas, E., Fuhlbrügge, S., Hepach, H., Hossaini, R., Wittke, F., Quack, B.: Oceanic VSLS contribution to the stratosphere: Comparing tropical East Atlantic with tropical West Pacific emissions, EGU 2012, Poster, Vienna, Austria, April 2012.
34. Tegtmeier, S., Chemical Composition of the Tropical Tropopause Layer, invited presentation, School of GeoSciences, Oral, University of Edinburgh, UK, 21.5.2013.
35. Tegtmeier, S., K. Krüger, B. Quack, E. Atlas, D. R. Blake, H. Boenisch, A. Engel, H. Hepach, R. Hossaini, M. A. Navarro, S. Raimund, S. Sala, Q. Shi, and F. Ziska, Contribution of oceanic halocarbons to the stratosphere, Lunch seminar, Oral, GEOMAR, Germany, 27.6.2013.
36. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Bieligk, H., Wittke, F.: Oceanic VSLS contribution to stratospheric ozone, EGU 2012, IGAC-SPARC-CCMVal workshop, Poster, Davos, Switzerland, 21–25 May, 2012.
37. Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Hepach, H., S. Raimund, S., Shi, Q., and Ziska, F.: Transport of VSLS from the ocean to the stratosphere, Sonne Statusseminar, Poster, Kiel, Germany, 14.2.
38. Tegtmeier, S., Krüger, K., Quack, B., Wittke, F., Atlas, E., Bieligk, H., Hepach, H., Hossaini, R., Raimund, S., Shi, Q.: Oceanic VSLS contribution to stratospheric ozone, Quadrennial Ozone Symposium, Oral, Toronto, Canada, 27-31 August 2012.
39. Tegtmeier, S., M. I. Hegglin, J. Anderson, S. Brohede, L. Froidevaux, R. Fuller, B. Funke, J. Gille, A. Jones, Y. Kasai, E. Kyröla, G. Lingenfelser, C. McLinden, J. Neu, E. Remsberg, A. Rozanov, L. Smith, M. Toohey, J. Urban, T. von Clarmann, K. A. Walker, and R.Wang, SPARC Data Initiative – Climatology comparisons for O3, N2O, NOy, NOx, ClO, and BrO WCRP Open Science Conference, Denver, USA, Poster, 2011.
40. Tegtmeier, S.: Meridional structure of the downwelling branch of the BDC, invited presentation, SPARC Brewer-Dobson Circulation Workshop, Oral, Grindelwald, Switzerland, 25-29 June 2012.
41. Walker, H., Ingham, T., Lampel, J., Wittrock, F., Heard, D., Huang, R.-J, Hoffman,T. ,Reactive iodine species in the western Pacific atmosphere during SHIVA, BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster
42. Wittke, Franziska, Birgit Quack, Kirstin Krüger and HalOcAt contributors, Global VSLS emission estimates based on in-situ measurements for the past and future, CCMVAL work-shop, Davos, 21.-24. May, 2012, Poster, 2012.
43. Ziska F., Quack B. und HalOcAt Beitragende, Emissions of halogenated trace gases from the South China and Sulu Sea in a global context (Comparison of the SO218 emissions with climatological values)BMBF Statusseminar "Meeresforschung mit FS SONNE" vom 13. bis 15. Februar 2013, Kiel, Poster

In the following, **SHORT REPORTS FROM THE PARTICIPATING INSTITUTIONS** are presented which give an insight into their objectives, methods and results.

Theme 1 - HALOCARBONS: Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons.

Report 1: *Halocarbons in the South China and Sulu Sea: distributions emissions and sources,* Birgit Quack, Helmke Hepach, Stefan Raimund, Qiang Shi, Wee Cheah, Astrid Bracher

Theme 2 - PHYTO-OPTICS and PLANKTON: Phytoplankton pigments, species and size distribution, radiation and absorption spectra of seawater and plankton content

Report 2a: *Natural phytoplankton communities and optical properties of phytoplankton during SHIVA-Sonne expedition in November 2011 in the South China Sea and Sulu Sea, Infinity ME,* Astrid Bracher, Wee Cheah, Sonja Wiegmann, Mariana Altenburg-Soppa, Joseph Dominic Palermo, Birgit Quack, Stefan Raimund, Gerd Krahmann

Report 2b**:** *Community structure of Pseudo-nitzschia (Bacillariophyceae) from the SHIVA expedition,* Sing-Tung Ten, Po-Teen Lim, Hong-Chang Lim, Aazani Mujahid, Chui-Pin Lea

Report 2c: *Microbial communities of the eastern South China Sea and the Celebes Sea and their possible roles in the DMS(P) Cycle,* Felicity W.I. Kuek, Aazani Mujahid, Moritz Müller

Report 2d: *Culturable bacteria from Talang-Talang Reef and its surrounding waters,* Felicity W.I. Kuek, Lin-Hui Ngu, Li-Fang Lim, Aazani Mujahid, Moritz Müller

Theme 3 - OCEANIC TRACE GASES: Oceanic concentrations of dimethyl sulfide and related compounds (DMS, DMSO, DMSP), nitrous oxide and methane

Report 3: *Interaction of climate active gases during the SHIVA-Sonne SO218 campaign: Dimethylsulfide, oxygenated volatile organic compounds, nitrous oxide (N_2O), and methane (CH_4),* Christa Marandino, Cathleen Zindler, Hermann W. Bange (not on board), and Franziska Ziska (on board for H. Bange)

Theme 4 – OCEAN SENSORS: Identification of carbon dioxide and oxygen sources and sinks; separation of physical and biological factors for observed sources and sinks, temperature and salinity

Report 4: *Underway measurements of pCO_2, oxygen and total gas pressure*, Tobias Steinhoff, Anke Schneider and Arne Körtzinger

Theme 5 - RADIOSOUNDING: Identification of meteorological vertical and ozone profiles in order to evaluate the mixing layer and tropopause height and to calculate air mass back trajectories

Report 5: *SHIVA SONNE SO218: Radio- and Ozonesounding*, Kirstin Krüger, Steffen Fuhlbrügge

Theme 6 – AIR SAMPLING: Determination of anthropogenic and natural trace gas concentrations by flask sampling

Report 6: *Determination of trace gas concentrations in the marine boundary layer,* Elliot Atlas, Steffen Fuhlbrügge, Kirstin Krüger, Birgit Quack

Theme 7 - SPECTROSCOPY: Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy (MAX DOAS) in a three dimensional field and Cavity Ring Down

Report 7: *Trace Gas Measurements using MAX-DOAS and CE-DOAS instruments,* Johannes Lampel, Folkart Wittrock

Theme 8 - µ-DIRAC: Quasi-continuous measurements of some VSLS in the marine atmospheric boundary layer (15 m altitude) for real time concentrations

Report 8: *µ-Dirac – continuous measurements of halogenated trace gases,* Neill Harris, Andrew Robinson, Karin Kreher, Elliot Atlas, Julian Kinzel, Birgit Quack

Theme 9 – ATMOSPHERIC TRACE GASES: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH_4, O_3, CO_2)

Report 9: *Atmospheric CO_2, CH_4, H_2O, O_3 and CO (DLR- Instrumentation),* Hans Schlager, Justin Sentian, Nur Aleesha Abdullah*:*

Theme 10 - CIMS-REACTIVE COMPOUNDS: Continuous measurements of Br_2, BrCl, HOBr, BrO, and $ClNO_2$ and HNO_3, HCl, SO_2, and HBr in the marine boundary layer with two Atmospheric Chemical Ionization Mass Spectrometers, a LIF Instrument for IO and a NOx detector

Report 10a: *DLR- CIMS measurements: Investigation of anthropogenic emissions affecting air quality in the marine boundary layer of the South China and Sulu Sea,*Tina Jurkat, Christiane Voigt, Dominik Schäuble

Report 10b: *Sonne-Falcon Lagrangian tracer experiment and continuos carbon monoxide and ozone measurements,* Hans Schlager, Yu Ren, Michael Lichtenstern, Monika Scheibe, Nur Aleesha Abdullah, Justin Sentian, Tina Jurkat, Dominik Schäuble

Report 10c: *In situ measurements of IO by Laser-Induced Fluorescence Spectroscopy,* Hannah Walker, Trevor Ingham, Dwayne Heard

Report 10d: *Measurements of I_2 and the sum of HOI + ICl during SHIVA,* Hannah Walker, Trevor Ingham, Dwayne Heard, Ru-Jin Huang, Thorsten Hoffmann

Theme 11 - ATMOSPHERIC AEROSOL: Major ions and halogens in aerosols

Report 11: *Aerosol chemistry of halogens during SHIVA,* Alex Baker and Chan Yodle,

Theme 12 – OCEANIC SURFACE CURRENTS

Report 12: *Oceanic Circulation -Transient tracer measurements during cruise Sonne-218,* Toste Tanhua, Peng Huang, Anke Schneider

Theme 13 – LOCAL BOAT DEPLOYMENTS

Report 13a: *Results of the local boat deployments Kuching, Kota Kina Balu, and Semporna*

Felicity W.I. Kuek, Aazani Mujahid, Lim Po Teen, Leaw Chui Pin, Moritz Müller, Ann Anton

Report 13 b: *Results of the local boat deployment Kuching* , Moritz Müller, Aazani Mujahid, Felicity W.I Kuek, Hong-Chang Lim, Sing-Tung Teng, Chui-Pin Leaw, Ann Anton, Lim Po Teen

Report 13c: *Results of the local boat deployment Kota Kinabalu,* Ann Anton

Theme 14 – TRANSPORT INTO THE STRATOSPHERE

Report 14: *The contribution of oceanic halocarbons to the stratospheric halogen loading,* Susann Tegtmeier, Kirstin Krüger, Birgit Quack

REPORT 1: HALOCARBONS IN THE SOUTH CHINA AND SULU SEA: DISTRIBUTIONS EMISSIONS AND SOURCES

Birgit Quack[1], Helmke Hepach[1], Stefan Raimund[1], Qiang Shi[1], Wee Cheah[2], Astrid Bracher[2]

[1]GEOMAR, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany.
[2]Alfred-Wegener-Institute für Polar und Meeresforschung, Klima, Bremerhaven, Germany

Objective: The oceans have strong influence on the trace gas concentrations in the atmosphere by sea-air-exchange processes. Halogenated hydrocarbons (halocarbons) such as methyl iodide (CH_3I), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) are important trace gases and are biologically and (photo) chemically produced in the water column. Macroalgae along the coast and waters with high phytoplankton densities are known sources for such compounds. River outflow, photochemical reactions and anthropogenic discharges (e.g. treatment of waste water) are other important sources and together with the biological sources cause a highly variable pattern of oceanic halocarbon distribution.

Halocarbons influence the atmospheric chemistry by contributing to the atmospheric halogen pool and consequently influencing the 'oxidizing capacity' of the troposphere and the stratosphere. Whereas naturally produced halocarbons mostly supply to the bromine and iodine pool, anthropogenic halocarbons elevate the atmospheric chlorine pool. In the troposphere, halocarbons influences the NO/NO_2 cycle, stimulates catalytic ozone depletion cycles and influences the life times of other trace. Rapid deep convection can transport halocarbons to the lower stratosphere where they may represent significantly to stratospheric halogens and consequently contribute to ozone depletion.

For a better understanding of chemical processes in the atmosphere (especially in a changing atmosphere with elevated greenhouse gases), it is necessary to measure oceanic halocarbon concentrations in so called “hot spots” around the globe. Tropical gas emissions from the ocean towards the atmosphere are highly interesting, because in those areas, trace gases can enter the stratosphere where ascending warm air lifted them upwards. Here, when deep convection events occur, air masses are transported from the troposphere to the lower stratosphere (passing the tropical tropopause layer, which is the typical barrier for ascending air masses in higher latitudes).

Method

During SO218, the first halocarbon measurements in waters of the coastal western Pacific were performed in the South China and Sulu Sea along the coast off Singapore, Malaysia, Borneo and the Philippines on board the German research vessel *SONNE* during the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) campaign.. Halocarbon concentrations where determined in water and air, and sea-to-air fluxes calculated.

Samples were taken along the cruise track at 73 different positions using a submerged water pump under the ship`s keel. Moreover, profiles were taken at 10 CTD stations with a 24-bottle CTD rosette (10-L-Niskin bottles). At each station samples were collected in the entire water column with the focus on the upper 150m (surface layer, chlorophyll maximum layer, lower layers).

Halocarbons were analysed on two different purge-and-trap (PT) gaschromatographic systems one with an electron capture detector (ECD) and one with a mass-spectrometric detector (GC-MS), where the halocarbons were quantified in single ion mode. Quantification of volatiles was

performed by external liquid standards. Liquid standards were diluted in seawater and treated like a normal sample. For more details see Quack et al. (2007).

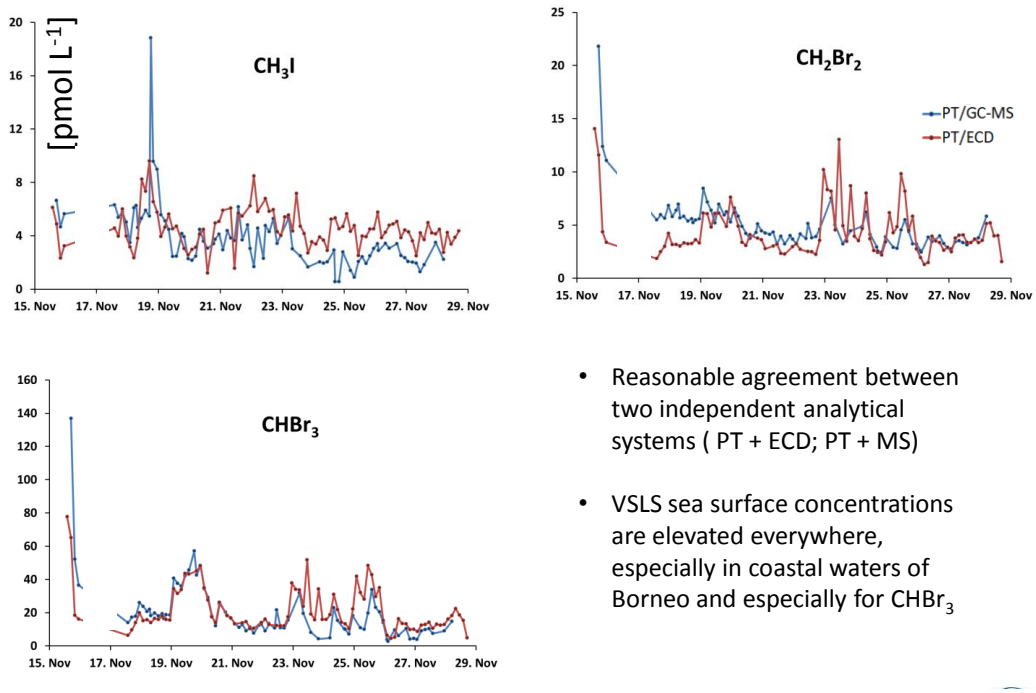


Figure 1: Concentrations of methyl iodide (CH_3I), dibromomethane (CH_2Br_2) and bromform ($CHBr_3$) in surface water, measured with two independent analytical systems.

The halocarbon distribution is highly variable along the cruise track. Near shore samples show typically elevated concentrations, especially for the brominated compounds while samples off shore generally contain lower halocarbons concentrations (Figures 1, 2, 3).

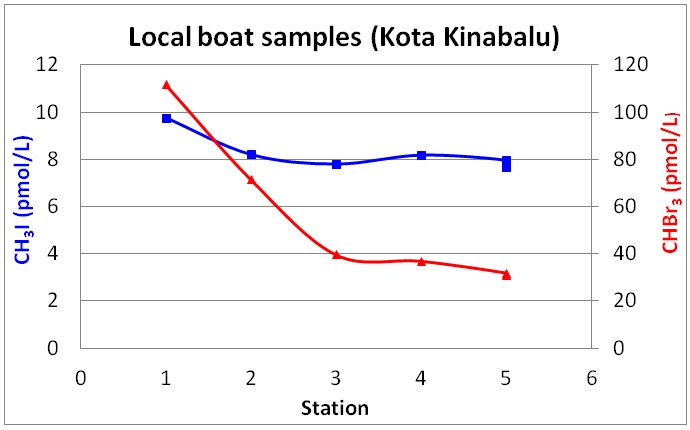


Figure 2: The local boat samples by Kota Kinabalu. Station 1 was closest to the shore, followed in short distance by No, 2 while stations No 3 to 5 where further off shore (see map in Report 13a)
.

At Kota Kinabalu, the concentration of bromoform at the local boat station 1 was more than 100 pmol/L, then decreased to 30 pmol/l at station 5. For methyl iodide, the variation of concentration was much smaller.

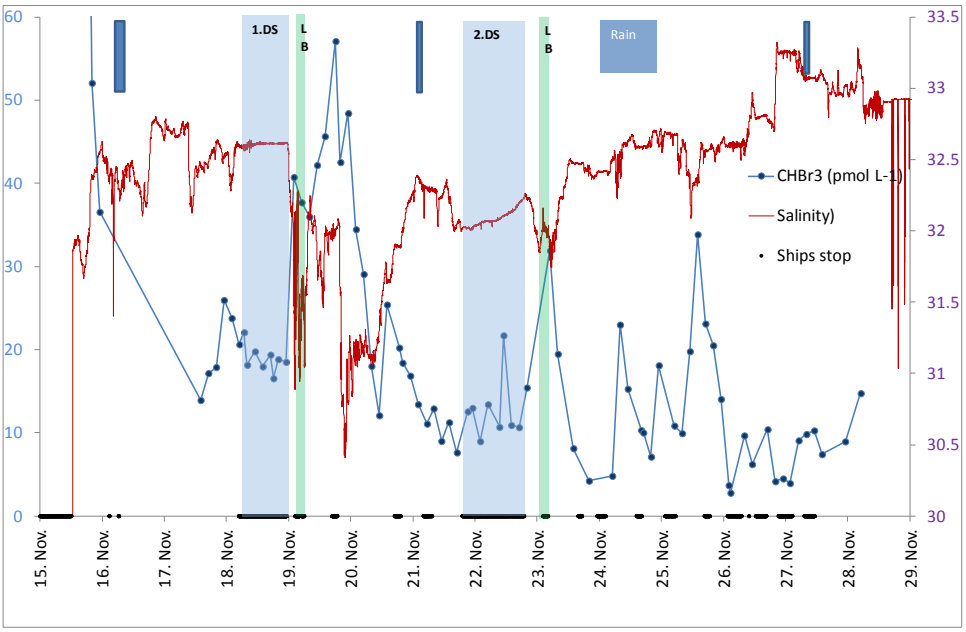


Figure 3: Bromoform and salinity along the cruise track of SO218. Marked are also the diurnal stations (DS), where the ship was positioned on station (ships stop) and the contact with the local boats (LB) at Kuching on the 19th and in Kota Kinabalu on the 23rd of November 2011. Rain events are also marked.

For bromoform which was the most concentrated halocarbon in sea water, also river run off from the coasts of the Malaysian peninsula and the Borneo coast accounted for a rise in sea water concentrations, which may have several reasons as coastal runoff with natural input (corals?, mangroves?, macro algae?) or anthropogenic sources. Atmospheric $CHBr_3$ during the SHIVA-*SONNE* campaign generally ranged between 2 and 3 ppt in coastal regions and decreased above the more open ocean waters (see also report No 6). The overall regional pattern between oceanic and atmospheric concentration trends was opposite for sea water and atmosphere, while sea water concentrations decreased towards the Sulu Sea, the atmospheric mixing ratios increased, leading to a decreasing concentration gradient between air and sea water in the Sulu Sea compared to the South China Sea (Figure 4).

Form the sea water concentrations and the atmospheric mixing ratios and wind speed, oceanic emissions were calculated, revealing the South China Sea and Sulu Sea as strong source regions of halocarbons for the atmosphere (Figure 4)

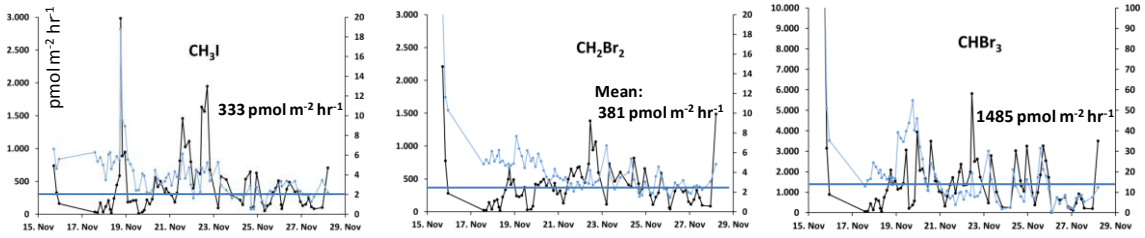


Figure 4: Oceanic emissions (pmol m^{-2} hr^{-1}) of methyl iodide (CH_3I), dibromomethane (CH_2Br_2) and bromoform ($CHBr_3$) from the South China and Sulu Sea (black line), mean emissions and the corresponding saturation anomaly (pmol L^{-1}, blue line).

Halocarbon maxima in deeper waters are often coincided with chlorophyll a maxima suggesting a biological source (Figure 5).

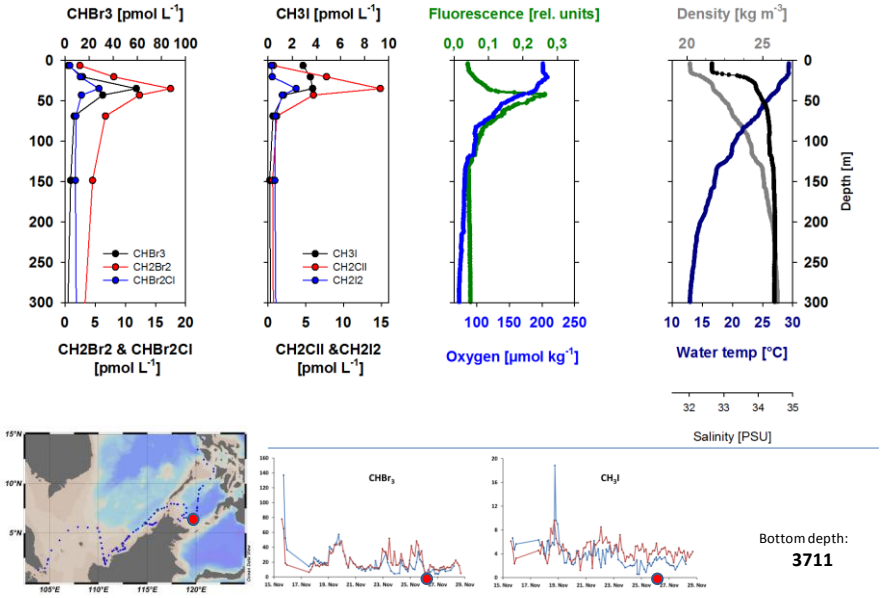


Figure 5: Depth profile of various halocarbons, fluorescence (as measure for chl a), oxygen, water temperature , salinity and density in the Sulu Sea.

The data are available from the GEOMAR data server: https://portal.geomar.de/ and from the SHIVA ftp server: ftp://shiva.iup.uni-heidelberg.de and from Birgit Quack (bquack@geomar.de).

To summarize, the observations show highly variable distributions along the cruise track, hinting to multiple sources and sinks. CTD profiles show elevated concentrations for brominated halocarbons (CH_2Br_2, $CHBr_3$ and $CHBr_2Cl$) in the Chl a maximum layer. This strongly indicates a phytoplanktonic source for those compounds. This feature is also visible for the iodinated halocarbons (CH_2I_2 and CH_2BrI). However, profiles for CH_3I show highest concentration in the subsurface. This indicates a photochemical or biological source at the surface. In some cases, there is a second CH_3I maximum in deeper layers pointing to a second biological source.

Phytoplankton measurements collected during SHIVA-Sonne (SO2018) and analyzed (further details in Report 2a) were used for studying the relationship of phytoplankton to VSLS concentratioons in water.

The statistical analysis of the relationship of phytoplankton to different halocarbon species identified significant ($p < 0.01$) relationships between zeaxanthin, cyanobacteria, but also for particulate organic matter (POC and PON) with methyl iodide (CH_3I) and Kendall's coefficients of 0.45, 0.44, 0.42 and 0.30, respectively. This shows that cyanobacteria likely contribute significantly to the production of CH_3I in the study area, while possible co-correlating factors as sea water temperature and light need to be considered also. Also significant relationships to bromoform ($CHBr_3$) and dibromomethane were identified for total phytoplankton biomass (TChl-a), hexanoyl-fucoxanthin (the marker pigments for haptophytes) and monovinyl-chlorphyll-b (the marker pigment for prasinophytes). These findings are based on statistical analysis based on Kendall's rank correlation, which examine the ranking relationship between VSLS and phytoplankton groups' marker pigments and total chl a concentration. These results are still written up in a manuscript which is also planned to be submitted to the Special Issue of SHIVA in Biogeosciences (Raimund et al in prep.).

Brominated and iodinated halocarbons also show significant correlations to phytoplankton groups, besides their correlations to the individual pigments (report 2a). Strong correlations were found for the diatoms, haptophytes, prasinophytes and prochlorophythes. The dominant group during the campaign were haptophytes and the prochlorophytes (report 2). Underway data along the cruise track reveal that shallow waters with low salinities show a large influence on near shore halocarbon concentrations.

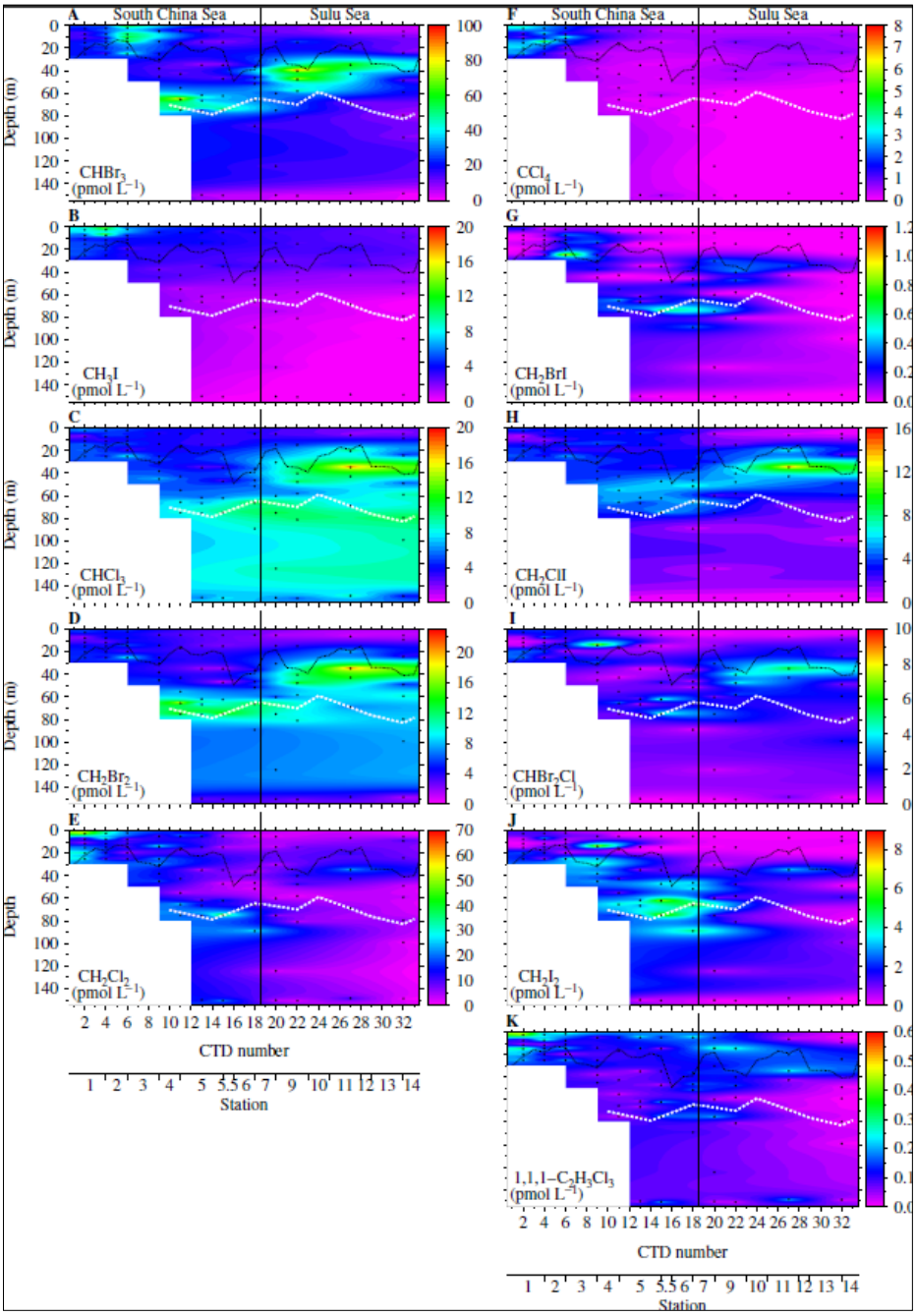


Figure 6: Halocarbon concentrations during SO218 SHIVA-Sonne cruise in the South China and Sulu Sea. Mixed layer (black line) and euphotic (white line) depth (Ref: Wee Cheah, August 2013).

REPORT 2A: NATURAL PHYTOPLANKTON COMMUNITIES AND OPTICAL PROPERTIES OF PHYTOPLANKTON DURING SHIVA-SONNE EXPEDITION IN NOVEMBER 2011 IN THE SOUTH CHINA SEA AND SULU SEA, INFINITY ME

Astrid Bracher[1], Wee Cheah[1], Sonja Wiegmann[1], Mariana Altenburg-Soppa[1], Joseph Dominic Palermo[2], Birgit Quack[3], Stefan Raimund[3], Gerd Krahmann[3]

[1]Alfred-Wegener-Institute für Polar und Meeresforschung, Klima, Bremerhaven, Germany

[2]University of the Philippines , Diliman, The Marine Science Institute, Biological Oceanography and Modeling of Ecosystem Lab., Quezon City, Philippines,

[3]GEOMAR, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany.

All phytoplankton measurements collected during SHIVASonne (SO2018) and analysed for pigment and group composition, absorption characteristics, physiological conditions were used for studying the relationship of phytoplankton to nutrients and environmental factors (salinity, temperature, wind). First results were presented at the South China Sea Science Conference in Kuala Lumpur (Cheah et al. 2012). Then the phytoplankton parameters such as pigment concentration, functional group type, and PSII efficiency were undergoing a detailed analysis to investigate the relationship between phytoplankton and physical parameters and nutrients. The high horizontal and vertical resolved survey showed that physiological conditions of natural phytoplankton communities in the southern SCS and SS were influenced mainly by light and nutrients concentrations, especially at the surface. Overall, photoacclimation at the shallow coastal stations was affected by high mixing rates and challenged by high surface irradiance. At the deeper offshore stations phytoplankton below the mixed layer were able to maintain higher photochemical efficiency (Fig. 1). Nutrients limitation was the main limiting factor for growth of phytoplankton in these regions as shown by low TChl a concentrations, domination of pico-eukaryotes and cyanobacteria in the open ocean areas. High TChl a concentrations observed at the surface in the shelf areas, especially at stations close to the coast were due to an enhancement in nutrient supplies, probably from river outflows. A manuscript on these results was submitted to Biogeosciences (Cheah et al. BGD 2013).

Satellite monthly mean maps for Nov 2011 for the SHIVASonne cruise area of biomass distributions of different dominant PFTs (Phytoplankton Functional Types; with 30 km by 60 km spatial resolution) derived from measurements of the satellite sensor SCIAMACHY on ENVISAT analyzed with PhytoDOAS, a method of Differential Optical Absorption Spectroscopy (DOAS) specialized for diatoms, dinoflagellates, coccolithophores and cyanobacteria (Bracher et al. 2009, improved by Sadeghi et al. 2012) agree well with the in-situ phytoplankton group data sampled during SHIVASonne (see Fig. 2 for cyanobacteria and coccolithophores). Validation of the HYGEOS-POLYMER MERIS satellite chl-a data showed good correlations (r^2 of 0.77 for 24 collocations) for collocations between in-situ and satellite chl-a, but a general underestimation close to 50% by the satellite product, which is even more pronounced for higher chl-a conc. (>0.4 mg/m^3). Using the chemtax program the HPLC pigment data were used to calculate the chl-a conc. major phytoplankton groups. These data will supplement other in-situ HPLC phytoplankton data for the validation of the PHYTODOAS retrievals. The outcome of the analysis is expected to result in improved satellite algorithms for deriving phytoplankton characteristics which than can be used for inferring VSLS in water conc. We plan to write up these results together with a more profound analysis of the in-situ optical data in order to improve the satellite products for this region in another paper to be submitted to the SHIVA Special Issue in Ocean Sciences (Bracher et al. in prep.).

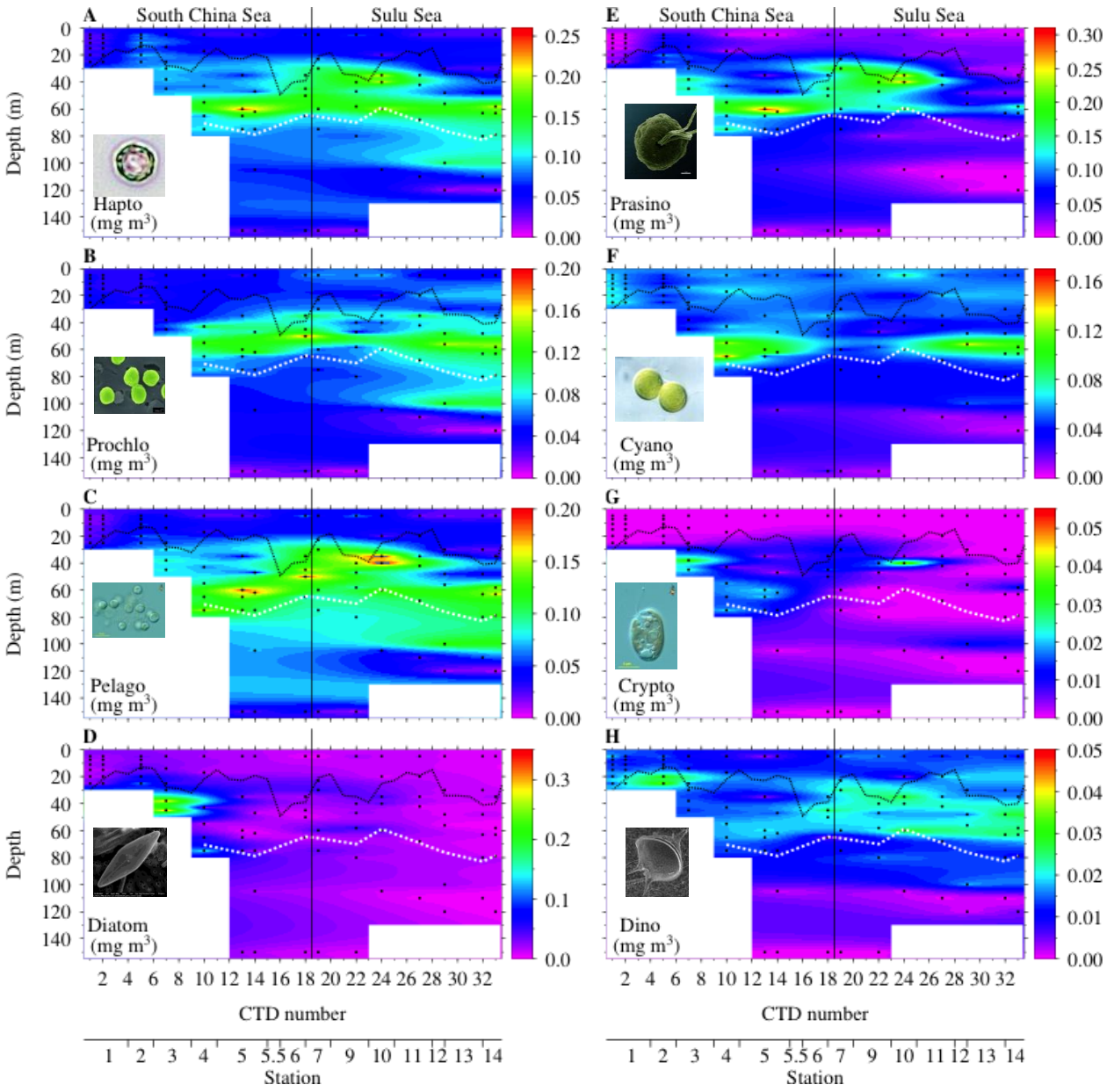


Figure 1: Biomass of different phytoplankton groups during SO218 SHIVA-Sonne cruise as derived from HPLC pigment conc. using the CHEMTAX analysis. In contrast to the surface water, vertical distribution of phytoplankton groups from CTD profiles show phytoplankton communities were dominated by prasinophytes and haptophytes, followed by prochlorohytes and pelagophytes. In general, phytoplankton were observed mostly below the mixed layer and above the euphotic depth correspond to high total chlorophyll a concentration. Figure adapted from Cheah et al. (BGD, 2013)

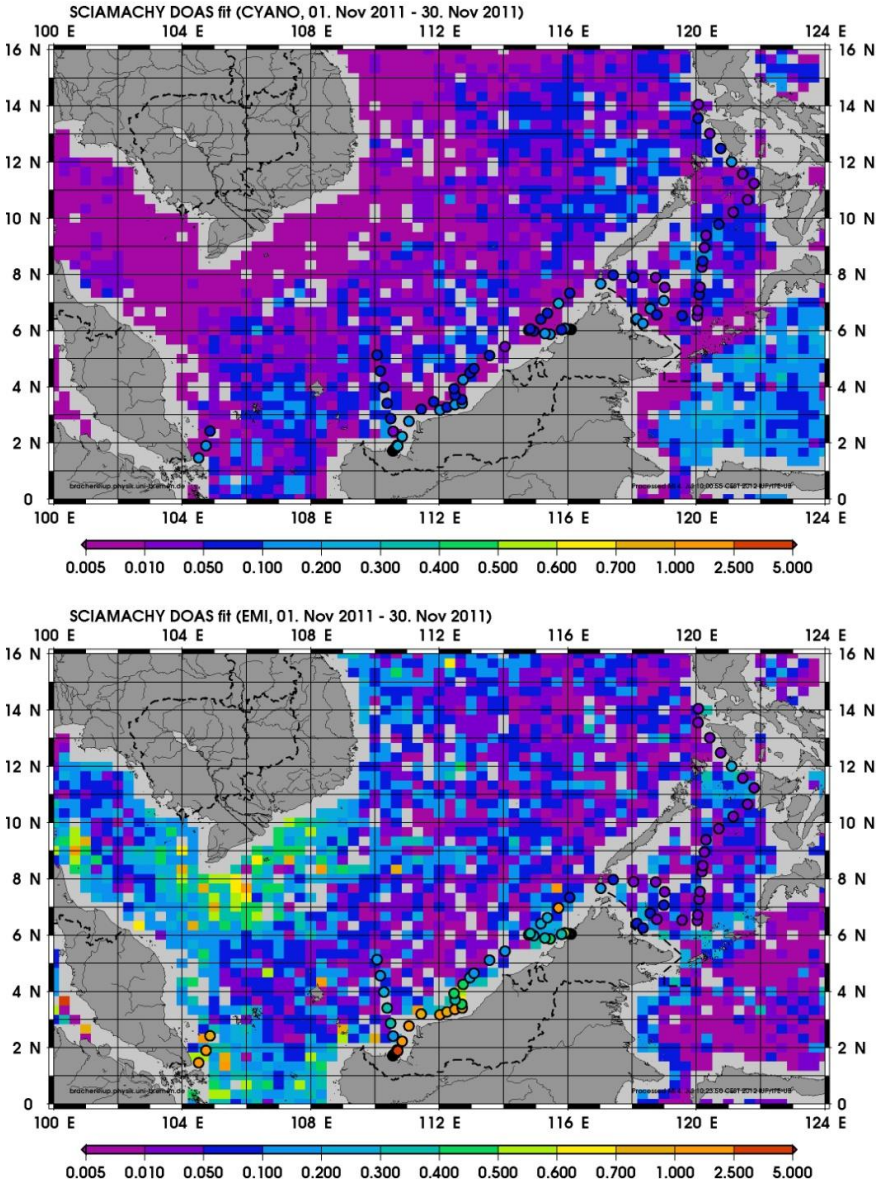


Fig.2: Mean Nov 2011 cyanobacteria (upper level) and coccolithophore (a major group belonging to haptophytes, lower level) chl-a conc. derived from ScIAMCHY with PhytoDOAS method. Plotted with the same color scale are the chl-a conc. of cyanobacteria and haptophytes determined via HPLC and CHEMTAX technique at water samples collected in Nov 2011 during the SHIVASonne cruise

References:

Cheah W., Taylor B.B., Wiegmann S., Raimund S., Krathmann G., Quack B., Bracher A. (2013) Photophysiological state of natural phytoplankton communities in the South China Sea and Sulu Sea. Biogeosciences Discussion 10: 12115-12153

Conference Talk: Cheah W., Taylor B., Dinter T., Raimund S., Quack B., Bracher A. (2012) Community structure and optical properties of phytoplankton during SHIVA-Sonne expedition: From in-situ and satellite. South China Sea Conference 2012, Kuala Lumpur, Malaysia, 22 October 2012 - 26 October 2012

Conference Poster: Hepach H., Raimund S., Taylor B., Bracher A., Fischer T., Quack B. (2013) "Contributions to tropical VSLS emissions from the equatorial Atlantic upwelling regions". Poster: SOPRAN Annual Meeting 2013, 19.-20.03.2013, Leipzig, Germany

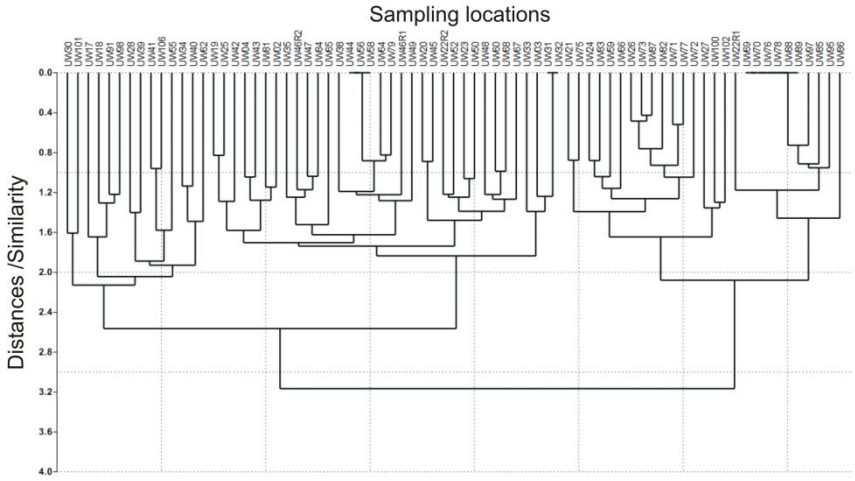
REPORT 2B: COMMUNITY STRUCTURE OF *PSEUDO-NITZSCHIA* (BACILLARIOPHYCEAE) FROM THE SHIVA EXPEDITION

Sing-Tung Teng[1], Po-Teen Lim[2], Hong-Chang Lim[2], Aazani Mujahid[1], Chui-Pin Leaw[1]

[1] Institute of Biodiversity and Environmental Conservation,[2] Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, Corresponding email: ptlim@frst.unimas.my

A study was undertaken to determine the community structure of *Pseudo-nitzschia* species based on genetic information by using the automated ribosomal intergenic spacer analysis (ARISA). The molecular approach was performed based on the secondary structural information of the first internal transcribed spacer (ITS1) transcripts to characterize the genetic variability of *Pseudo-nitzschia* species along the eastern South China Sea (SCS) during the SHIVA expedition in November 2011. Phytoplankton samples were collected through a 20-µm plankton net and retained onto Nylon filter membranes via filtration. Samples were preserved with saline ethanol, and environmental genomic DNAs were obtained in the laboratory. *Pseudo-nitzschia* species- and genus-specific oligonucleotide primers were designed *in silico* based on the secondary structure information. Specificity of the primers was tested on clonal cultures prior to SHIVA samples. Each fragment profile showed the corresponding single fragment and matching ITS1 length *in silico* for each species. Amplification was carried out on a total of 75 surface water samples, and the amplicons were analyzed by fragment analysis using DNA analyzer. Total of 50 ribotypes were detected. Community structure of *Pseudo-nitzschia* along the eastern SCS was characterized. Clustering analysis revealed a degree of community structuring in *Pseudo-nitzschia*. The results showed two linkages, one cluster with locations being dominated by *P. caciantha* ribotype 2; and the other with locations where *P. caciantha* is absent. However, no significant variation was found between samples collected from coastal water or open ocean.

Keywords: *Pseudo-nitzschia*, ribosomal intergenic spacer analysis, species-specific oligonucleotide primers, genotyping



REPORT 2C: MICROBIAL COMMUNITIES OF THE EASTERN SOUTH CHINA SEA AND THE CELEBES SEA AND THEIR POSSIBLE ROLES IN THE DMS(P) CYCLE

Felicity W.I. Kuek[1], Aazani Mujahid[2], Moritz Müller[1]

[1]*Faculty of Engineering, Computing and Science, Swinburne University of Technology, Sarawak campus, 93350 Kuching, Sarawak, Malaysia.*

[2]*Department of Aquatic Science, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 93400 Kota Samarahan, Sarawak, Malaysia.*

The South China Sea is a marginal sea that is part of the Pacific Ocean, encompassing an area from the Singapore and Malacca Straits to the Strait of Taiwan (Morton & Blackmore 2001). The Celebes Sea is connected to the South China Sea through the Sulu Sea (Yoshida, Nishimura & Kogure 2007). While the bacterial community structure in these two regions have been previously reported to display some similarities when compared (Yoshida, Nishimura & Kogure 2007) not much is known about the diversity and function of the microbial communities in the South China Sea, especially regarding the eastern region (Kuching and Kota Kinabalu) and the Celebes Sea and no studies on culturable communities in the region have been made at this time. One major and globally important role of surface bacteria is their involvement in the breakdown or osmoregulation of DMSP to DMS or MeSH.

The present study tries to expand our knowledge on microbial communities in the South China Sea by assessing the surface bacterial communities along the eastern region of the South China Sea as well as the Celebes Sea. Over 200 isolates obtained were also screened for the existence of key genes involved in the competing, enzymatically mediated DMSP degradation pathways (dmdA, dddP) to identify potential key players in the local DMS(P) cycle. This is to our knowledge the first comprehensive study looking at the diversity of culturable bacteria in the eastern South China Sea and also their potential roles in the DMS(P) cycle.

The bacterial communities from the sampling sites in Kuching, Kota Kinabalu and Semporna were found to be diverse with representatives from several groups. The total bacterial assemblage had representatives within the *Alpha-*, *Beta-* and *Gammaproteobacteria*, as well as *Firmicutes* (see Fig. 1). The general similarity in groups (Figure 1) can be explained by the use of a singular isolation media (marine agar at half strength). However, the total number of bacterial isolates obtained and assemblages at the three sampling sites were different as briefly discussed in the following.

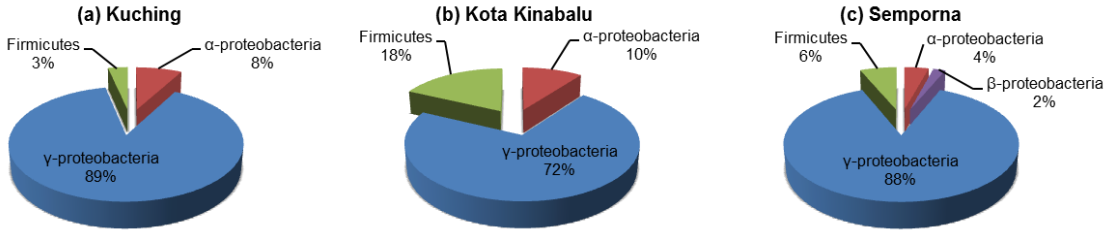


Figure 1: Pie charts illustrating the diversity of bacterial groups based on partial 16S rRNA gene sequences from bacteria isolated from (a) Kuching, (b) Kota Kinabalu and (c) Semporna.

Gammaproteobacteria are the dominant phylogenetic group at all three locations and at all sampling depths, followed by *Alphaproteobacteria* (see Fig. 1). *Betaproteobacteria* were only found at Semporna at 1m depth. From Kuching waters, 89 isolates were obtained over two sampling periods (November 16 and 19, 2011). The diversity of bacterial phylotypes is presented in Figures 2 to 5. Overall, 89% of the cultured bacteria were clustered within the *Gammaproteobacteria*, 8% within the *Alphaproteobacteria* and 3% within the *Firmicutes* (Figs. 2+3). In Kota Kinabalu waters, 39 isolates were obtained and the majority (72% of the cultured bacteria) were clustered within the *Gammaproteobacteria*. The remaining isolates were members of the *Firmicutes* (18%) and *Alphaproteobacteria* (10%) (Fig. 4). In Semporna waters, 48 isolates were obtained from four phylogenetic groups. In total, 88% of the cultured bacteria were members of the

Gammaproteobacteria, 6% of the *Firmicutes*, 4% of the *Alphaproteobacteria* and 2% *Betaproteobacteria* (Fig. 5).

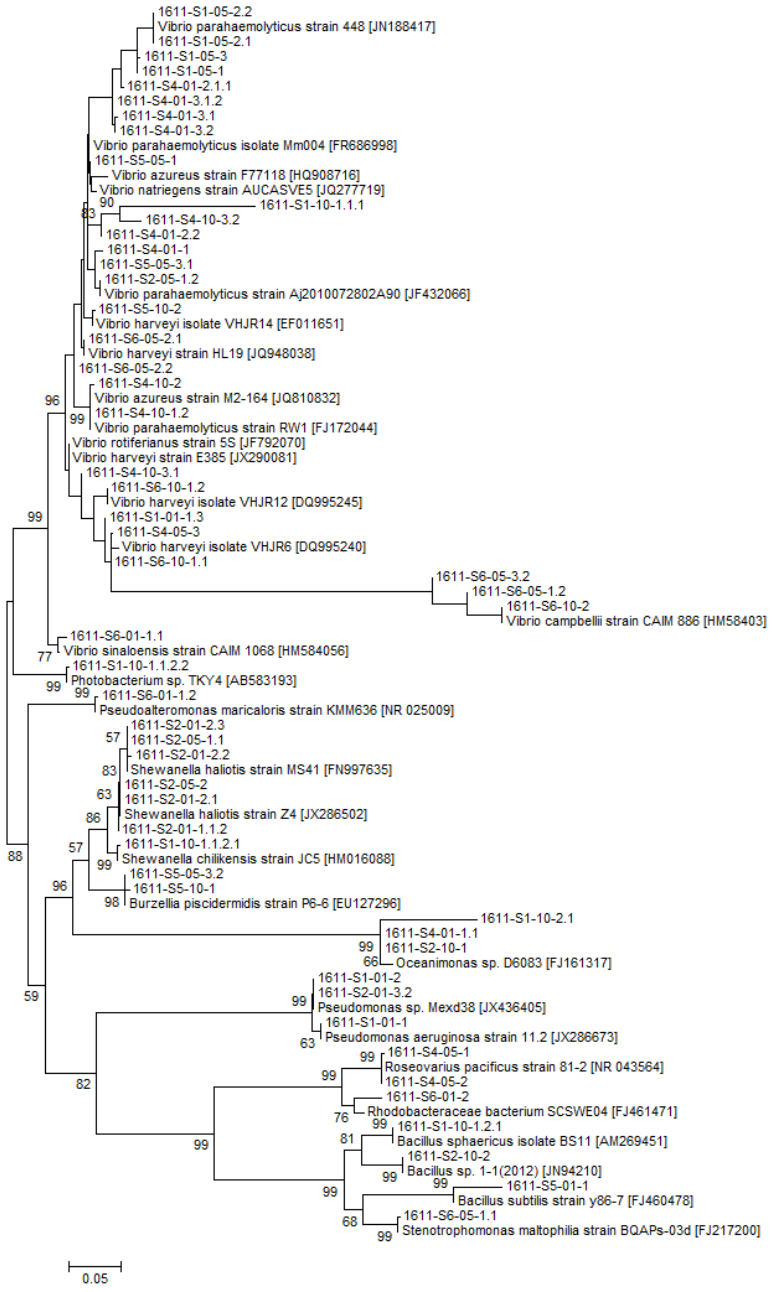


Figure 2: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kuching 1611. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbour-joining method. Bootstrap values ≥50 are shown and the scale bar represents a difference of 0.05 substitution per site. Accession numbers for the reference sequences are indicated.

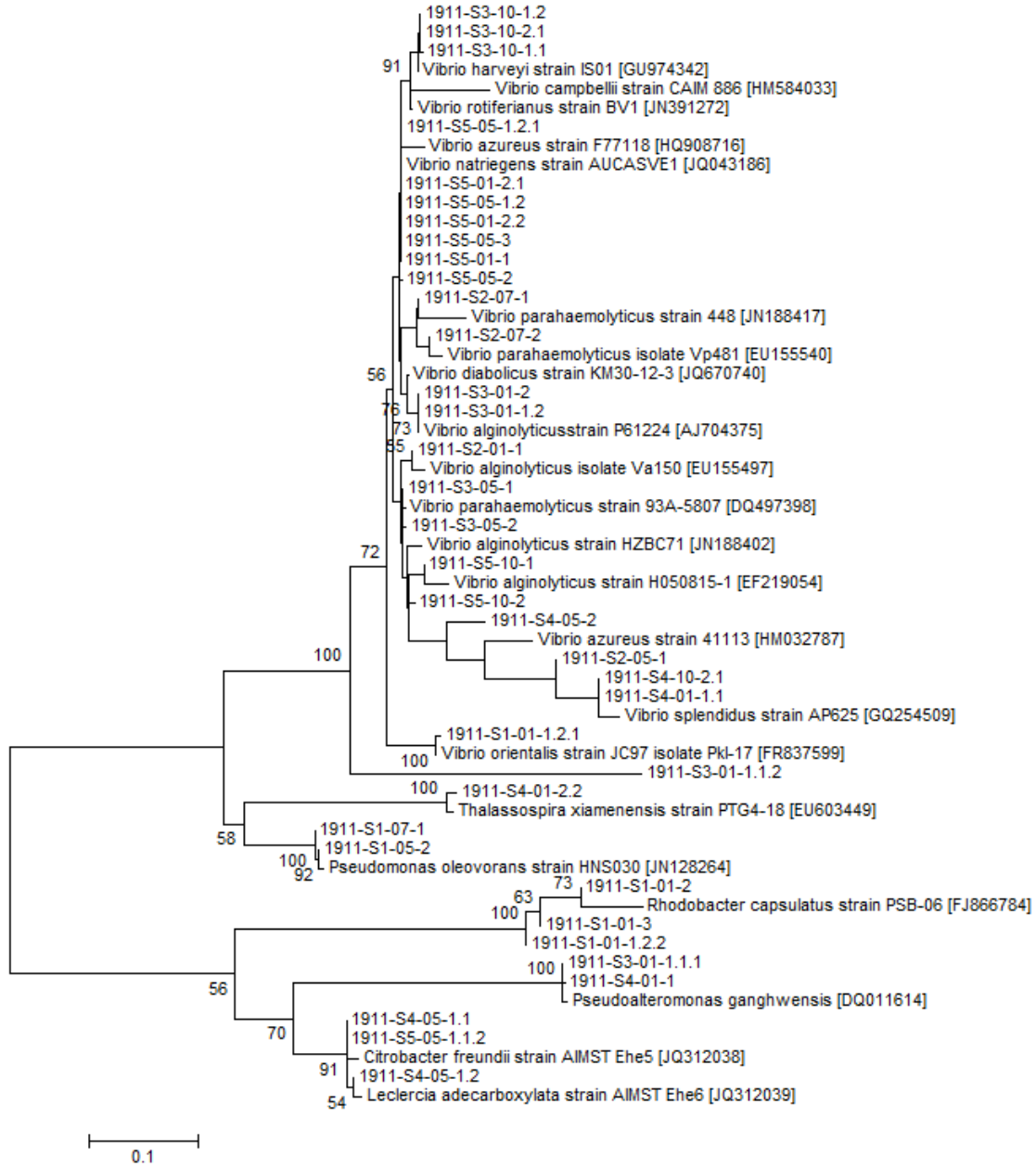


Figure 3: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kuching 1911. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbor-joining method. Bootstrap values ≥50 are shown and the scale bar represents a difference of 0.1 substitution per site. Accession numbers for the reference sequences are indicated.

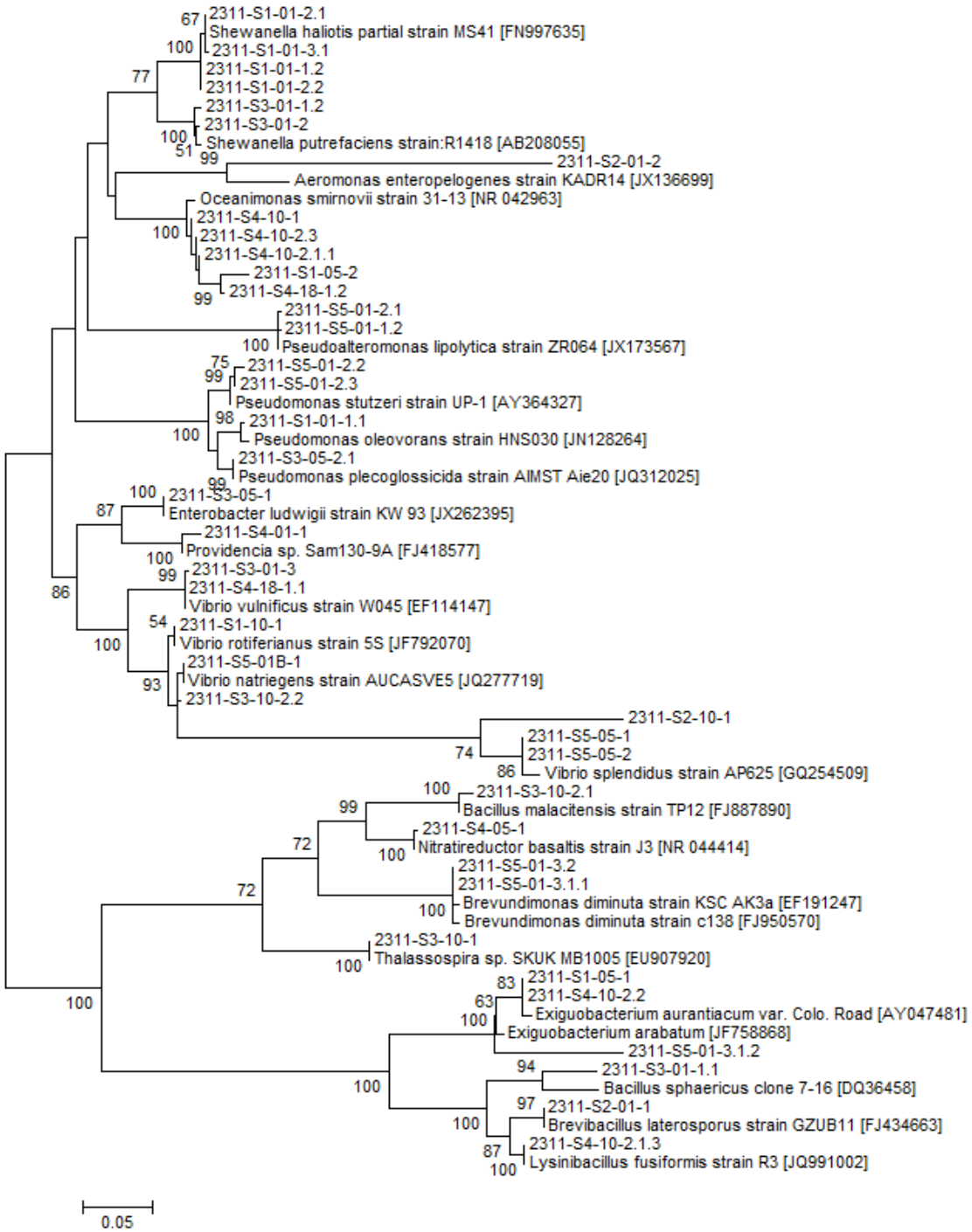


Figure 4: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Kota Kinabalu. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbor-joining method. Bootstrap values ≥50 are shown and the scale bar represents a difference of 0.05 substitution per site. Accession numbers for the reference sequences are indicated.

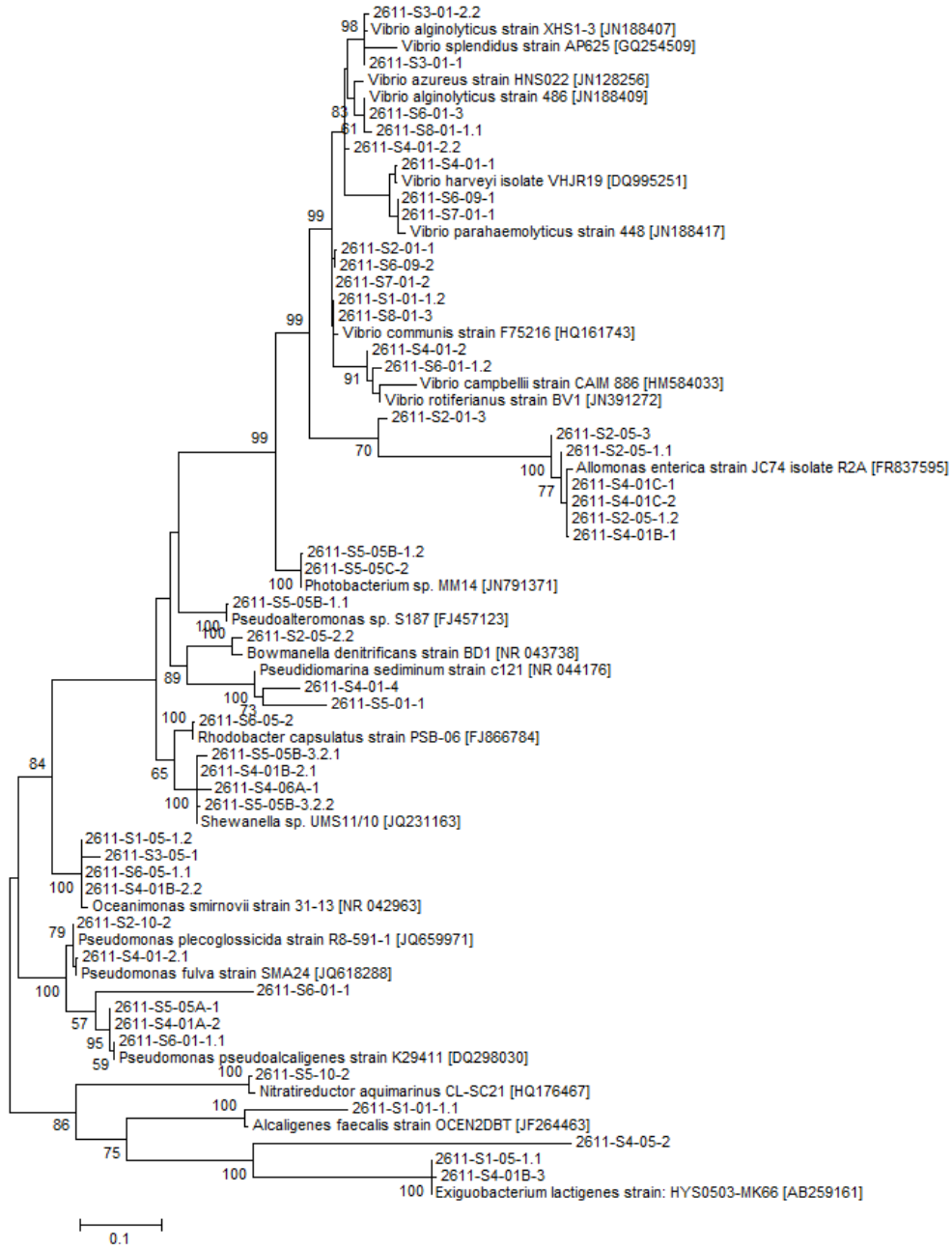


Figure 5: 16S rRNA gene-based phylogenetic tree representing bacterial sequences found in Semporna. The phylogenetic tree was generated with distance methods, and sequence distances were estimated with the neighbour-joining method. Bootstrap values ≥50 are shown and the scale bar represents a difference of 0.1 substitution per site. Accession numbers for the reference sequences are indicated.

Our results correlate with existing records of microbial communities found in coastal and open-ocean environments (Bernard et al. 2000) although samples from Kuching display significant riverine influence. Differences between the three areas can partly be explained by differences in physico-chemical parameters. The Kuching community is influenced by higher nutrients and riverine input, and is dominated by potentially pathogenic *Vibrios*, while the Kota Kinabalu community is more indicative of an open ocean environment. Isolates obtained from Kota Kinabalu and Semporna show that the communities in these areas have potential roles in bioremediation, nitrogen fixing and sulphate reduction.

Since there are no published reports on the microbial biodiversity in the eastern region of the South China Sea, their role in local biogeochemical cycles is also unclear. To date, there are no available reports on the sulphur cycle in the region, or of DMSP catabolism from bacterial communities of Kuching, Kota Kinabalu and Semporna; neither are any bioinformatics data available on the prevalence of dmdA and dddP genes in bacteria from these regions. As part of our effort to understand the importance of bacteria in the region for the local sulphur cycle, we screened our isolates for the existence of dmdA and dddP genes. Since our isolates have been cultured in a very general way using a method that does not involve selection for DMSP utilisation, any presence of these genes in our isolates is most likely a fundamental trait of these bacteria.

Bacteria isolated from Kuching displayed the highest abundance of both DMSP degrading genes (36%) compared to communities isolated from Kota Kinabalu and Semporna with 13 and 19 %, respectively. The bacterial community in Kota Kinabalu has the highest percentage of dmdA gene occurrence (28%) while the dddP gene responsible for DMS production appears to be most abundant (29%) within the bacterial community Semporna (see Fig. 6)

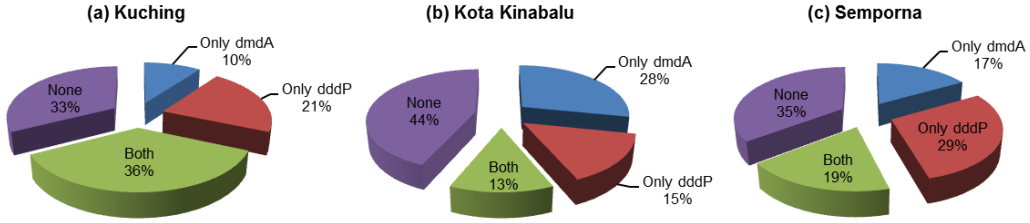


Figure 6: Relative abundance of dmdA and dddP genes in cultured bacterial communities from the waters of (a) Kuching, (b) Kota Kinabalu and (c) Semporna.

The *Gammaproteobacteria* group is the largest identified fraction within the communities at all three sampling sites with the potential for DMSP-assimilation. Interestingly, the composition of the DMSP-assimilating community generally mirrored the composition of the total bacterial community at each sampling site which is unlike previous studies at the Gulf of Maine and the Sargasso sea where the dominating group are the *Alphaproteobacteria* (Malmstrom, Kiene & Kirchman 2004). Our findings indicate that the community structure of *Gammaproteobacteria* in the area could be tightly linked to the local sulphur and also possibly the nitrogen cycle.

It was previously hypothesized that DMSP production is an overflow mechanism for when growth is unbalanced by lack of nutrients and the need to release excess energy and excess reduced sulphur (Stefels 2000). These carbon-energy overflow substances might evolve through natural selection to be useful in the cell (e.g. through auxiliary structures or defence mechanisms) (Hill, White & Cottrell 1998). Based on our findings, it seems likely that at low nutrient conditions, the distribution of dmdA and dddP genes within the bacterial community become more specific (e.g. more dmdA in KK and more dddP in Semporna; see Figure 3.11) to adapt to a preferred pathway to degrade DMSP.

Further in-depth characterization of these communities through a combination of physical, chemical and molecular biological studies will improve our understanding of the role of bacteria in DMS(P) cycling in the eastern South China Sea and the Celebes Sea and their impacts on climate change.

REPORT 2D: CULTURABLE BACTERIA FROM TALANG-TALANG REEF AND ITS SURROUNDING WATERS

Felicity W.I. Kuek[1], Lin-Hui Ngu[1], Li-Fang Lim[1], Aazani Mujahid[2], Moritz Müller[1]

[1]*Faculty of Engineering, Computing and Science, Swinburne University of Technology, Sarawak campus, 93350 Kuching, Sarawak, Malaysia.*

[2]*Department of Aquatic Science, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 93400 Kota Samarahan, Sarawak, Malaysia.*

Coral reefs are a rare feature in Sarawak due to its shallow sea shelf extending a long way into the ocean. The reefs of Sarawak are limited to the areas off the shores of Bintulu, Miri and offshore islands including the Talang-Satang region in Kuching. The Talang-Satang region is situated off the coast of Sematan and is especially important as it is one of the most diverse ecosystems found off Sarawak, including a healthy coral reef.

The coral surface mucus layer (SML) contains a complex microbial community that respond to changes in the environment (Ritchie & Smith 2004). The normal microbial flora within the SML can protect the coral against pathogen invasion and disturbances which may have led to coral diseases (Sutherland, Porter & Torres 2004). On average, 20-30 % of bacterial isolates originating from coral SML possess antibacterial properties (Ritchie 2006) that may assist the coral holobiont as a first line of defence against pathogens (Shnit-Orland & Kushmaro 2009). It has been suggested that these antimicrobial compounds are temperature sensitive (Ritchie 2006). Antibacterial activity was found to be optimal at 26 °C and slightly decreased at 30 °C, with partial inactivation occurring at 60 °C and complete loss of activity occurring at 80 °C (Shnit-Orland & Kushmaro 2009).

Coral reefs are also potentially significant sources of dissolved DMS and DMSP, particularly when corals are stressed or exposed during low tides (Broadbent & Jones 2004). The concentrations of DMS and DMSP measured in mucus are the highest reported in the marine environment, with values exceeding those reported from highly productive polar waters (Fogelqvist 1991; Trevena et al. 2000, 2003) and sea algal communities (Kirst et al. 1991; Levasseur, Gosselin & Michaud 1994; Trevena et al. 2003). The high levels of DMSP and DMS produced by corals, coupled with involvement of bacteria in DMSP and DMS conversion, suggest that corals are likely to harbor bacterial species involved in the cycling of these compounds (Raina et al. 2009, 2010).

The present study provides what we believe is the first analysis of cultured bacterial communities from the reefs of Talang- Talang. The bacterial communities from coral mucus, reef sediment and water column were found to be diverse with representatives from several bacterial groups. The total bacterial assemblage had representatives within the *Actinobacteria*, *Proteobacteria* (*Alpha-* and *Gammaproteobacteria*), as well as *Firmicutes* (see Fig. 1 for an overview of the major groups). The total number of bacterial isolates obtained and assemblages from the three reef environments are discussed in the following.

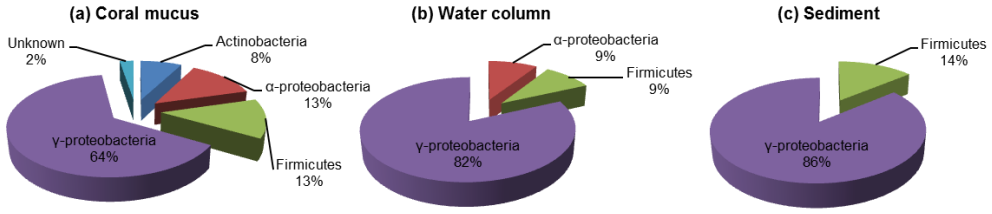


Figure 1: Pie charts illustrating the diversity of bacterial groups based on partial 16S rRNA gene sequences from bacteria isolated from (a) coral mucus, (b) water column and (c) sediment.

A total of 93 isolates were cultured from coral mucus, water column and reef sediment of the Talang-talang reef. Overall, 3% of the cultured bacteria were clustered within the *Actinobacteria*, 76% within the *Gammaproteobacteria*, 6% within the *Alphaproteobacteria* and 13% within the *Firmicutes*. From the coral mucus, 39 isolates were obtained with the majority clustered within the *Gammaproteobacteria* (64%), followed by *Alphaproteobacteria* (13%), *Firmicutes* (13%) and *Actinobacteria* (8%). There is an unknown isolate that was cultured from coral mucus. Its closest related sequence is unidentified. Within the water column, 82% of the isolates were *Gammaproteobacteria*, 9% *Actinobacteria* and 9% *Firmicutes*. Isolates from reef sediment were less diverse with cultures from only two bacterial groups: the Gammaproteobacteria (86%) and Firmicutes (14%).

The mucus associated isolates are related to representatives of bacteria documented in earlier studies, including a subset of *Vibrio spp.* consistently found in association with healthy corals (Ritchie & Smith 1995a, 1995b, 2004). There is a higher percentage of *Vibrios* (91%) when comparing mucus attached isolates to mucus associated isolates (29%). This illustrates the defensive qualities of coral mucus, and how a potential composition shift from beneficial bacteria to *Vibrio* dominance (which are known to be opportunistic) under conditions of increased temperature can occur.

Isolates related to the *Alphaproteobacteria* are only found in coral mucus samples. A couple of the cultures are related to uncultured sequences suggesting possible novel species. Isolates related to *Roseobacter spp.* and *Sphingobium amiense* strain D3AT58 (GenBank accession number JF459959; 97% similarity) were also obtained. *Roseobacter spp.* are widely associated with corals (Frias-Lopez et al. 2002; Rohwer et al. 2002; Bourne & Munn 2005; Kooperman et al. 2007; Bourne et al. 2008) and are potentially central to the health of corals. Antibacterial activities of *Roseobacter* have been observed against a wide range of marine pathogens (Hjelm et al. 2004). Coral associated bacteria from this genus have also been previously implicated in the degradation of DMSP (Raina et al. 2009, 2010). Thiotropocin, an antibiotic produced by *Roseobacter*, is a sulfur compound that might be derived from DMSP metabolism (Wagner-Döbler et al. 2004). These bacteria are suspected to be involved in a symbiotic relationship with coral-cultured zooxanthellae (Raina et al. 2009) which produces high concentrations of DMSP (Hill, Dacey & Krupp 1995; Broadbent, Jones & Jones 2002; Van Alstyne, Schupp & Slattery 2006). It is likely that the occurrence of *Roseobacter spp.* within the coral mucus may be due to the availability of DMSP produced by the zooxanthellae. *Roseobacter*-related strains (BCM 37 and 56; 100% similarity) were isolated from the coral mucus. Both isolates may play a possible role in the biogeochemical cycling of sulphur within the mucus as they appear to have both DMSP degrading genes. The *Roseobacter* genus is potentially central to the health of corals. The *Roseobacter spp.* are widely associated with corals (Frias-Lopez et al. 2002; Rohwer et al. 2002; Bourne & Munn 2005; Kooperman et al. 2007; Bourne et al. 2008) and suspected to be involved in a symbiotic relationship with zooxanthellae (Raina et al. 2009). An antibiotic produced by *Roseobacter*, thiotropocin, is a sulphur compound derived from DMSP metabolism (Wagner-Döbler et al. 2004).

To our knowledge, screening of dmdA and dddP genes in coral SML bacterial communities has not been done before. This preliminary study is part of our effort to understand the importance of bacteria in the region for the local sulphur cycle. Our isolates were not cultured in a method that involves specific selection for DMSP utilisation, therefore any presence of these genes in our isolates is most likely a fundamental trait.

The dddP gene which is responsible for DMS production appears to be most abundant (26%) within the coral mucus bacterial community (see Fig. 2). Many of our isolates also show potential in undergoing both DMSP degrading pathways as 20% of them have both dmdA and dddP genes.

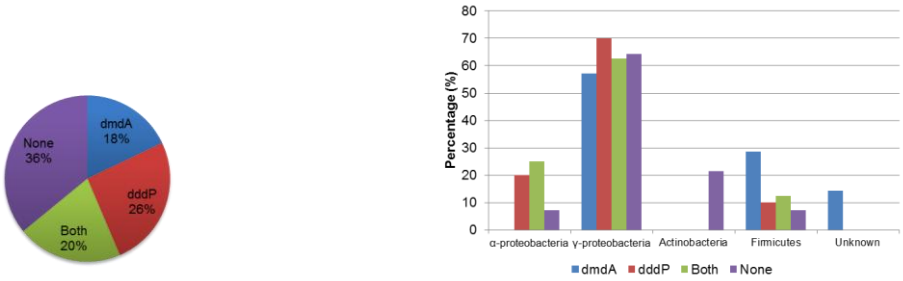


Figure 2: a) Relative abundance of dmdA and dddP genes in cultured bacterial communities from coral mucus. b) Presence of dmdA and/or dddP genes in bacterial isolates from coral mucus.

The presence of DMSP degrading genes in the coral mucus bacterial groups is similar to their occurrence in bacterial communities in the Kuching area of the South China Sea (see report on Bacterial diversity in SCS) where their composition generally mirrored the bacterial community. The *Gammaproteobacteria* group is the largest identified fraction within the community with the potential for DMSP-assimilation, followed by the *Alphaproteobacteria* and *Firmicutes*.

Within the coral mucus, bacteria are extremely dependent on photosynthetic products produced by zooxanthellae which play a role in regulating microbial communities present in corals (Ritchie & Smith 2004). Studies into coral-associated bacteria capable of metabolizing DMSP and DMS have emerged only recently (Raina et al. 2009, 2010). Little information is available and the nature of their interactions with the coral host remains an important research question.

REPORT 3: INTERACTION OF CLIMATE ACTIVE GASES DURING THE SHIVA-SONNE SO218 CAMPAIGN: DIMETHYLSULFIDE, OXYGENATED VOLATILE ORGANIC COMPOUNDS, NITROUS OXIDE (N_2O), AND METHANE (CH_4)

Christa Marandino, Cathleen Zindler, Hermann W. Bange (not on board), and Franziska Ziska (on board for H. Bange)

GEOMAR, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany

Objective: To investigate seawater cycling and the air-sea gradient of a variety of climate-active trace gases. Specifically, nitrous oxide (N_2O), methane (CH_4), dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), dimethylsulfoxide (DMSO), isoprene, and 11 different oxygenated volatile organic compounds (OVOCs): methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, acetaldehyde, propanal, butanal, acetone, and butanone were measured. The relationship between the concentrations of these compounds with each other and a variety of biological, chemical and physical parameters will be examined in order to determine what factors control the magnitude and distribution of the compounds in the surface ocean.

Background

Nitrous oxide and methane

Nitrous oxide (N_2O) and methane (CH_4) are atmospheric trace gases, which, directly and indirectly, influence the present-day climate of the Earth. Thus, an assessment of the natural and anthropogenic sources and sinks as well as the formation pathways of N_2O and CH_4 is essential both to understand past Earth's climate variability and to estimate the future development of Earth's climate. The world's oceans including its coastal zones, as natural sources of N_2O and CH_4, play a major role in the global budget of atmospheric N_2O, but only a minor role in the global budget of atmospheric CH_4. However, measurements of oceanic N_2O and CH_4 are still sparse and the derived emission estimates are associated with large uncertainties. N_2O in oceanic environments is mainly formed as a byproduct during nitrification ($NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$) and as an intermediate during denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$). In both processes, the yield of N_2O strongly depends on the concentration of dissolved oxygen (O_2). Both, nitrification and denitrification are microbial processes and can occur in the water column, in the sediments and in the interior of suspended particles.

CH_4 is formed during the decomposition of organic material by microbial methanogenesis. Since CH_4 formation requires strictly anaerobic conditions, CH_4 is produced in anoxic environments such as sediments, in the interior of suspended particles, in zooplankton guts during grazing or from biological cleavage of dissolved precursors such as DMSP and methylphosphonate. Additionally, CH_4 is oxidized under aerobic as well as anaerobic conditions in the water column and in the sediments. On the continental shelf so-called geological CH_4 can be released directly to the water column through mud volcanoes, via groundwater input, or seepage from gas/oil fields.

DMS(P/O)

DMS is the most abundant biogenic sulfur compound emitted to the atmosphere. It is mainly produced in the surface ocean from the precursor DMSP, a compound excreted by phytoplankton. Once in the atmosphere, DMS is rapidly oxidized to sulfur dioxide (lifetime approximately 1 day). The oxidation products of DMS can form aerosols and cloud condensation nuclei, thereby influencing the Earth's radiative properties and climate. It was proposed by Charlson et al. (1987) that this air-sea cycling of DMS may be a natural negative feedback loop on Earth's climate system. This so called CLAW hypothesis has yet to be proven. In addition, it is still not possible to predict the concentrations and distribution of DMS in the surface ocean. Although many individual components of surface ocean DMS cycling have been studied, such as production of DMSP by dinoflagellates and cleavage of DMSP into DMS via DMSP lyase, the surface ocean concentrations of DMS seem to be due to a combination of factors. One part of the cycle, DMS oxidation, produces the product, DMSO. DMSO is found throughout the water column, even into the deep ocean. More studies investigating exactly what

factors (e.g. phytoplankton species, bacteria abundance, UV radiation, etc.) control the surface ocean cycling and concentrations of DMS are still needed.

OVOCs
OVOCs can influence the oxidative capacity of the atmosphere by contributing to peroxyacetylnitrate and secondary organic aerosol formation, and HO_x and ozone chemistry. They are especially important in regions of the atmosphere where water vapor levels are low, such as in the upper troposphere. The region of the Shiva Sonne cruise track is especially interesting because of the highly convective air in this region. Gases produced at the air-sea interface can be transported more quickly and directly to the upper troposphere/lower stratosphere, where they have the greatest impact on atmospheric chemistry. Whether the ocean is a source or a sink of these compounds to the atmosphere is still an open question. In addition, surface ocean processes of OVOCs are largely uncharacterized, but it is largely thought that OVOCs are produced by photochemical reactions of color dissolved organic matter (CDOM) and by biology in the surface ocean. Uptake of these compounds also seems to be related largely to biological processes.

Methods

Samples for the determination of dissolved N_2O and CH_4 have been taken in triplicates from both the continuous surface seawater supply and the CTD/rosette casts. Samples have been poisoned with $HgCl_{2(aq)}$ immediately after sampling. All samples were shipped back to our lab in Kiel for the analysis of dissolved N_2O and CH_4. N_2O and CH_4 will be determined by applying the static headspace equilibration method. Gaseous subsamples of the equilibrated headspace will be injected onto a separation column filled with 5A molsieve followed by detection of N_2O and CH_4 with an electron capture detector (ECD) and a flame ionization detector (FID), respectively. 106 underway samples have been sampled for N_2O and CH_4 in triplicates every 3h from the continuous surface seawater supply. 14 CTD/rosette casts and 7 CTD/rosette casts have been sampled for N_2O and CH_4, respectively. The final N_2O and CH_4 data will be archived in MEMENTO (The MethanE and NiTrous Oxide database: https://memento.ifm-geomar.de/).

DMS, DMSP (dissolved and particulate), and DMSO are measured by purge and trap gas-chromatography (GC) coupled to a flame photometric detector (FPD). Triplicate samples, 10 mL in volume, are sparged for 10 minutes with a helium flow of approximately 30 mL per minute. The samples are dried with potassium carbonate and trapped with liquid nitrogen before being injected on the GC with boiling water. DMSP and DMSO are quantitatively converted to DMS via 26 chemical reaction after the sample has been sparged of the ambient DMS. The subsequent concentrations of DMS are measured in the way described above.

OVOCs, isoprene, and DMS were also measured via purge and trap gas chromatography coupled to a mass spectrometer detector (GC-MS). 10 mL samples were sparged with 30 mL per 27 minute of helium for 20 minutes through a potassium carbonate drying trap. The trap was then flushed at 40 mL per minute for an additional 10 mins. The sparged gases were trapped with liquid nitrogen then injected onto the GC column with boiling water. The masses of each compound were detected with the MS. Trace gases in air were trapped for 10 minutes in liquid nitrogen headspace from the bow of the ship using a small pump (flow = approx. 80 mL per minute). Potassium carbonate was again used to dry the samples. The gases were desorbed with boiling water and refocused using liquid nitrogen before being injected on the GC and detected in the same way as the liquid samples. Standards for both air and water were measured daily and 3 4 to 5 point calibrations for air and water were performed over the entire cruise track. CDOM fluorescence was measured to characterize the chemical makeup of the CDOM. CDOM absorbance was measured to determine the quantity in the seawater samples.

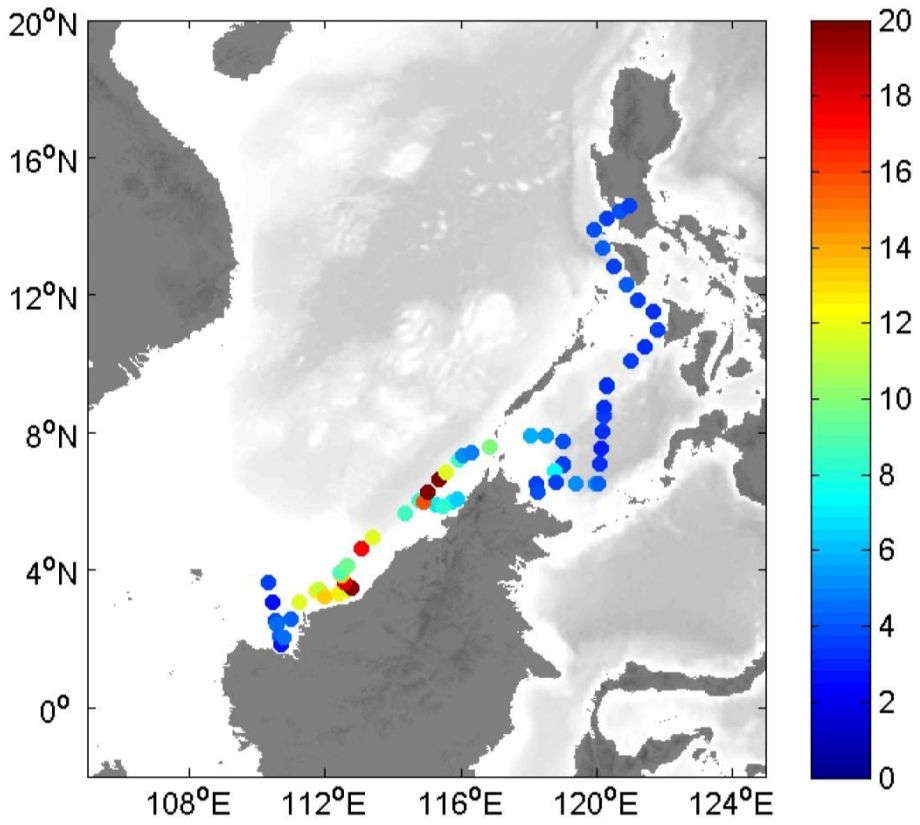


Figure 1. Surface seawater CH_4 levels (nM) over the SHIVA-Sonne cruise track.

DMS(P) as a source of CH_4

Methane is oversaturated in the subsurface layer of ocean relative to the atmosphere (Figure 1). Methanogenesis, the only known source of methane, is strictly anaerobic. Therefore, since these conditions do not exist in the upper ocean, another source of methane should exist. Some hypotheses suggest that methane is formed in anoxic niches or in the intestines of fish. Recent investigations propose two alternative CH_4 production mechanisms, both implicating nutrient limitation in the control of mixed layer CH_4 formation. In the first hypothesis bacterioplankton successfully exploit phosphate-depleted waters, where nitrate (NO_3^-) is in excess, by deriving phosphorus from phosphonates such as methyl phosphonate (Karl et al. 2008). Methane is thus produced aerobically as a byproduct of methyl phosphonate decomposition. The second hypothesis proposes that certain microbes can catabolise DMSP as a carbon source through methylotrophic methanogenesis in NO_3^- depleted waters, where phosphate (PO_4^{3-}) is plentiful (Damm et al. 2010). Based on the conversion of DMSP to hydrogen sulphide (H_2S) and CH_3SH by DMSP-utilising bacteria (Kiene et al. 2000) and a recent proposal for the intermediate formation of CH_3SH during CH_4 oxidation (Moran et al. 2008), Damm et al. (2010) proposed a thermodynamically plausible reverse reaction for the aerobic production of CH_4 from CH_3SH. The two mechanisms are entirely compatible and raise the intriguing possibility that deviations from the Redfield N:P ratio could be indirectly responsible for the marine CH_4 paradox through planktonic succession favouring species able to exploit alternative marine phosphorus and nitrogen stores. On the SHIVA-Sonne cruise, it is clear that there are similarities in the spatial distribution of the DMS and methane, possibly indicating DMSP as the main source for both (Figure 1 and 2).

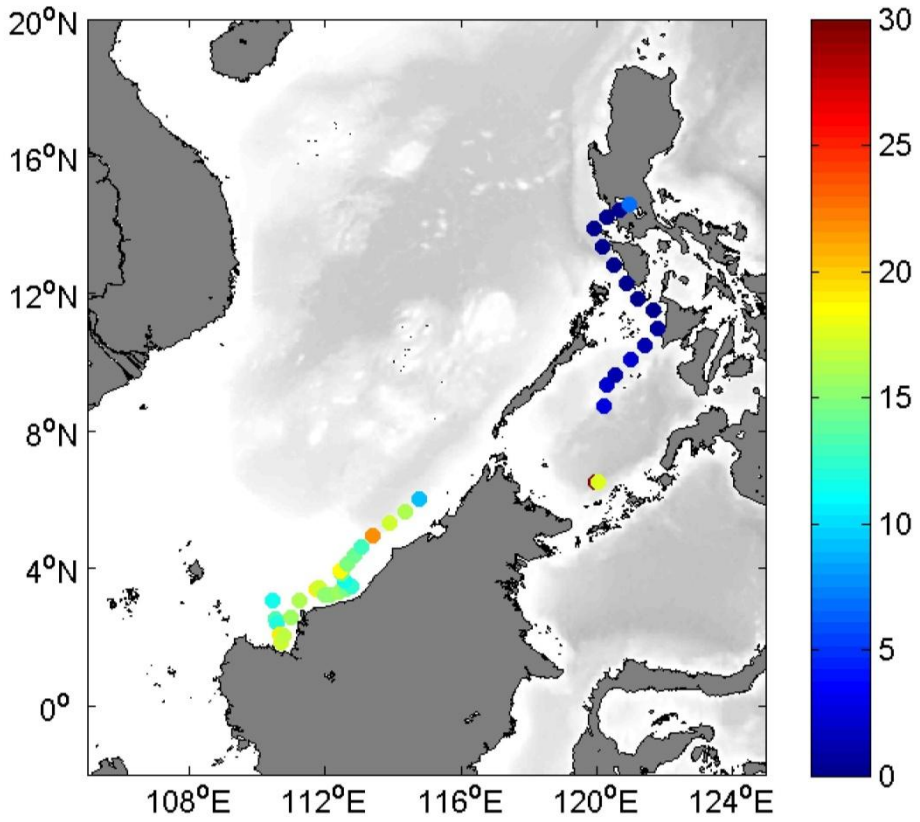


Figure 2. Surface seawater DMS concentrations (nM) over the SHIVA-Sonne cruise track.

Further preliminary results and data analysis plan

Unfortunately, the GC-FPD system did not exhibit adequate sensitivity during the cruise. Most samples were measured with the gas chromatograph-mass spectrometer system. Separate samples were preserved for DMS, DMSP, and DMSO detection later. The DMS values measured in situ do not compare well with those preserved (Table 1). The explanation for this discrepancy is not currently apparent and tests to understand the analytical differences are on-going. DMS concentrations were between 0 and 25 nM (Figure 2). There are clear hot spots along the Borneo coast in the South China Sea, while the levels drop markedly in the Sulu Sea off the Philippines coast. Analyses of phytoplankton pigment distribution for comparison with the DMS surface seawater data are currently underway. Methanol, acetone, isopropanol, DMS and 1-butanol were observed in almost every sample. Acetaldehyde, ethanol, propanol, and 2-butanol were also regularly measured. Propanal, isoprene, butanal, and butanone were either extremely small (below the detection limit) or not present in most of the samples measured.

More detailed analysis is planned for DMS(P/O), OVOCs, and N_2O. The air-sea gradient and spatial distribution over the cruise track is yet to be determined. CTD profiles for DMS and the CTD chlorophyll maximum depth for OVOCs and isoprene were also measured but the results will be analyzed in Fall 2013. CDOM absorbance values cannot be determined because the spectrophotometer lamp was not functioning properly. CDOM fluorescence data has been examined for quality control and data will be finalized in Fall 2013.

Table 1. Comparison of GC-MS DMS measurements made on board to GC-FPD measurements preserved and measured at IFM-GEOMAR. ND indicates samples values below the detection limit.

Day of Year	DMS (mol L^{-1}, GC-FPD)	DMS (mol L^{-1}, GC-MS)
322.05	ND	1.033E-08
322.17	ND	1.247E-08
322.30	ND	8.557E-09
322.80	ND	8.350E-09
322.92	ND	6.732E-09
323.05	ND	1.130E-08
323.17	ND	8.874E-09
323.29	ND	8.523E-09
323.42	ND	7.375E-09
323.55	ND	7.916E-09
323.67	ND	1.108E-08
323.79	ND	8.965E-09
323.92	ND	6.729E-09
324.04	ND	6.851E-09
324.17	ND	7.572E-09
324.29	ND	6.305E-09
324.42	ND	3.608E-09
324.55	ND	2.582E-09
324.67	ND	5.842E-09
324.80	ND	1.087E-08
324.92	ND	6.164E-09
325.05	ND	5.613E-09
325.17	ND	6.102E-09
325.29	ND	4.379E-09
325.42	ND	1.430E-08
325.55	ND	9.022E-09
325.67	ND	8.072E-09
325.80	ND	5.764E-09
325.92	ND	1.411E-10
326.04	ND	5.176E-09
326.30	5.530E-08	5.422E-09
326.42	ND	4.049E-09
326.54	ND	4.732E-09
326.68	ND	4.102E-09
326.92	ND	3.599E-09
327.04	ND	1.464E-08
327.17	2.970E-08	9.886E-09
327.29	1.047E-08	1.013E-08
327.42	2.970E-08	1.595E-08
327.55	1.045E-08	1.969E-08
327.67	1.664E-08	1.125E-08
327.79	ND	6.882E-09

327.92	8.320E-09	8.668E-09
328.04	1.951E-08	1.202E-08
328.17	8.746E-08	2.703E-08
328.29	ND	2.068E-08
328.54	7.050E-09	2.755E-08
328.67	4.265E-08	2.056E-08
328.83	1.779E-08	2.551E-10
328.92	4.237E-08	1.197E-08
329.17	1.040E-08	1.213E-08
329.29	2.622E-08	1.041E-08
329.42	ND	1.115E-08
329.54	2.478E-08	2.009E-08
329.67	2.217E-08	8.465E-09
329.79	ND	7.578E-09
329.92	1.435E-08	6.806E-09
330.04	8.300E-09	1.257E-08
330.17	5.350E-09	1.341E-08
330.29	5.800E-09	7.446E-09
331.17	ND	2.848E-08
331.29	1.380E-08	2.533E-08
331.54	3.900E-09	1.516E-08
331.67	8.300E-09	2.548E-08
331.79	3.044E-08	1.912E-08
331.92	3.676E-08	1.185E-08
332.04	1.811E-09	5.926E-09
332.17	5.029E-08	5.864E-09
332.29	1.158E-08	8.515E-09
332.42	2.269E-08	8.453E-09
332.54	ND	8.297E-09
332.67	ND	6.550E-09
332.79	ND	9.139E-09
332.92	3.506E-08	4.679E-09
333.04	1.120E-08	6.903E-08

References

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G. (2010) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655–661.

Damm E, Helmke E, Thoms S, Schauer U, Nöthig E, Bakker K, Kiene R (2010) Methane production in aerobic oligotrophic surface water in the central Arctic Ocean. Biogeosciences 7:1099–1108

Karl DM, Beversdorf L, Björkman KM, Church MJ, Martinez A, Delong EF (2008) Aerobic production of methane in the sea. Nature Geoscience 1:473-478

Kiene RP, Linn LJ, Bruton JA (2000) New and importantroles for DMSP in marine microbial communities. J Sea Res 43:209–224

Moran JJ, Beal EJ, Vrentas JM, Orphan VJ, Freeman KH, House CH (2008) Methyl sulphides as intermediates in the anaerobic oxidation of methane. Environmental Microbiology 10:162–173

REPORT 4: UNDERWAY MEASUREMENTS OF pCO_2, OXYGEN AND TOTAL GAS PRESSURE

Tobias Steinhoff, Anke Schneider and Arne Körtzinger (GEOMAR, Chemical Oceanography, Kiel)

Land, rivers, atmosphere, sediments and biota play a role in coastal ocean and shelf sea biogeochemical cycling of carbon. All these processes lead to highly variable (spatial and temporal) systems. Even if the area of coastal systems is small compared to the open ocean it plays an important role in the global carbon budget. The amount of carbon being fixed or released in coastal systems is still a number of debate [*Chen and Borges*, 2009] because of its high variability. The South China Sea is a poorly understood marginal sea in terms of its biogeochemistry [*Morton and Blackmore*, 2001] . Its circulation pattern is influenced by the Monsoon system. During winter the surface flow of the South China Sea is driven by the Northwest Monsoon and creates an anti-clockwise circulation pattern. This results in a northeasterly flow along the coast of Borneo and Philippines. Only in the near vicinity of the coast of Borneo the surface flow could reverse in southwesterly direction.

Measurements

During SO218 cruise underway measurements of pCO_2, dissolved oxygen and gas tension were conducted. All sensors were deployed in a bath (Coleman® cooling container) that was flushed with the seawater at a typical flow rate of 10 L min^{-1}. The instruments were fed with a seawater flow from a submersible pump that was installed in the ships moonpool (~ 5m depth). Sea surface salinity (SSS) and temperature (SST) were taken from the ships thermosalinograph.

pCO_2: For the determination of pCO_2 a submersible sensor was used (HydroC-CO_2). A flat silicone membrane acts as an equilibrator between the seawater and the inner gas volume of the sensor. The CO2 concentration in the air circuit is measured by means of NDIR detection. The sensor was calibrated before the cruise and zero values were used to account for a possible drift of the sensor following the recommendations of *Fietzek et al.* [2013].

Dissolved *Oxygen:* Dissolved Oxygen was determined with an oxygen optode (Aanderaa Instruments AS, Bergen, Norway). This technique is based on dynamic luminescence quenching. The raw data were calibrated by applying a temperature and oxygen dependent calibration polynomial that was recorded before the cruise [*Bittig et al.*, 2012].

Gas Tension: The PSI-GTD-Pro (Pro-Oceanus Systems Inc., Halifax, Canada) measures the total dissolved gas pressure of all gases. A small sample volume of air is equilibrated to all dissolved gases in the water through a special membrane. The GTD was also installed in the water bath.

Results

Fig. 1 shows SSS and SST along the cruise track. The study area can be divided into two parts. A part along the coast of Borneo with lower salinity values but higher variability and the Sulu Sea with higher values but lower variability. The Sulu Sea shows more open ocean condition as it is also deeper than the section along the coast of Borneo. Between 112 and 113°W salinity values fall even below 29 what might be caused by river runoff.

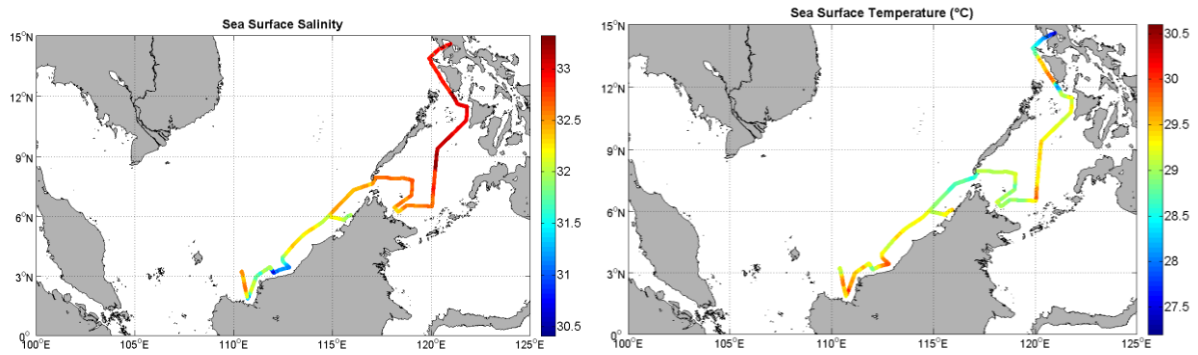


Figure 1: Sea Surface Salinity and Temperature along the cruise track of SO218.

For atmospheric xCO_2 data we used data from station SCSN09-01 from the Globalview network [*GLOBALVIEW-CO2*, 2011]. These data were used to calculate the pCO_2 difference between ocean and atmosphere (ΔpCO_2). Fig. 2 shows the ΔpCO_2 values and the oxygen anomaly what is the difference between the observed oxygen concentration and the saturation concentration (calculated from SST and SSS). Positive values mean an oversaturation and vice versa. CO_2 is oversaturated during the whole cruise track with maximum values at the coast of Borneo and the Philippines. The oversaturation at the coast of Borneo coincides with the salinity minimum. Again this might be due to river runoff, as riverine water transports huge amounts of inorganic and organic carbon into the coastal ocean. The organic carbon is respired and CO_2 increases. This can be also observed in the oxygen data, as along the coast of Borneo oxygen is slightly undersaturated.

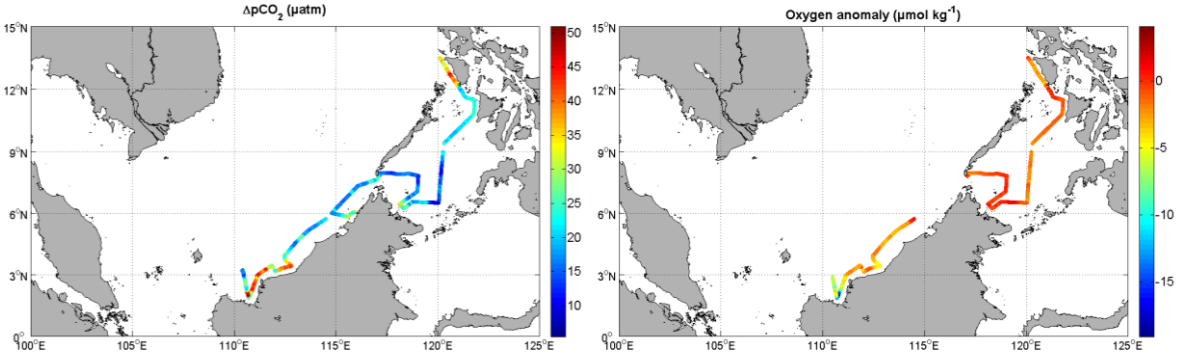


Figure 2: ΔpCO_2 and Oxygen anomaly.

The observed oversaturation of CO_2 is in good agreement with the data of [*Rehder and Suess*, 2001] who measured CO_2 in the same region in 1994. Using the ship's wind speed data we calculated the CO_2 flux F for the dataset:

where k is the wind speed dependent transfer coefficient that was calculated following the parameterization of *Nightingale et al.* [2000]. Fig. 3 shows the calculated flux values for CO_2. Even if there were high concentration gradients between the ocean and the atmosphere only minor fluxes were observed during most of the cruise track due to low wind speeds. However these fluxes compare well with the results of *Zhai et al.* [2005] showing the South China Sea is a CO_2 source.

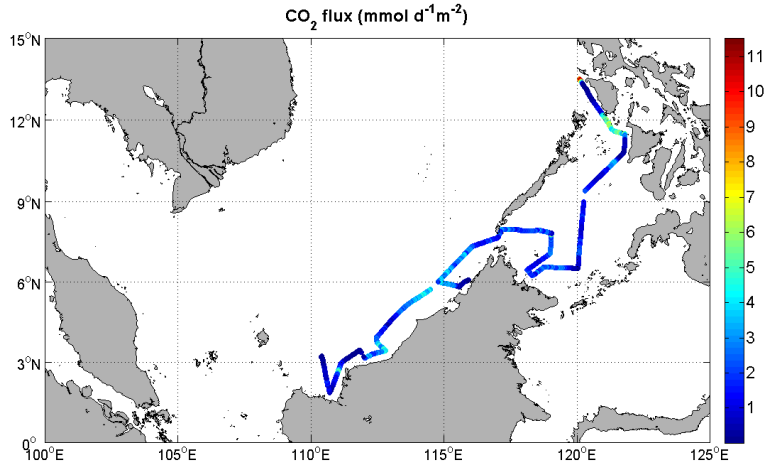


Figure 3: CO_2 flux along the cruise track. Positive values mean a flux from the ocean to the atmosphere.

References

Bittig, H. C., B. Fiedler, T. Steinhoff, and A. Körtzinger (2012), A novel electrochemical calibration setup for oxygen sensors and its use for the stability assessment of Aanderaa optodes, *Limnology and Oceanography: Methods*, *10*, 921–933, doi:10.4319/lom.2012.10.921. [online] Available from: http://www.aslo.org/lomethods/free/2012/0921.html (Accessed 3 December 2012)

Chen, C.-T. A., and A. Borges (2009), Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO2, *Deeep-Sea Res. II*, *56*, 578–590.

Fietzek, P., B. Fiedler, T. Steinhoff, and A. Körtzinger (2013), In situ quality assessment of a novel underwater p CO 2 sensor based on membrane equilibration and NDIR spectrometry, *Journal of Atmospheric and Oceanic Technology*, 130827113218000, doi:10.1175/JTECH-D-13-00083.1. [online] Available from: http://journals.ametsoc.org/doi/abs/10.1175/JTECH-D-13-00083.1 (Accessed 28 August 2013)

GLOBALVIEW-CO2 (2011), Cooperative Atmospheric Data Integration Project - Carbon Dioxide, *CD-ROM, NOAA ESRL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLOBALVIEW]*.

Morton, B., and G. Blackmore (2001), South China Sea., *Marine pollution bulletin*, *42*(12), 1236–63. [online] Available from: http://www.ncbi.nlm.nih.gov/pubmed/11827109

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycl.*, *14*(1), 373–387.

Rehder, G., and E. Suess (2001), Methane and pCO 2 in the Kuroshio and the South China Sea during maximum summer surface temperatures, *Marine Chemistry*.

Zhai, W., M. Dai, W.-J. Cai, Y. Wang, and Z. Wang (2005), High partial pressure of CO2 and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China, *Marine Chemistry*, *93*(1), 21–32, doi:10.1016/j.marchem.2004.07.003. [online] Available from: http://linkinghub.elsevier.com/retrieve/pii/S030442030400218X (Accessed 30 August 2013)

REPORT 5: SHIVA SONNE SO218: RADIO- AND OZONESOUNDING

Kirstin Krüger and Steffen Fuhlbrügge

GEOMAR, Marine Meteorology, Kiel, Germany.

Scientific background

Although the first signs of the ozone recovery have been recognized in the upper stratosphere since the beginning of 2000 (WMO, 2007), still unexpected high ozone loss is eventually reported over polar latitudes since then, i.e. the record ozone loss over Antarctica in 2006 und more recently the first "Arctic ozone hole" during the winter 2010/2011 (Manney et al., 2011 *Nature*). Especially the timing of full ozone recovery in the Northern hemisphere (NH) is quiet uncertain due to the high natural variability of stratospheric temperatures during winter and the impact of naturally produced halocarbons chemical compounds, which are yet not adequately addressed in current ozone projections for the 21st century (SPARC CCMVal 2010; WMO, 2011; Manney et al., 2011 *Nature*).

Despite the well known threat of anthropogenic produced halo fluorocarbons (HFCs) on the ozone layer, very short-lived substances (VSLS) as bromine and iodine compounds and other natural trace gases have to be considered for the ozone depletion as well. These chemical species are produced in the ocean, probably through the metabolism processes of microorganisms called phytoplankton. To better understand the relationship between marine biochemistry and atmospheric chemistry and physics our SO218 SONNE expedition aims to investigate these relations into more detail. The tropical Western Pacific is especially suitable for these VSLS-transport examinations for two reasons: First, the tropical West Pacific is known to be a source region for halocarbons and has not yet been examined especially the southern part of the South China Sea. Second, this region exhibits strong convective activity throughout the year. Thus, active gas exchange between the marine boundary layer and the stratosphere (altitudes: 17-50 km), where the protective ozone layer exists. Regular (6-hourly) weather balloons are launched to improve the global meteorological assimilations, which are used as input data for trajectory and chemical transport calculations within SHIVA project, starting from the ocean surface well into the stratosphere. The ozonesonde measurements should detect direct chemical effects of the halocarbons or other chemical relevant trace gases in the atmosphere along and above our ship track.

Scientific goals

From the SO218-SONNE expedition we derived new results concerning the atmospheric structure and content over the southern part of the South China Sea from the marine boundary layer well into the stratosphere. Given that the expedition cruised well within the tropical belt, we do not expect high variations in the meteorological parameters. Along the ship cruise from 1° N to 15° N deeper cold point temperatures within the Tropical Tropopause Layer (TTL) should be measured during November compared to boreal transition or summer seasons. Given that the cruise takes place in November starting in Singapore, we expect to be close to the Inner Tropical Convection Zone (ITCZ) with enhanced convective activity. The radiosounding of temperature, wind, humidity and ozone are used to validate the meteorological input data and serve as a starting point for the trajectory calculations with the Lagrangian dispersion model FLEXPART.

Measurements

We have carried out 6-hourly radiosoundings of temperature, wind, and humidity, using 350 gr balloons inflated with roughly 25 kbar Helium. This routine observational program was carried out with DFM-09 radiosonde from GRAW. These radiosondes are characterized by their small lightweight package and easy handling which bears great advantage on an expedition that does not provide dedicated balloon filling and launching facilities. Also, the ground receiver equipment (antenna, radio

data acquisition) was made available at no cost from the Germany Weather Service (DWD) in Lindenberg and could be easily installed on the vessel.

Ozone sondes were launched along the western and northern coast of Borneo usually at 19 LT (11 UTC) together with a GRAW radiosonde (DFM-97), using a TOTEX balloon with 1200 gr weight and about 80 kbar Helium filling. In total 6 ozone sondes were started during our South China Sea passage as well as more 73 radiosondes. For the ozonesonde launch a DFM-97 radiosonde was tight together with the ozone instrument equipped with a 30 m enroller. These large balloons had to be filled in on deck. In order to avoid premature burst of the balloons during filling, a special cover net ("balloon launcher") was used for protection. The balloons and the balloon launcher were produced by the Japanese company TOTEX. The balloon launches were greatly supported by the scientists and the ship crew by securing the filling and launching equipment on deck. The balloons reached frequently altitudes above 25 km. Only one small balloon burst just before starting off due to the narrow passage between the fill-in and another 20 feed container. The individual starts of the two described instruments are listed in the appendix.

Results

The atmosphere along our trip showed throughout tropical character with minimum temperatures reaching below -85° C around 17 km altitude (90 hPa), marking the lower boundary of the stratosphere (Figure 1 left). The tropical wind regime in the stratosphere the Quasi Biennial Oscillation (QBO) is in its Easterly phase above ~23 km altitude (50 hPa) (Figure 1 bottom).

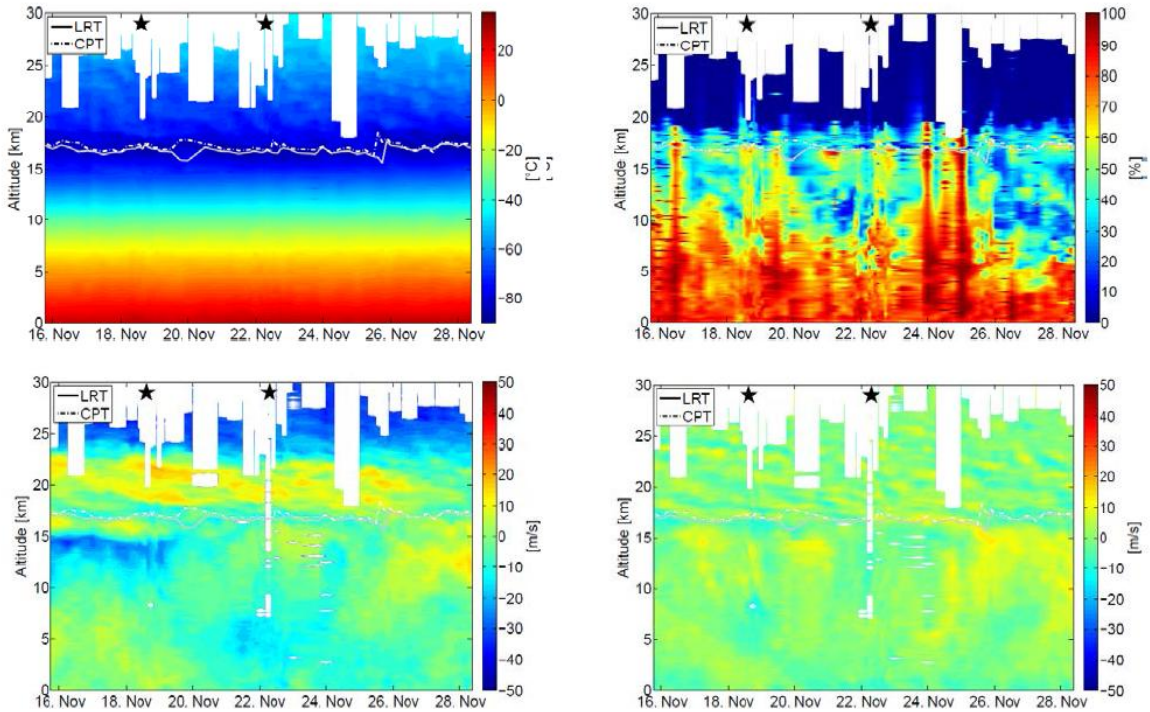


Figure 1: Profiles obtained from the radio sounding: Left: Temperature (°C), the dashed line shows the cold point temperature (CPT) and the solid line displays the lapse rate temperature (LRT); Right: Relative humidity (in %); Bottom: zonal and meridional wind components (m/s).

Surface winds were dominantly North Easterlies with maximum wind speeds reaching regularly above 10 m/s, the typical trace winds (Figure 2 top). Surface air temperature varied between maximum 29° C minimizing up to 26 °C (Figure 2 bottom). Sea surface temperatures (SSTs) stayed above 29 °C most of the time, which may be influenced by the La Nina in the tropical West Pacific. Enhanced convective activity with thunder storms and lightning occurred in Singapore and at the Northwestern tip of Borneo (Figure 3). The ozone profiles revealed low tropospheric ozone values between 15 to 70

ppb, which were however higher than the observed very low ozone mixing ratios (<10 ppb) detected during the TransBrom Sonne cruise, which crossed the tropical West Pacific further to the East (not shown here).

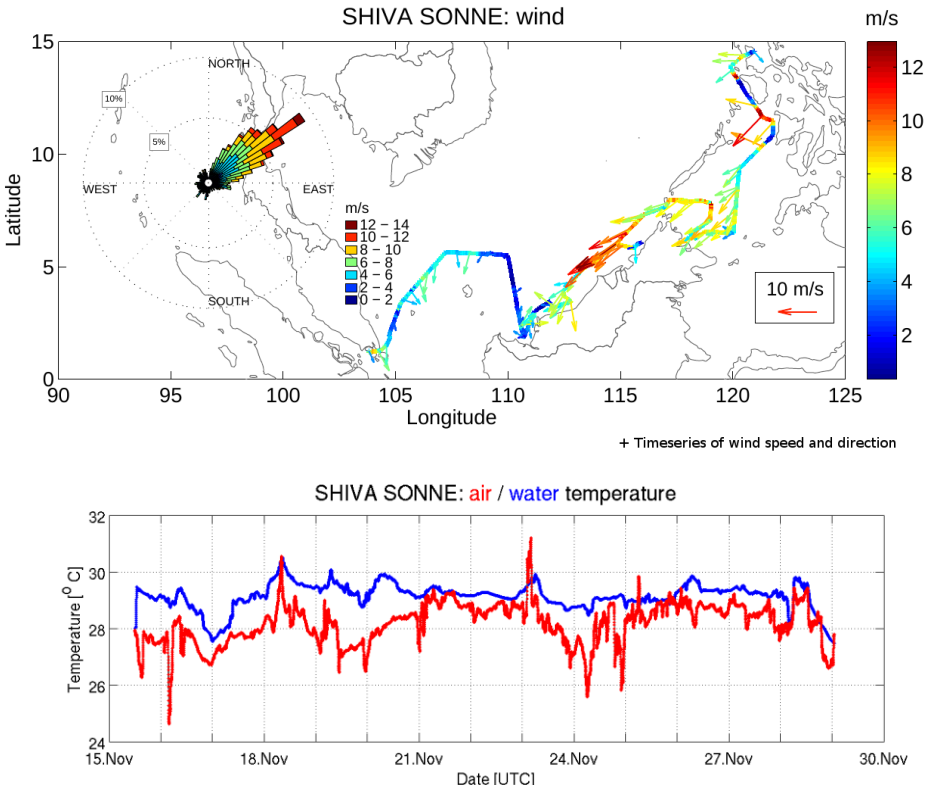


Figure 2: Top panel: wind speed (m/s) and direction; bottom panel: air and water temperature (°C) measured on board of RV SONNE during the SO218 cruise.

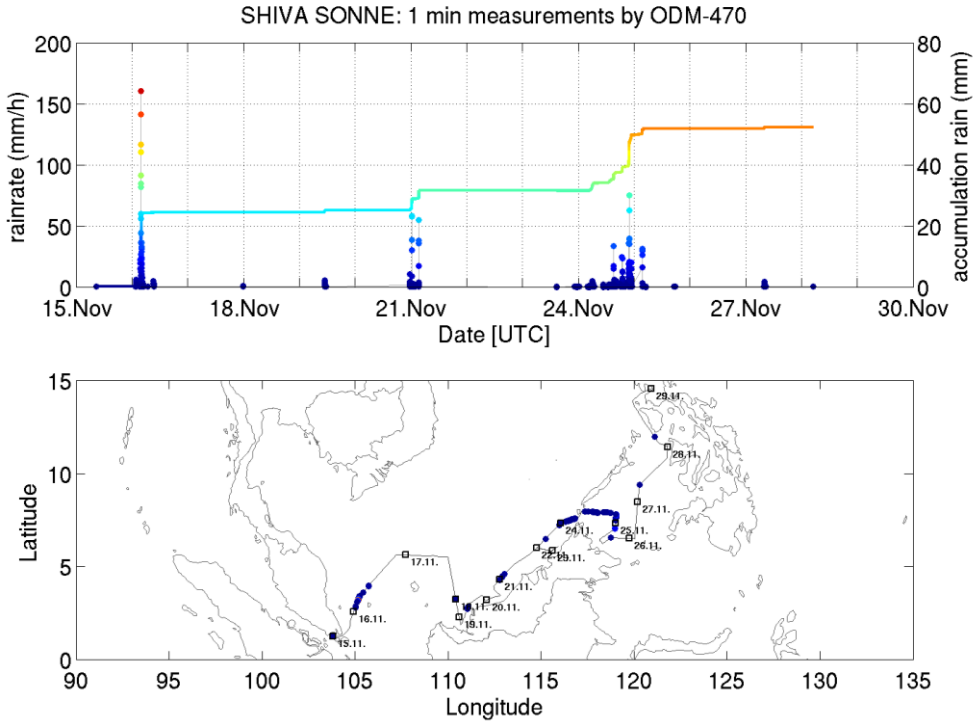


Figure 3: Precipitation measurements: rain rate (mm/h) and accumulation rain (mm).

Tegtmeier et al. (2013) analysed the air mass pathways (trajectories) from the surface into the stratosphere. With the trajectory model FLEXPART we found that the entrainment of methyl iodide into the stratosphere is projected to be higher above the tropical West Pacific than available aircraft observations showed so for. However, these aircraft measurements mainly took place in the East Pacific/ Central America. In another study the air mass exchange of VSLS through the marine boundary layer to the free troposphere is examined along the cruise and is compared with the SHIVA FALCON aircraft measurements (Fuhlbrügge et al. in preparation).

References:

Manney, G. et al., Unprecedented Arctic ozone loss in 2011, Vol. 478, 468-477, doi:10.1038/nature10556, Nature, 2011.

SPARC CCMVal Report on the Evaluation of Chemistry-Climate Models, SPARC No. 5, WCRP-132, *WMO/TD-No. 1526*, 2010.

Tegtmeier, S., K. Krüger, B. Quack, E. Atlas, D. R. Blake, H. Boenisch, A. Engel, H. Hepach, R. Hossaini, M. A. Navarro, S. Raimund, S. Sala, Q. Shi, and F. Ziska, The contribution of oceanic methyl iodide to stratospheric iodine, *ACPD*, 13, 11427-11471, 2013.

WMO, Scientific Assessment of Ozone Depletion: 2006, World Meteorological Organization, Geneva, Switzerland, *WMO Report No. 50*, 2007.

WMO, Scientific Assessment of Ozone Depletion: 2010, World Meteorological Organization, Geneva, Switzerland, *WMO Report No. 52*, 2011.

REPORT 6: DETERMINATION OF TRACE GAS CONCENTRATIONS IN THE MARINE BOUNDARY LAYER

Elliot Atlas1, Steffen Fuhlbrügge[2], Kirstin Krüger[2], Birgit Quack[2]

[1] Rosenstiel School of Marine and Atmospheric Sciences, Miami

[2]GEOMAR, Kiel, Germany

Measurements

200 Canister air samples were taken for GC/MS- Analysis of trace gases in Miami. The air samples were taken three hourly and the sampling frequency was increased to 1 sample per hour at the diurnal stations and close to the northern coastal Borneo, where we expected interesting diurnal patterns as well.

Results

The wind observations already reveal two different air mass origins (Figure). From 15.11. – 19.11.2011 the mean wind speed accounts 3.7 ± 1.8 m/s with a northern wind direction, while the wind changes to Northeast after 20.11.2011 until 29.11.2011 and increases to a mean wind speed of 6.4 ± 3.0 m/s (Figure 1, Report No. 5). Thus, the dominating wind regime at the South China and Sulu Seas is the trade wind regime. This is reflected by an overall mean wind direction of Northeast (50° – 60°) and a mean wind speed of 5.5 ± 2.9 m/s. From 18.11. – 19.11.2011 the wind direction changes additionally to West before the ship reaches the coast of Kuching.

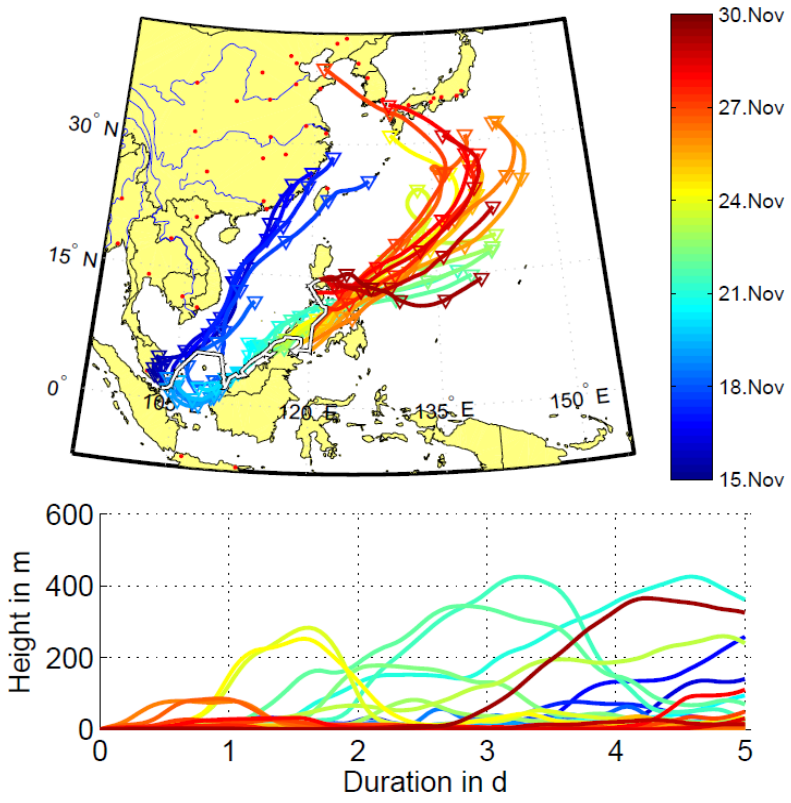


Figure 1: 5-day backward trajectories starting at the surface, meterologicalet input data NCEP/NCAR Reanalysis Data 1.

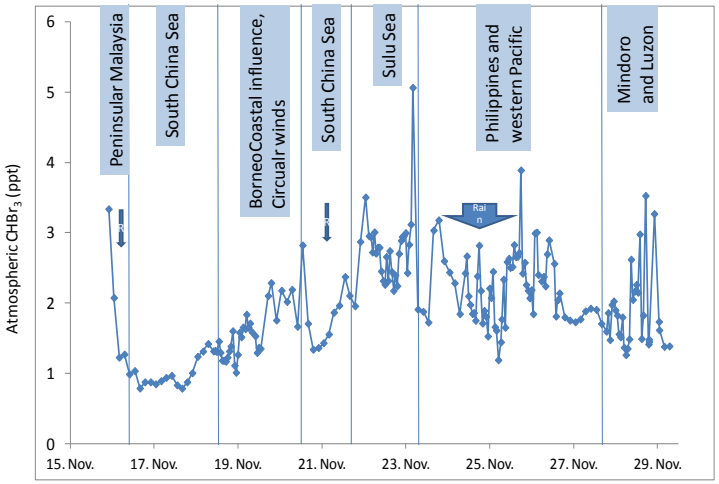


Figure 2: Origin of air-masses, determining the atmospheric mixing ratios of bromoform.

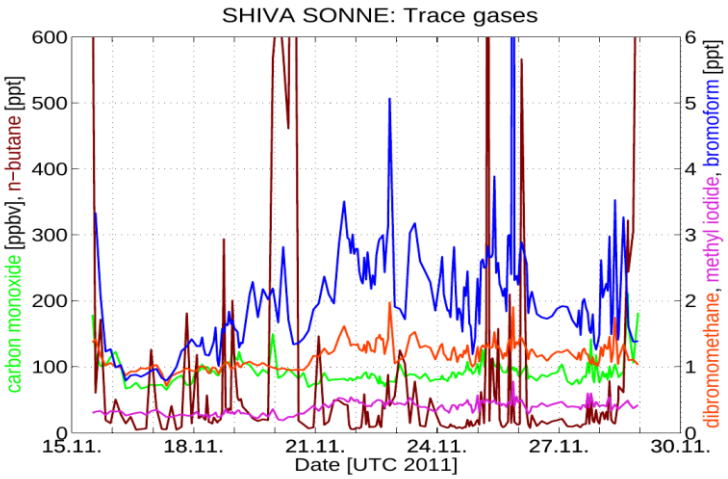


Figure 3: Anthropogenic and natural trace gases in the atmosphere of the South China and Sulu Sea.

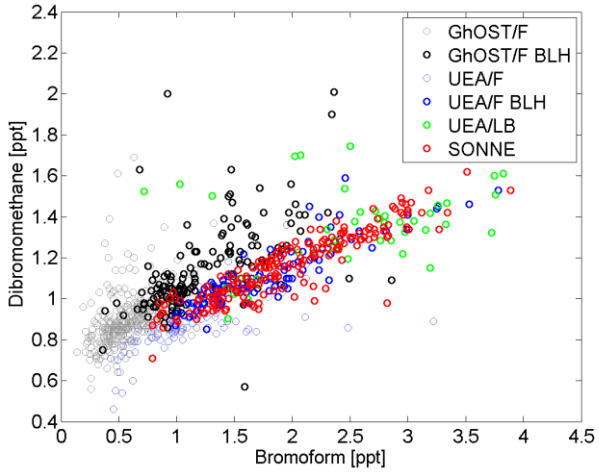


Figure 4: Bromoform vs. Dibromomethane volume mixing ratio (ppt).

REPORT 7: TRACE GAS MEASUREMENTS USING MAX-DOAS AND CE-DOAS INSTRUMENTS

Johannes Lampel[1], Folkard Wittrock[2]

[1]Institute of Environmental Physics, University of Heidelberg, johannes.lampel@iup.uni-heidelberg.de

[2]Institute of Environmental Physics, University of Bremen, folkard@iup.physik.uni-bremen.de

Motivation

Reactive halogen species (RHS) are known to play an important role in the troposphere as well as in the stratosphere by, among other processes, catalytically taking part in ozone destruction, NO_x and HO_x cycles and thus actually influencing the oxidation capacity of the atmosphere.

They can be created by oxidizing directly emitted halogen compounds, by photolysis of VSLS emitted from the ocean or in chemical reactions upon surfaces. Iodine compounds can significantly increase ozone destruction compared to bromine compounds. Additionally eventually form aerosol particles via self-reactions.

MAX-DOAS measurements provide the possibility of calculating trace gas profiles. It is possible to measure RHS as well as providing NO_2, formaldehyde, glyoxal, and SO_2 data at the same time. Some uncertainties of concentrations can originate from radiative transport modeling. The in-situ cavity measurements have a rather well-defined path-length and thus enable us to have additional ground measurements, even though only a few trace gas species can simultaneously be measured with one instrument due to technical limitations.

Method

DOAS: (Differential Optical Absorption Spectroscopy) is a method to detect trace gases within air by measuring light spectra, calculating optical thicknesses and finally fitting trace gas absorption cross sections known from literature to these to obtain column densities and finally mixing ratios. Differential means that Mie and Rayleigh scattering are accounted for by removing the broad band structures from the optical thickness and also reducing the trace gas cross sections to their differential part. The type and number of trace gas mixing rations which can simultaneously be retrieved depends on the wavelength range used.

MAX-DOAS: (Multi AXial DOAS): This particular method uses the scattered sun light as a light source prevailing measurements during night. Due to changes in the solar zenith angle and especially by looking at different elevation angles close to the horizon results in different light paths in the atmosphere. Radiative transport models are used to obtain the actual path of light and aerosol profiles. It is then possible to calculate stratospheric abundances and tropospheric trace gas profiles up to a height of usually 2-4km at a resolution of 100-1000m.

CE-DOAS: (Cavity Enhanced DOAS): This method is an active method and does not rely on sunlight. By means of 2 highly reflective mirrors the actual light-path from light-source to spectrometer can be several kilometers. This value is determined using a Helium calibration to minimize Rayleigh scattering or via analysis of ringdown signals. The usable wavelength window is often limited by the mirror reflectivity and usually of the order of a few 10nm.

Trace gases within the wavelength range of the MAX-DOAS systems on SO218:BrO, IO, HCHO, HONO, CHOCHO, H_2O, O_4, NO_2, SO_2, O_3, OIO, I_2

Trace gases within the wavelength range of the CE-DOAS system on SO218:IO, NO_2, H_2O, CHOCHO

"Samples"

The MAX-DOAS instruments recorded spectra during daytime from the time RV Sonne left Singapore. The Heidelberg MAX-DOAS was shut down and dismantled on the evening of November, 28th, 2011. The MAX-DOAS system from Bremen continued to measure until reaching the port of Manila around 10:00 LT on the following day. Bremen's MAX-DOAS was looking towards starboard, Heidelberg's instrument towards portside. The time resolution of profiles is about 10 to 15 minutes, the detection limit for the different trace gases depend on viewing conditions with typical values for IO of 0.8 ppt, for BrO 1ppt, and for NO_2 around 100 ppt.

The Cavity system was operated outside on the monkey deck portside on November 16th, 2011 and from October 19th, 2011 until it stopped measuring on November 29th, 2011 around 08:00 LT. On November 17th and 18th it had to be transported back to the lab to be cleaned and readjusted. Heavy rain together with wind from the side resulted in a small drop of seaspray on of the mirrors which had lowered the sensitivity significantly. Time resolution for single spectra was usually 30s, which results in a detection limit of about 2ppt VMR for IO (for clean mirrors). For a time resolution of around 5 minutes the best achievable detection limit for IO was 0.8ppt due to systematic problems during the evaluation.

The actual air measurements were interrupted a few times for zero air and calibration measurements. Rainfall and/or sea spray was a reason for long zero air measurements to protect the instrument.

Results

The MAX-DOAS measurements of Heidelberg failed during SHIVA, even though it functioned well before during MSM18 and afterwards during SOPRAN M91. The reason for this problem was not found onboard due to the high workload operating the other MAX-DOAS and especially the CE-DOAS. The Bremen MAX-DOAS worked fine during the whole cruise

CE-DOAS data has not shown any IO mixing ratios above 0.8ppt. The detection limit has been degrading towards the end of the cruise, caused by a decrease in mirror reflectivity. In contrast to this finding fit was possible to derive from MAX-DOAS measurements small IO mixing ratios between 0.5 ip and 2 ppt and in the lowest layer (0 to 500 m) with slightly higher values in the Sulu sea. These observations are in reasonable agreement to measurements from the LIF instrument operated during SO228 by the Univeryity of Leeds.

For BrO no positive detection was possible for the whole cruise.

NO_2 mixing rations were also calculated and were used during the cruise to roughly estimate the influence of the ship's stack on air measurements on the monkey deck. The detection limit was usually approximately 100ppt, significantly worse during the last day approaching Manila. Direct wind from the back as well as wind from starboard seem to cause exhaust air to be mixed into air on the monkey deck. Figure1 shows six minutes averaged NO_2 mixing ratios and a situation with possible mixing of relatively clean air with stack air on November, 25th. Distant Sources of NO_2 usually appeared as broader peaks.

Passing through the plume of a wildfire on the Philippines on November 28th, 10-11 LT, a clear NO_2 signal was seen, correlating again with Ozone and CO. Glyoxal stayed below detection limit for the CE-DOAS. The Bremen MAX-DOAS was able to detect glyoxal up to 350 ppt when approaching

Manila. SO2 up to a few ppb was measured in the beginning of the cruise close to the shipping lane from Singapur through the South China Sea and occasionally during the whole cruise whenever plumes of passing ships were sampled.

Data sets both from the CE-DOAS and the Bremen MAX-DOAS can be found on the SHIVA data server.

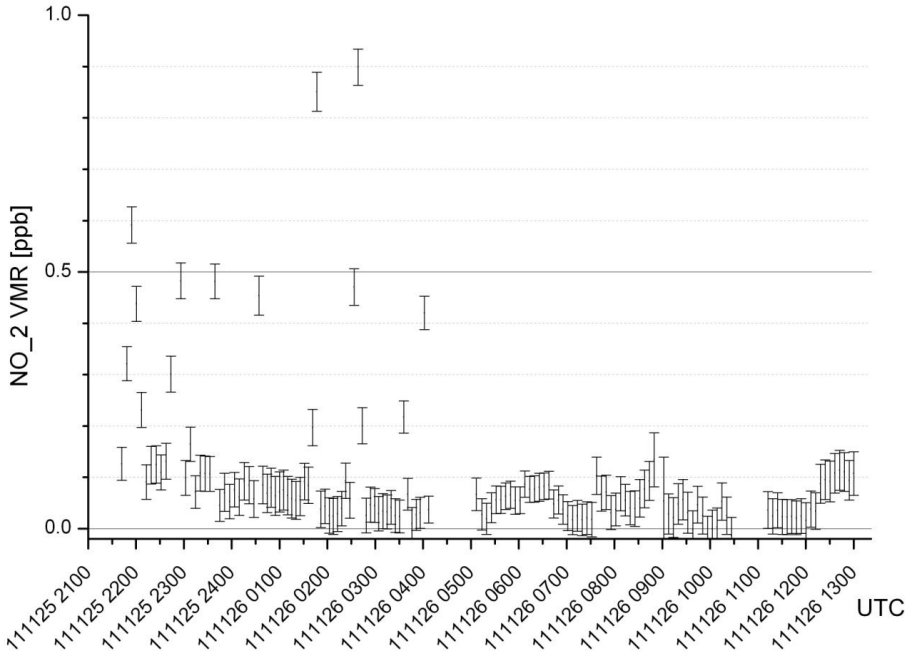


Figure 1: NO_2 Mixing ratios for a period where the ship exhaust might have been detected.

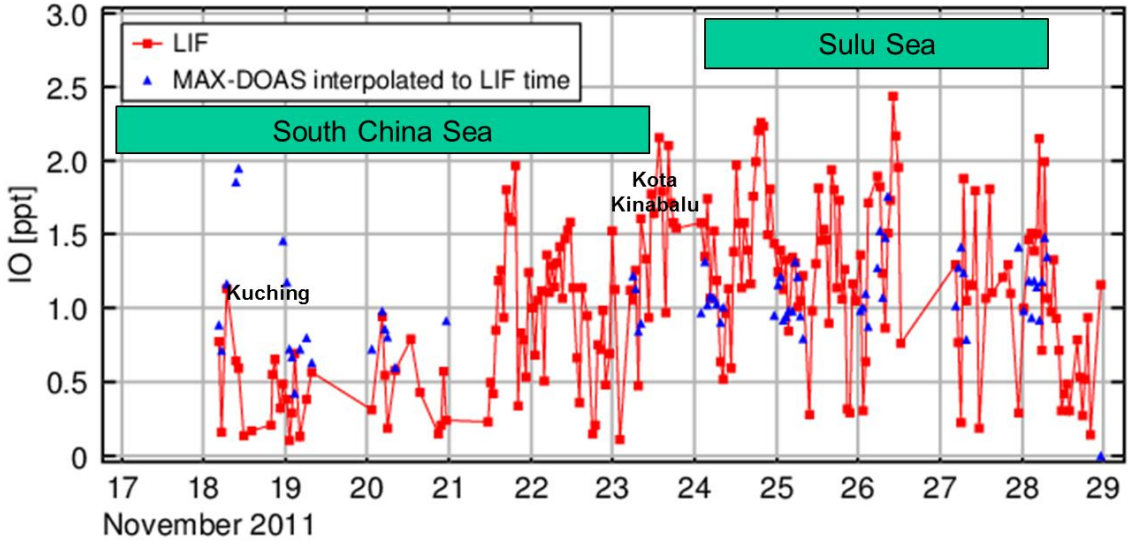


Figure 2: IO mixing ratios derived from the MAX-DOAS and from the LIF instrument.

REPORT 8: µ-DIRAC – CONTINUOUS MEASUREMENTS OF HALOGENATED TRACE GASES

Neill Harris[1], Andrew Robinson[1], Karin Kreher[1], Elliot Atlas[3], Julian Kinzel[4], Birgit Quack[4],

[1] University of Cambridge; Chemistry Department, UK
[2]Lauder, New Zealand
[3]RSMAS, Miami
[4]Geomar, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany

On this cruise, one of few world-wide existing, non-commercial µ-Diracs (micro-Dirac) was operated . Apart from being lighter in weight and less expensive compared to a conventional GC-MS system, it does not require a high degree of human operation, as it runs automatically. The focus lay on detecting short-lived halocarbons in the tropical marine boundary layer. Bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and iodomethane (CH_3I) were of special interest during this cruise campaign. In addition to the µ-Dirac used for the cruise, an earlier version of the instrument was operating at the GAW station on Bukit Atur (Sabah) during the period of the SHIVA campaign.

Methodology - The µ-Dirac

The marine boundary layer air mass measurements were performed using a gas chromatograph (GC) equipped with an electron capture detector (ECD). This so-called µ-Dirac was designed in Great Britain and has been detecting halocarbons in New Zealand since March 2010 (before being deployed on RV Sonne). The µ-Dirac is capable of measuring halocarbons in the atmosphere having mixing ratios lower than 1ppt (parts per trillion).

Brief description of µ-Dirac setup: The halocarbons contained in an air sample (typical sample size: 20cm3) pass through an inlet to a Valco Valve, on top of which an adsorption/ desorption tube is situated containing two different Carboxen materials. Depending on the respective boiling points the individual halocarbons are being adsorbed by either one of the Carboxen materials.

Flash-heating of the adsorbent tube is subsequently carried out, with temperatures reaching values up to 180° C. The target compounds are readily desorbed and pass onto the separation column along with the Helium purge gas (optimal Flow rate: 0.3cm3/ min). This so-called carrier gas is purified in advance in order to remove moisture and other contaminants. Flowmeters control the helium gas (and sampling gas) flow entering the system which is essential for reproducing peak retention times.

The separation capillary column is 10 meters long (MXT-502.2), furnished with an inner wall coating and is mounted in a temperature-controlled oven enclosure made from foam board. Here, it serves as the stationary phase of the GC. Dependent on respective partial vapor pressures and temperature, the sample partitions between the mobile (Helium) and stationary phase and is separated into individual components. Each halocarbon passes through the detector at a unique speed and thus reaches the detector at a characteristic retention time which is defined as the sum of residence time within the mobile and stationary phase. A whole sample run lasts approximately 35 minutes, depending on the column temperature.

Figure 1: µ-Dirac deployment on RV Sonne on the scientific bridge. Photo: Julian Kinzel

The column outlet is connected to the heated detector. Target halocarbons pass into the micro-volume ECD which is highly temperature- and pressure-sensitive. Here, they are ionized within an electron field formed by ionization of a nitrogen make-up gas from primary electrons emitted from a 63Ni foil (acting as a beta emitter). An ionization background current is thus established and maintained at a constant level due to an electrometer. Since the halogenated compound's electron affinity is high, the current is reduced, proportional to the compound concentration. A 16 bit ATD-converter finally produces the 10Hz output which yields the final chromatogram. On the basis of retention times and corresponding peak heights, one can identify numerous halocarbons and convert the signal into ppt-volumes by referring to separately conducted calibration runs.

µ-Dirac - Deployment on RV Sonne

The µ-Dirac was deployed on the scientific bridge (see Fig.1), where access to the outside was provided for the sampling tube. The outside-end of the tube was attached to a reeling on the port side of the monkey deck. An attached funnel prevented too much moisture from entering the system. This sampling spot was chosen to avoid the influence of the ship's exhaust, which was situated further 'downwind'. The Helium and Nitrogen cylinders were installed outside of the scientific bridge and connected to the µ-Dirac via stainless steel tubes.

Air samples were taken approximately once every 45 minutes, thus allowing for a relative high measurement frequency throughout the cruise (i.e. roughly 18 air samples per day). Calibrations and blank runs were conducted every 4 hours, respectively. Apart from focusing on bromoform, dibromomethane and iodomethane, the analysis also comprised ppt-concentrations of chloroform ($CHCl_3$), PCE (C_2Cl_4), chloroiodomethane (CH_2ClI) and dibromochloromethane ($CHBr_2Cl$). Due to installation issues, reliable real time data is not available until several hours after departing from Singapore. Measurements were taken until the arrival in Manila, i.e. the morning hours of November 29th.

Results

The results show, that there is qualitative agreement between the air concentrations measured in the air canister and the µ-Dirac (Figures 2 to 6). Differences may be the result in the time resolution of the measurements, the general offsets are likely the results of calibration differences while extreme outliers, e.g. for methyl iodide can't be explained by those reasons.

Concentrations of bromoform ($CHBr_3$) vary between 1-5 ppt (Figure 2). Higher values tend to be observed close to the coast (e.g. 113/114°E) and near Kuching (111° E), especially when the persisting wind direction had a considerable off-land component. Extraordinarily large concentrations (e.g. greater than 10ppt) were not observed.

Dibromomethane concentrations (CH_2Br_2) tend to be slightly lower than those of bromoform (generally 0.3-1.5 ppt) (Figure 3). Regions characterized by elevated CHBR3 levels (see above) also resolve relatively high dibromomethane concentrations. Overall, levels prior to cruising near Kuching were considerably smaller than during the second week of the cruise.

Methyliodide concentrations (CH_3I) generally remained below 1.5 ppt (Figure 4). Again, highest values occurred in the coastal areas (exception in the open sea near 110°E). Temporal and spatial variability is especially evident during the second local boat contact.

Chloroform ($CHCl_3$) ppt's varied between 8-14 ppt throughout the cruise (Figure 5). During the first week of the cruise, it seems as if a multi-diurnal cycle of CHCl3 concentrations occurred. However, this structure was not reproduced during the last days of the cruise.

A time series of PCE (C_2Cl_4) mixing ratios showed an exponential decrease within the first days (starting with roughly 7 ppt) of the cruise and remaining rather constant (1-2 ppt), once fresh anthropogenic impact became negligible (Figure 6).

The data were calibrated based on the pre- and post-cruise analysis of the decanted NOAA calibration gas, against the NOAA SX standard cylinder in the UCAM lab.

The pre-cruise comparison of the Sonne calibration was done straight after decanting from the main NOAA-SX standard can. This showed changes in the composition of the decanted can as follows:
CH_2Br_2 fell by ~0.2 ppt (~ 7 % fall), C_2Cl_4 fell by ~0.3 ppt (~15 % fall), CH_3I fell by ~0.1 ppt (~ 4 % fall), $CHCl_3$ rose by ~0.6 ppt (~ 7 % rise), $CHBr_3$ fell by ~0.3 ppt (~ 6 % fall)

After the cruise the decanted cal was again measured against the original NOAA SX can and the following changes in composition inside the decanted can were found:
CH_2Br_2 fell by ~0.3 ppt (~14 % fall), C_2Cl_4 rose by ~0.3 ppt (~13 % rise), CH_3I rose by ~0.3 ppt (~ 9 % rise), $CHCl_3$ fell by ~0.6 ppt (~ 7 % fall), $CHBr_3$ rose by ~0.1 ppt (~ 1 % rise)

These changes where applied to the cruise samples based on linear interpolation between the pre- and post-cruise calibration dates and the mid-date of the cruise.

The changes to the cruise samples are not huge as can be seen in the time series plots. The error bars in the plots are the 1-sigma cruise precision from the onboard cals:
CH_2Br_2 12 %, C_2Cl_4 13 %, CH_3I 14 %, $CHCl_3$ 15 %, $CHBr_3$ 16 %

The estimated 1-sigma accuracy based on the NOAA uncertainty and those from our pre and post-cruise calibrations are as follows (not included in the plot error bars):
CH_2Br_2 10 %, C_2Cl_4 8 %, CH_3I 16 %, $CHCl_3$ 7 %, $CHBr_3$ 9 %

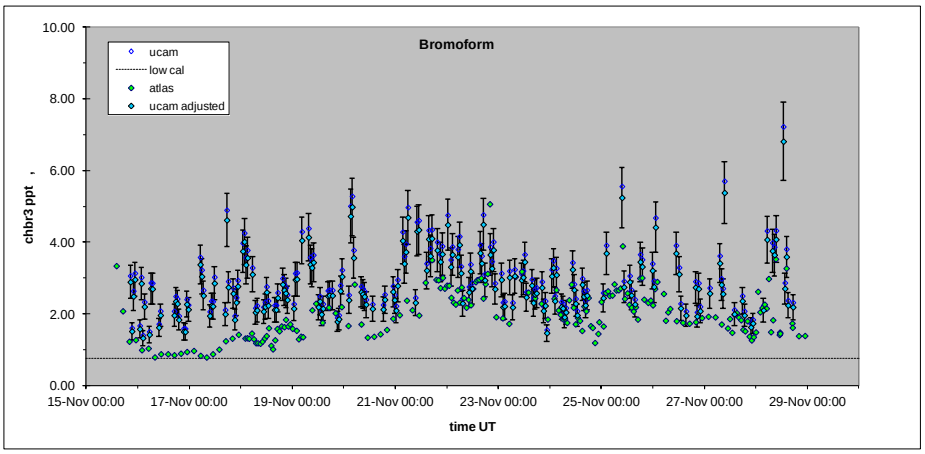


Figure 2: Atmospheric mixing ratios of bromoform ($CHBr_3$)of canister samples from RSMAS (atlas), and µ-dirac data (ucam and ucam adjusted to postcruise calibration).

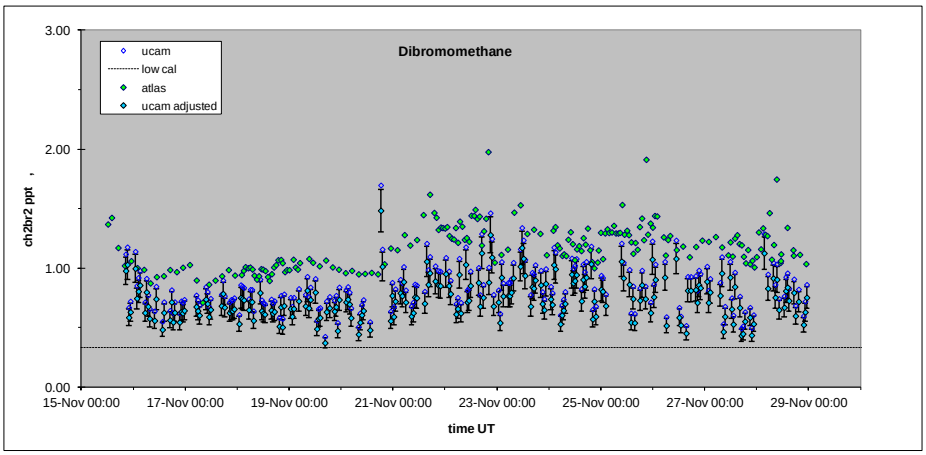


Figure 3: Atmospheric mixing ratios of dibromomethane (CH_2Br_2)of canister samples from RSMAS (atlas), and µ-dirac data (ucam and ucam adjusted to postcruise calibration).

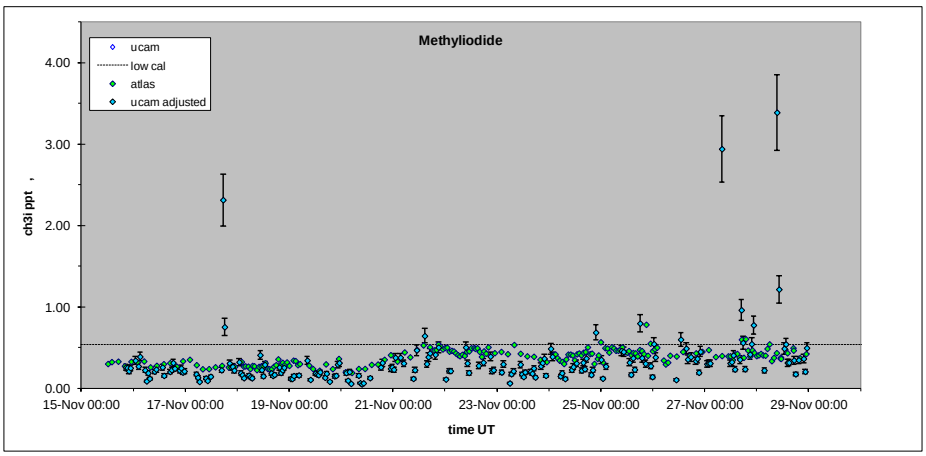


Figure 4: Atmospheric mixing ratios of methyl iodide (CH_3I)of canister samples from RSMAS (atlas), and µ-dirac data (ucam and ucam adjusted to postcruise calibration).

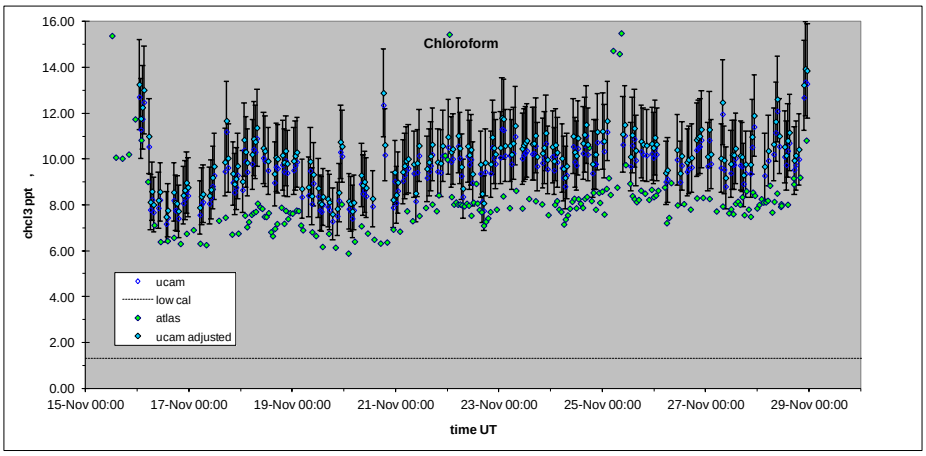


Figure 5: Atmospheric mixing ratios of chloroform ($CHCl_3$)of canister samples from RSMAS (atlas), and µ-dirac data (ucam and ucam adjusted to postcruise calibration).

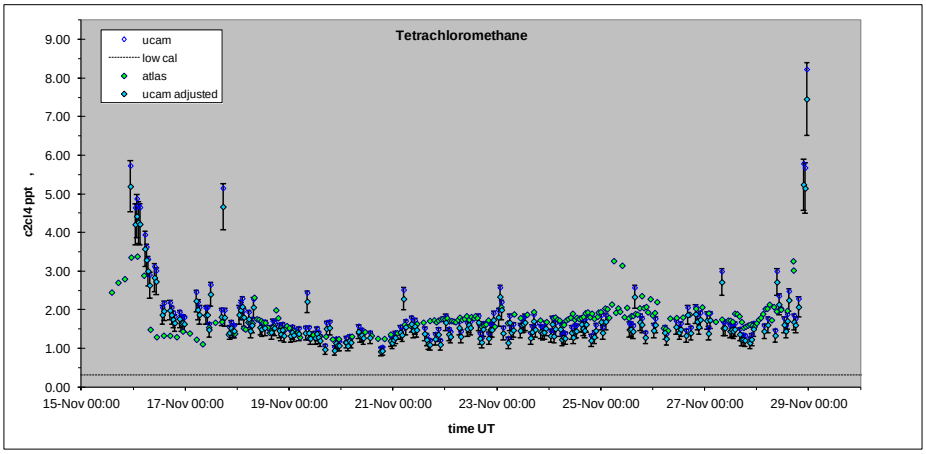


Figure 6: Atmospheric mixing ratios of tetrachloroethene (C_2Cl_4) of canister samples from RSMAS (atlas), and µ-dirac data (ucam and ucam adjusted to postcruise calibration).

REPORT 9: CONTINUOUS MEASUREMENTS OF THE ATMOSPHERIC MIXING RATIOS OF A SUITE OF POLLUTION INDICATORS AND GREENHOUSE GASES (CO, CH_4, O_3, CO_2)

Exepditioner: Justin Sentian / Nur Aleesha Abdullah, UMS, Kota Kinabalu, MMD Malaysia

Principle investigator: Hans Schlager (DLR, not on board)

1.0 Objective

a) To measure carbon monoxide and tropospheric ozone levels and to investigate spatial and temporal variability in lower tropical marine boundary layer.
b) To measure greenhouse gases (CO_2, CH_4 and H_2O) levels and to investigate spatial and temporal variability in lower tropical marine boundary layer.

However, due to the technical problem with the Picarro instrument, the measurement of the greenhouse gases was halted and therefore no greenhouses gases data were obtained during this campaign.

2.0 Method

In general, the 3 instruments namely TE49 Ozone Analyzer, Carbon Monoxide Analyzer and Picarro is being mounted to two racks and placed at the scientific bridge on-board the RV Sonne. All the inlets of the instruments are integrated into only one main inlet which is connected to the ambient air at the top of the Scientific bridge through the ducting system.

The setup of the whole instrument at the scientific bridge of the RV-Sonne is shown in Figure 1

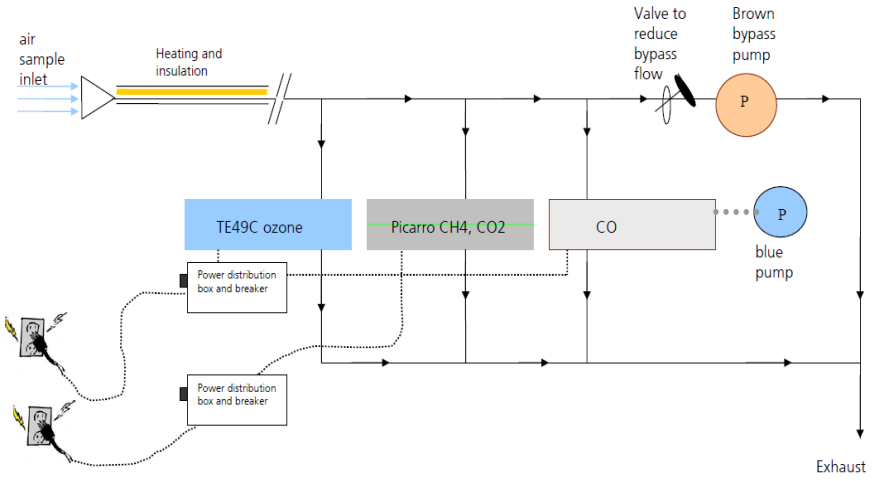


Figure 1: The instrument setup on-board RV-Sonne

Table 1: Instrument and operating status

Instrument	Parameter	Operation Principle
Model 49C UV Photometric Ozone Analyzer	O_3	UV absorption at 254 nm
Model AL 5001 CO-Monitor	CO	Non-Dispersive Infra-Red (NDIR)
Picarro G1301 Analyzer (not operational)	CO_2, CH_4, H_2O	Optical absorption spectroscopy – based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS)

REPORT 10A: DLR- CIMS MEASUREMENTS: INVESTIGATION OF ANTHROPOGENIC EMISSIONS AFFECTING AIR QUALITY IN THE MARINE BOUNDARY LAYER OF THE SOUTH CHINA AND SULU SEA

Tina Jurkat, Christiane Voigt, Dominik Schäuble

DLR -Deutsches Zentrum für Luft- und Raumfahrt, Oberpfaffenhofen, Germany

Measurements of reactive chlorine and bromine compounds in the marine boundary layer in the Western Pacific are rare. Reactive halogen compounds like Br_2, BrCl, and Cl_2 evolve from sea spray aerosol. Strong acids like H_2SO_4 or HNO_3, which are secondary products of anthropogenic combustion processes, change the acidity of the sea spray aerosol. Through acid displacement the release of reactive halogen species can be enhanced. Furthermore, Br_2 and BrCl evolve from HOBr by heterogeneous reactions on sea salt aerosol. Both are photolysed during the day and react with O_3 to form BrO. As a consequence MBL ozone is destroyed in a catalytic cycle. Apart from sea spray aerosol very short lived substances (VSLS) may be an important source for reactive bromine compounds in the MBL. However, their contribution is highly uncertain.

In polluted coastal regions elevated concentrations of $ClNO_2$ have been measured. $ClNO_2$ is a night-time reservoir for chlorine and active nitrogen oxides. After sunrise photolyses of $ClNO_2$ slowly releases Cl which oxidizes methane and volatile organic compounds.Local air pollution affects public health, environmental quality, agricultural industry and it changes the oxidation capacity of the Marine Boundary Layer (MBL), thus for example the lifetime of the greenhouse gas methane (CH_4).

For measurements of the reactive halogen compounds (Br_2, BrCl, HOBr, BrO, and $ClNO_2$) and as an indicator for inorganic acids (HNO_3, HCl, SO_2, and HBr) two Atmospheric chemical Ionization Mass Spectrometers, AIMS-1 and AIMS-2, were deployed inside a 10 ft container on the backdeck of the RV Sonne. This laboratory container was designed, modified, and equipped by DLR, Oberpfaffenhofen for this cruise. Furthermore, in cooperation with the University of Leeds the container was deployed with a LIF Instrument (for IO) and a NO_x detector (University of Leeds).

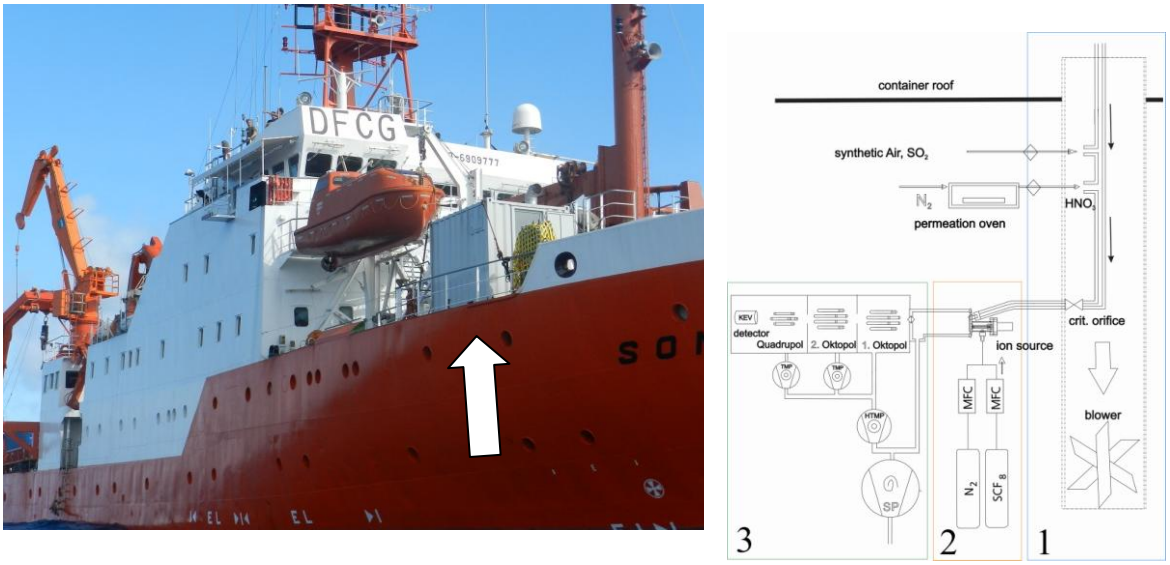


Figure 1: (left) DLR 10ft container with inlet system on the backdeck of RV Sonne. (right) Schematic setup of the AIMS instrument inside the container. Inlet (1), ionization (2) and detection region (3) are explained in the text.

AIMS-1 and -2 detect atmospheric trace gases with concentrations of a few ppt by chemical reactions with artificially produced ions (I^- and SF_5^-) from a corona discharge ion source (Fig 1, (2)). Product and educt ions are filtered by a quadrupole mass filter (Fig 1, (3)) and individually detected by a channeltron multiplier.

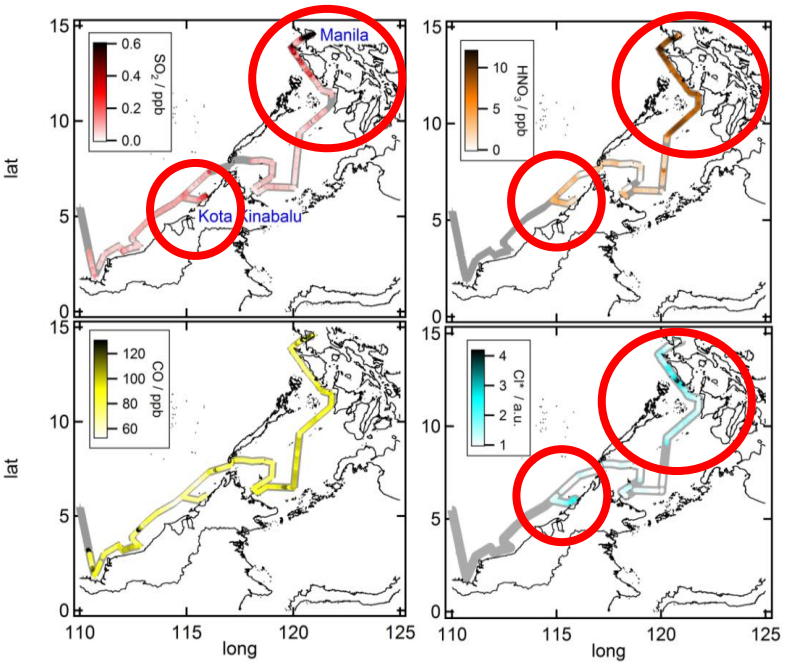


Fig 2 Atmospheric mole fractions of SO_2, HNO_3, CO (ppb) and Cl*(a.u.) along the SONNE ship track. Red circles show regions with elevated concentrations along the coast of large cities.

Using the I- reagent ions, SO_2 laboratory tests showed that the detection scheme is independent of the water vapor content thus it is very suitable for measurements at high relative humidity. Permeation devices were used for calibration. Occasional gaps in the time series evolve from calibration sequences. Mass spectra with a range from 20 to 300 amu were recorded every 8 min and continuous measurements of 16 different selected masses were done with a time resolution of 8s. High sensitivity for SO_2 and Br_2 of 1-3 Hz / ppt were determined during the cruise.

The instruments installed on SONNE were originally designed to measure trace gas concentrations at low mixing ratios under dry upper tropospheric conditions. Before the cruise, first extensive tests were conducted in the laboratory yielding high sensitivities and relatively low detection limits (3-10 ppt) for the components. In order to measure these components under MBL conditions additional effort was necessary to reduce high sea salt deposition on the inlet walls.

The inlet system has been adapted such that contact to the ship surface is avoided (Fig. 1, (1)). An inlet system was connected to a blower providing a large flow 1100 m^3/h through a 30cm stainless steel tube on the container roof. Air from above the ship was sampled presumably with minimal contact to the roof. In case of rain the tube was covered with a 90° angle piece on top of the straight inlet tube. The container was additionally equipped with two air conditioning system. Thus the instruments were operated at a constant temperature and humidity which proofed to be very important at these humid conditions in the tropical sea.

With the help of a critical orifice made of PFA, the biggest part of the inlet tube was kept at low pressure to reduce the relative humidity and residence time of the gases in the inlet. A small film of salted water at the upper, inner part of the PFA inlet tubes was however unavoidable. Due to the exposed position of the container occasionally sea spray entered the inlet tubing. Cleaning of the inlet tube was therefore performed on a regular basis.

Sensitive and high-resolution sulfur dioxide (SO_2), nitrogen oxides (HNO_3) and active chlorine (Cl*)(measured by AIMS) together with CO measurements (provided by E. Atlas) are shown in Fig 1. Along the cruise track both SO_2 and HNO_3 were elevated above the detection limit of 16 ppt. Short term pollution events from the ship stack and other close by ships were identified and separated from background measurements.

Background concentrations are 0.09 ppb (SO_2), 0.2 ppb (HNO_3) and 90 ppb (CO), respectively and suggest a moderately polluted MBL when compared to measurements in the remote North-Atlantic and West-Pacific MBL (e.g. Lee et al., 2010). Specifically in coastal regions near large cities such as Manila and Kota Kinabalu elevated concentrations were detected. Here, release of active chlorine (blue color coding) has been observed. This active chlorine is detected in the form of Cl^- in the mass spectrometer. The measurements support observations of halogen release due to acid displacement in the polluted MBL (Lawler et al.,2009).

Atmospheric concentrations for Br_2+HOBr, BrO, HBr and $ClNO_2$ were always below the detection limit during the cruise. Partly this was due to technical problems that caused an enhanced detection limit of around 30 ppt (one sigma standard deviation). These technical problems were only observed during the cruise and have been eliminated since.

The measurements will be used for validation of the global climate model EMAC at the Institut für Physik der Atmosphäre, DLR Oberpfaffenhofen and will contribute to a better understanding of anthropogenic emissions and their effects on local air pollution.

References

Lawler, M. J., Finley, B. D., Keene, W. C., Pszenny, A. A. P., Read, K. A., von Glasow, R., and Saltzman, E. S.: Pollution enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer, Geophys. Res. Lett.,n 36, L08810, doi:10.1029/2008GL036666, 2009.

Lee, J. D., McFiggans, G., Allan, J. D., Baker, A. R., Ball, S. M., Benton, A. K., Carpenter, L. J., Commane, R., Finley, B. D., Evans, M., Fuentes, E., Furneaux, K., Goddard, A., Good, N., Hamilton, J. F., Heard, D. E., Herrmann, H., Hollingsworth, A., Hopkins, J. R., Ingham, T., Irwin, M., Jones, C. E., Jones, R. L., Keene, W. C., Lawler, M. J., Lehmann, S., Lewis, A. C., Long, M. S., Mahajan, A., Methven, J., Moller, S. J., Müller, K., Müller, T., Niedermeier, N., O'Doherty, S., Oetjen, H., Plane, J. M. C., Pszenny, A. A. P., Read, K. A., Saiz-Lopez, A., Saltzman, E. S., Sander, R., von Glasow, R., Whalley, L., Wiedensohler, A., and Young, D.: Reactive Halogens in the Marine Boundary Layer (RHaMBLe): the tropical North Atlantic experiments, Atmos. Chem. Phys., 10, 1031-1055, doi:10.5194/acp-10-1031-2010, 2010.

REPORT 10B: SONNE- FALCON LAGRANGIAN TRACER EXPERIMENT AND CONTINUOS CARBON MONOXIDE AND OZONE MEASUREMENTS

Hans Schlager, Yu Ren, Michael Lichtenstern, Monika Scheibe, Nur Aleesha Abdullah, Justin Sentian, Tina Jurkat, Dominik Schäuble

DLR -Deutsches Zentrum für Luft- und Raumfahrt, Oberpfaffenhofen, Germany
Malaysian Meteorological Department, Jabatan Meteorologi Malaysia,
Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS

A Lagrangian experiment has been performed during SHIVA using a new perfluorocyclocarbon tracer system (PERTRAS) developed at DLR (Ren et al. 2013). The Lagrangian approach is to follow a single air mass with multiple measurements and study the dispersion and change of composition as it moves. The objectives of the SHIVA experiment were to study the transport and dispersion of emissions (e.g. very short lived species) in the tropical marine boundary layer (MBL) and the handover of the emissions to the free troposphere, the comparison of the measurement data with transport model simulations, and the demonstration of this novel experimental technique. PERTRAS consists of three main modules: a tracer release unit (RU), an adsorption tube sampler (ATS) and a tracer analytical system. The tracer release unit was used on board the Sonne for release of a perfluoromethylcyclopentane (PMCP) tracer (8.8 kg) on 21 Nov 2011 near Miri, Malaysia, from 0224 to 0303 UTC. The PMCP tracer was sampled downstream of the Sonne by the DLR Falcon research aircraft with the ATS on 21 and 22 Nov. 2011 about 5 and 25 hours after the release. The Falcon sampling flights were planned using forecasts calculated with the particle dispersion model HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) driven by GSF and ECMWF meteorological forecast data.

The adsorption tube samples collected during the Falcon flights were analyzed after the field campaign in the laboratory at DLR using a thermal desorber/gas chromatography/mass spectrometry (TD/GC/MS) system. Figure 1 shows measured PMCP mixing ratios during the Falcon flight on 21 Nov 2011 along five transects through the tracer plume predicted by HYSPLIT.

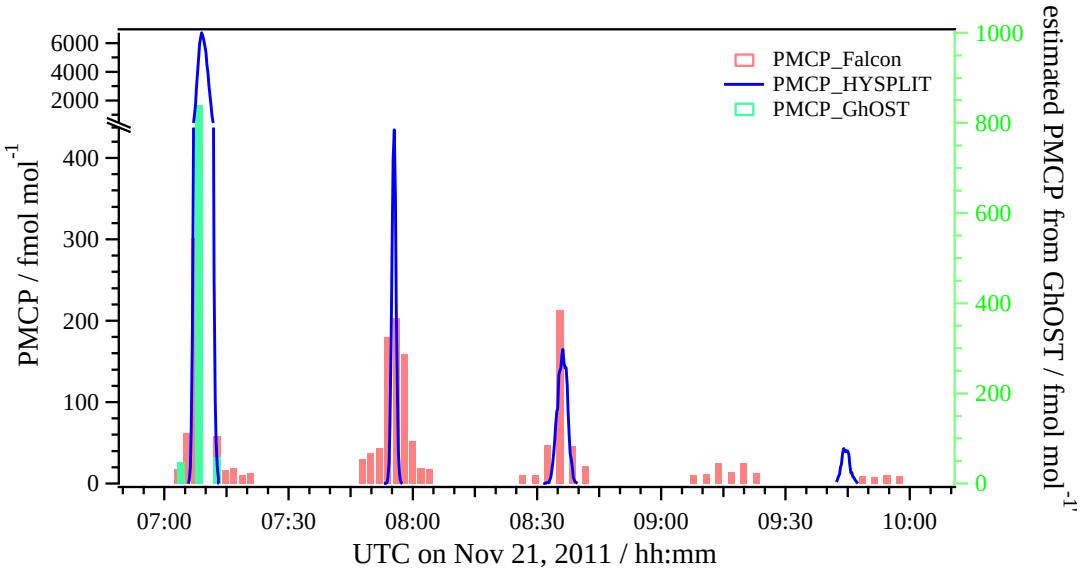


Fig. 1: Time series of PMCP tracer measurement (red bars) on November 21 and HYSPLIT simulation using GFS data (blue lines). Green bars indicate PMCP estimates from GhOST in-flight GC data.

During all five Falcon transects enhanced PMCP concentrations were detected with a maximum value of 301 fmol mol^{-1}. PMCP background mixing ratios measured outside of the tracer plume and during

other Falcon flights ranged between 5-7 fmol mol^{-1}. During the second sampling flight on 22 Nov 2011, PMCP concentrations between 15-20 fmol mol^{-1} were measured in the tracer plume aged 25 hours. Thus, the tracer plume has been intercepted successfully during both sampling flights. The PMCP measurements during the first three plume intercepts on 21 Nov 2013 (Fig. 1) compare reasonable with the HYSPLIT/GFS calculations, although, the simulated PMCP tracer plume is less dispersed with higher maximum concentrations. The HYSPLIT/ECMWF simulations compare worse with the PMCP tracer measurements. More details are given in Ren et al. (2013).

In addition to the Lagrangian tracer experiment continuous carbon monoxide (CO) and ozone (O_3) in-situ measurements were performed during the entire Sonne cruise. The measurement techniques used were vacuum UV fluorescence and UV absorption, respectively. The CO data can be used as tracer for pollution plumes from land-based combustion sources (biomass burning, anthropogenic emissions) and shipping.

Reference

Ren, Y., et al., Perfluorocyclocarbon tracer system: experimental technique and first application for a Lagrangian experiment during SHIVA, Atmospheric Measurement Technique (in preparation), 2013.

REPORT 10C: *IN SITU* MEASUREMENTS OF IO BY LASER-INDUCED FLUORESCENCE SPECTROSCOPY

Hannah Walker, Trevor Ingham, Dwayne Heard

School of Chemistry, University of Leeds

Measurements of IO were made by the Leeds Laser-Induced Fluorescence instrument positioned on the front deck of RV *Sonne*. Ambient air was drawn through an inlet (0.8 mm diameter) into a low-pressure (150 Torr) detection chamber. Laser light at λ = 440 nm excited the sampled IO radicals, and the resulting short-lived fluorescence at λ = 521 nm was detected by a channel photomultiplier tube on an axis perpendicular to both the gas flow and the laser beam. Measurements of IO and the background signal were achieved by modulating the laser wavelength between an 'online' and 'offline' position, respectively. The signal was recorded every second, and the data were averaged to 15 minutes of online data, which is equal to a total averaging time of 45 minutes. The instrument was calibrated during the cruise by generating a known concentration of IO by photolysis of N_2O in the presence of CF_3I.

Mixing ratios of IO remained close to the limit of detection of the instrument (~ 0.5 pptv), with the mean mixing ratio during the cruise being 0.8 pptv. The maximum value (2.4 pptv) was observed whilst the ship was crossing the Sulu Sea to the north of Borneo. Figure 1 shows a time series of IO during the whole cruise. The IO measurements made during cruise SO218 are slightly lower than the range of values measured during a previous cruise in the Western Pacific (Großmann *et al.*, 2013) but are within the range of values measured during previous studies in other open ocean regions (e.g. Allan *et al.*, 2000, Read *et al.*, 2008, Mahajan *et al.*, 2012, Dix *et al.*, 2013, Gómez Martín *et al.*, 2013).

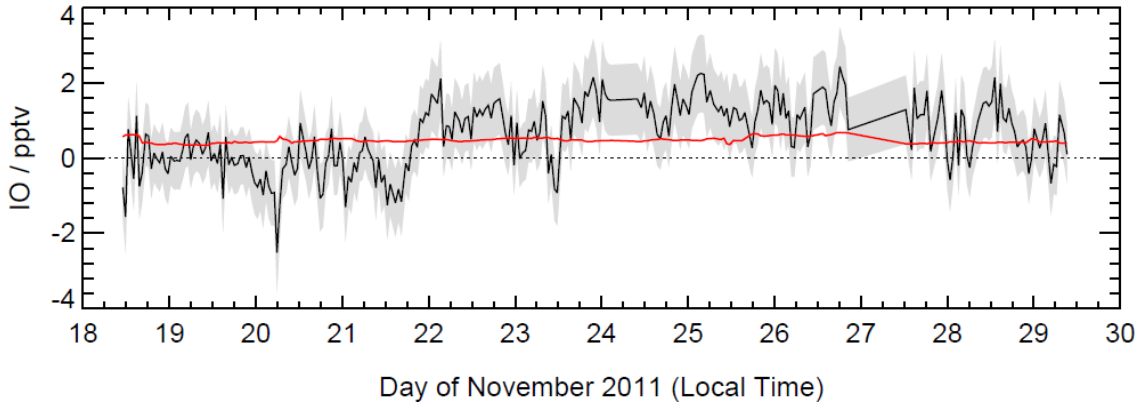


Figure 1. Time series of IO measured by LIF during cruise SO218. IO data are represented by black line, with the uncertainty in the measurements shown by the shaded grey area. Instrumental limit of detection is represented by the red line. The dotted black line indicates zero pptv. Data points below the limit of detection are shown to indicate the IO profile along the cruise.

The relationships between IO and its potential precursors have been investigated. No significant correlation was found between IO and air temperature (r = 0.027), sea surface temperature (r = −0.19), salinity (r = 0.25), or wind speed (r = 0.28), in contrast to previous studies (Mahajan *et al.*, 2012, Gómez Martín *et al.*, 2013, Großmann *et al.*, 2013), though the range of values of these physical parameters was small during cruise SO218 compared to during the previous studies. No significant

correlation ($r = -0.17$) was found between IO and oceanic concentrations of chlorophyll-*a*, suggesting that there was not a strong biogenic source of reactive iodine during cruise SO218. Surprisingly, IO was found to be negatively correlated to I_2 ($r = -0.59$) and the sum of HOI + ICl ($r = -0.41$). This relationship is as yet unexplained, though it may be explained in part by the reaction of IO with HO_2 to produce HOI, and uptake of HOI to sea-salt aerosol, which releases I_2 and ICl. No strong correlation was found between IO and atmospheric CH_3I ($r = 0.26$), indicating that CH_3I was not a major precursor of reactive iodine during the cruise. Significant negative correlation was found between IO and oceanic CH_3I ($r = -0.42$) and CH_2ICl ($r = -0.50$), suggesting that a biological mechanism inhibits production or release of iodine from the ocean, in agreement with previous work (Gómez Martín *et al.*, 2013).

A steady-state analysis of IO was conducted, using the measurements of I_2, HOI + ICl, CH_3I, O_3, and NO_2 made during the cruise, and estimated concentrations of OH, HO_2, and NO from measurements in the open ocean marine boundary layer reported in the literature. No heterogeneous reactions were included, so the analysis represents a first look at important production and loss processes, and a more detailed modelling study is required to examine the processes in more detail. Photolysis of I_2 was found to be the largest source of IO, with a smaller but significant contribution from photolysis of HOI. The reaction of IO with NO was found to be an important reactive iodine recycling mechanism.

Iodine was not found to play a significant role in tropospheric ozone destruction during the cruise.

Reasonable agreement was found between simultaneous measurements of IO by LIF and MAX-DOAS during cruise SO218, with the mean MAX-DOAS measurement being 0.74 pptv. Similar average daytime profiles of IO were measured by both instruments, with little variation in IO throughout the day. Slightly higher mixing ratios were measured by the LIF instrument, in accordance with the predicted vertical profile of IO above the sea surface (Mahajan *et al.*, 2010, Großmann *et al.*, 2013). Maximum IO columns of 3×10^{12} molecule cm^{-2} have been measured over the Western Pacific by the SCIAMACHY instrument onboard the Envisat satellite (Schönhardt *et al.*, 2008). Assuming an air mass factor of 1 and a boundary layer height of 1 km, following the work of Gómez Martín *et al.* (2013), this satellite-based measurement corresponds to a mixing ratio of 1.4 pptv. Given the large uncertainty in the satellite measurements (Schönhardt *et al.*, 2008), and the potential influence of IO in the free troposphere on the observed IO column (Dix *et al.*, 2013), there is no clear discrepancy between the satellite measurements and the *in situ* LIF measurements made during the cruise.

References

Allan, B. J., McFiggans, G., Plane, J. M. C. and Coe, H., *Observations of iodine monoxide in the remote marine boundary layer*, Journal of Geophysical Research: Atmospheres, 105 (D11), 14363-14369, 2000

Dix, B., Baidar, S., Bresch, J. F., Hall, S. R., Schmidt, S., Wang, S. and Volkamer, R., *Detection of iodine monoxide in the tropical free troposphere*, Proceedings of the National Academy of Sciences, 110 (6), 2035-2040, 2013

Gómez Martín, J. C., Mahajan, A. S., Hay, T. D., Prados-Román, C., Ordoñez, C., MacDonald, S. M., Plane, J. M. C., Sorribas, M., Gil, M., Paredes Mora, J. F., Agama Reyes, M. V., Oram, D. E., Leedham, E. and Saiz-Lopez, A., *Iodine chemistry in the eastern Pacific marine boundary layer*, Journal of Geophysical Research: Atmospheres, 118 (2), 887-904, 2013

Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., Tschritter, J., Sommariva, R., von Glasow, R., Quack, B., Krüger, K., Pfeilsticker, K. and Platt, U., *Iodine monoxide in the Western Pacific marine boundary layer*, Atmospheric Chemistry and Physics, 13 (6), 3363-3378, 2013

Mahajan, A. S., Plane, J. M. C., Oetjen, H., Mendes, L., Saunders, R. W., Saiz-Lopez, A., Jones, C. E., Carpenter, L. J. and McFiggans, G., *Measurement and modelling of reactive halogen species over the tropical Atlantic Ocean*, Atmospheric Chemistry and Physics, 10 (10), 4611-4624, 2010

Mahajan, A. S., Gómez Martín, J. C., Hay, T. D., Royer, S.-J., Yvon-Lewis, S., Liu, Y., Hu, L., Prados-Román, C., Ordoñez, C., Plane, J. M. C. and Saiz-Lopez, A., *Latitudinal distribution of reactive iodine in the Eastern Pacific and its link to open ocean sources*, Atmospheric Chemistry and Physics, 12 (23), 11609-11617, 2012

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J. and Plane, J. M. C., *Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean*, Nature, 453 (7199), 1232-1235, 2008

Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H. K. and Burrows, J. P., *Observations of iodine monoxide columns from satellite*, Atmospheric Chemistry and Physics, 8 (3), 637-653, 2008

REPORT 10D: MEASUREMENTS OF I_2 AND THE SUM OF HOI + ICL DURING SHIVA

Hannah Walker, Trevor Ingham, Dwayne Heard, Ru-Jin Huang, Thorsten Hoffmann

School of Chemistry, University of Leeds

University of Mainz

Measurements of I_2 and the sum of HOI + ICl (collectively termed activated iodine compounds, or AIC) were made using the Denuder Diffusion technique (Huang and Hoffmann, 2009, Huang *et al.*, 2010). Samples were collected by drawing air through glass tubes, coated on the inside with 1,3,5-trimethoxybenzene (1,3,5-TMB) for collection of ICl and HOI, and α-cyclodextrin/$^{129}I^-$ for collection of I_2. The tubes were positioned on the port side of the front deck of the RV *Sonne* to minimise the influence of the ship on the sampled air. For each sample, air was drawn through the tubes for 30 minutes by a small diaphragm pump housed in the 10 ft shipping container on the front deck. The tubes were connected to the pump by Teflon tubing. Following sampling, the tubes were sealed and were stored in a freezer. The samples were analysed by Dr Ru-Jin Huang at the University of Mainz, using the gas chromatography/mass spectrometry technique described by Huang and Hoffmann (2009). 47 samples were taken in total.

Both I_2 and AIC remained above the detection limit (0.17 pptv) for most of the cruise. The mean I_2 mixing ratio was 1.98 pptv, and the maximum I_2 mixing ratio was 12.74 pptv, measured at night (22:00 local time) during the diurnal station near Kuching. Few measurements of I_2 in open ocean regions are reported in the literature. The I_2 mixing ratios measured during cruise SO218 are generally higher than the 1.5 pptv reported by Finley and Saltzmann (2008) in oceanic air on the Californian

coast, and lower than the 10–50 pptv reported by Harris *et al.* (2011) between Singapore and Wellington, New Zealand. The mean AIC mixing ratio was 2.74 pptv, and the maximum AIC mixing ratio was 7.56 pptv, also measured at 07:00 (local time) during the diurnal station near Kuching. No measurements of HOI and ICl over the ocean have previously been reported. Figure 1 and Figure 2 show the SO218 cruise track coloured by the mixing ratios of I_2 and AIC, respectively.

Previous modelling studies of IO have relied upon fluxes of I_2 from the ocean surface to reproduce observations (Furneaux *et al.*, 2010, Großmann *et al.*, 2013). A recent laboratory and modelling study found that HOI, produced in the heterogeneous reaction of O_3 with dissolved iodide at the sea surface, is the dominant inorganic iodine species emitted from the ocean, and is likely to be an important precursor of IO (Carpenter *et al.*, 2013). The measurements of I_2 and AIC made during the SHIVA cruise were therefore a useful tool in predicting the daytime IO concentrations using a steady-state analysis.

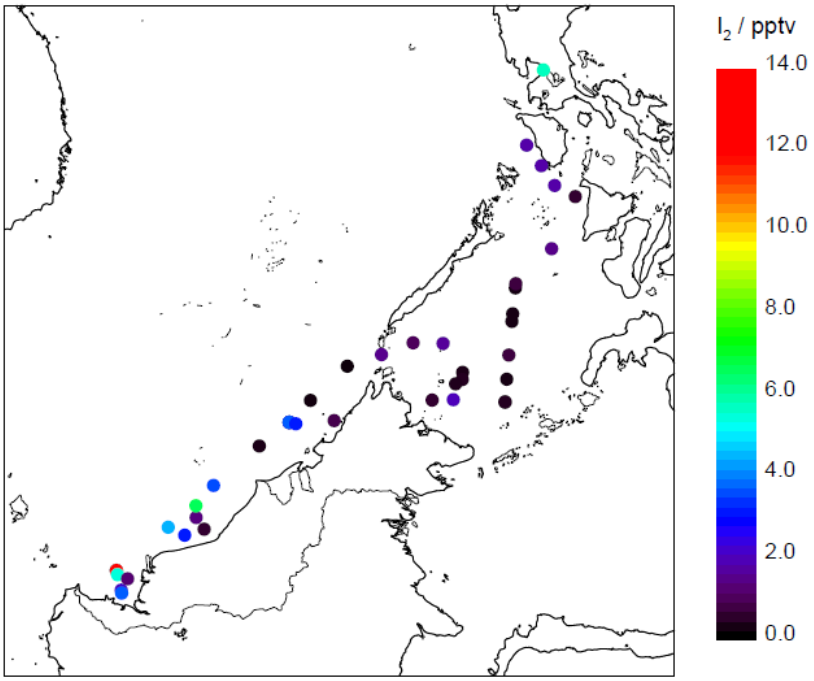


Figure 1. SO218 cruise track coloured by mixing ratio of I_2, with low mixing ratios in blue colours and high mixing ratios in red colours.

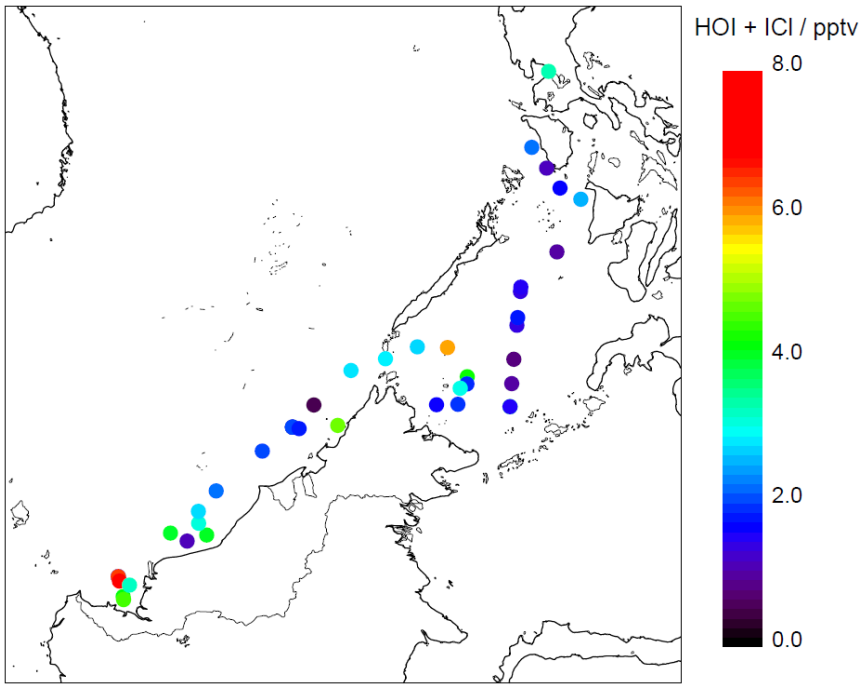


Figure 2. SO218 cruise track coloured by mixing ratio of HOI + ICl (AIC), with low mixing ratios in blue colours and high mixing ratios in red colours.

References

Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Parthipan, R., Wilson, J. and Plane, J. M. C., *Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine*, Nature Geoscience, 6 (2), 108-111, 2013

Finley, B. D. and Saltzmann, E. S., *Observations of Cl_2, Br_2, and I_2 in coastal marine air*, Journal of Geophysical Research: Atmospheres, 113 (D21), D21301-D21314, 2008

Furneaux, K., Whalley, L. K., Heard, D. E., Atkinson, H. M., Bloss, W. J., Flynn, M. J., Gallagher, M. W., Ingham, T., Kramer, L., Lee, J. D., Leigh, R., McFiggans, G. B., Mahajan, A. S., Monks, P. S., Oetjen, H., Plane, J. M. C. and Whitehead, J. D., *Measurements of iodine monoxide at a semi polluted coastal location*, Atmospheric Chemistry and Physics, 10 (8), 3645-3663, 2010

Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., Tschritter, J., Sommariva, R., von Glasow, R., Quack, B., Krüger, K., Pfeilsticker, K. and Platt, U., *Iodine monoxide in the Western Pacific marine boundary layer*, Atmospheric Chemistry and Physics, 13 (6), 3363-3378, 2013

Harris, N. R. P., Johnston, P. V., Kreher, K., Harvey, M., Hay, T. D., Robinson, A. D., Ashfold, M. J., Archibald, A., Pyle, J. A., Huang, R.-J. and Hoffmann, T., *Halogen species in the marine boundary layer between Singapore and Wellington, New Zealand*, AGU Fall Meeting, San Francisco, 2011

Huang, R.-J. and Hoffmann, T., *Development of a Coupled Diffusion Denuder System Combined with Gas Chromatography/Mass Spectrometry for the Separation and Quantification of Molecular Iodine and the Activated Iodine Compounds Iodine Monochloride and Hypoiodous Acid in the Marine Atmosphere*, Analytical Chemistry, 81 (5), 1777-1783, 2009

Huang, R.-J., Hou, X. and Hoffmann, T., *Extensive Evaluation of a Diffusion Denuder Technique for the Quantification of Atmospheric Stable and Radioactive Molecular Iodine*, Environmental Science & Technology, 44 (13), 5061-5066, 2010

REPORT 11: AEROSOL CHEMISTRY OF HALOGENS DURING SHIVA

Alex Baker and Chan Yodle,

School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

Introduction

Aerosols play a key role in halogen cycling in the marine atmosphere, with chlorine (Cl) being transferred to the gas phase by acid displacement reactions, bromine (Br) release being induced by reaction of ozone on seasalt particles and iodine (I) chemistry promoting transfer of Cl, Br and I to the gas phase via halogen activation reactions. Ultimately aerosols appear to be net sources for Cl and supermicron Br and net sinks for I and submicron Br.

Although these processes are intimately linked to ozone chemistry, the processes that lead to submicron Br enrichment and those that control aerosol iodine chemistry are very poorly understood at present. In the case of iodine, which has extremely rich and complex aerosol chemistry, there is a severe lack of field data available, with only one published study in the western Pacific region (Lai et al., 2008). The species of iodine commonly found in marine aerosol include iodide (I^-), iodate (IO_3^-) and a soluble organic iodine (SOI) fraction whose components have yet to be identified (Baker, 2005; Saiz-Lopez et al., 2012). The mechanisms responsible for interchanges between these species, and the overall impact of these interchanges on tropospheric ozone chemistry, are currently unclear.

Sampling and Analysis

During the SO218 cruise aboard RV *Sonne* 13 aerosol samples were collected for determination of Cl^-, Br^- and iodine speciation, as well as a number of other aerosol ionic components. Each sample was collected for ~24 hours onto pre-cleaned 20 x 25 cm glass fibre filters, using a Tisch total suspended particulate sampler operating at a flow rate of ~ 1 m^3 min^{-1}. Aerosol filters were stored frozen until analysis at the University of East Anglia, when soluble components were extracted into ultra-pure water using mechanical shaking at room temperature. Most analytes (including Cl^- and Br^-) were determined by ion chromatography (IC), while iodine analysis was done using both inductively coupled plasma mass spectrometry (ICP-MS) for total soluble iodine (TSI) and IC-ICP-MS for I^- and IO_3^-. Soluble organic iodine (SOI) concentrations were then determined as the difference between TSI and the sum of I^- and IO_3^-.

Results

Overall chemistry of the aerosol samples collected during the SHIVA campaign is consistent with the composition of other marine-dominated environments. Here we focus on the results obtained for bromide and the iodine species.

In Figure 1 we show enrichment factors (EF) relative to seawater composition (Eqn 1) for both Br^- and iodine (TSI). EF values greater than 1 indicate that the element concerned is enriched relative to seawater composition, while values less than 1 indicate that the element is depleted.

Eqn 1. ————, where *X* is Br or I and the subscripts *aero* and *sw* refer to the aerosol sample and seawater respectively.

For bromide, all samples were depleted. This indicates that aerosols are a net source of bromine to the atmosphere in this region, and that depletion processes in super-micron aerosol particles probably outweigh enrichment in sub-micron particles (Sander et al., 2003). For iodine, the opposite behaviour

was observed, with all samples being enriched (to factors of 35-320 above seawater composition). This behaviour has been observed in several other marine (and terrestrial) environments (Baker et al., 2000; Duce et al., 1967) and indicates that aerosol is a net sink for iodine emitted from the sea surface.

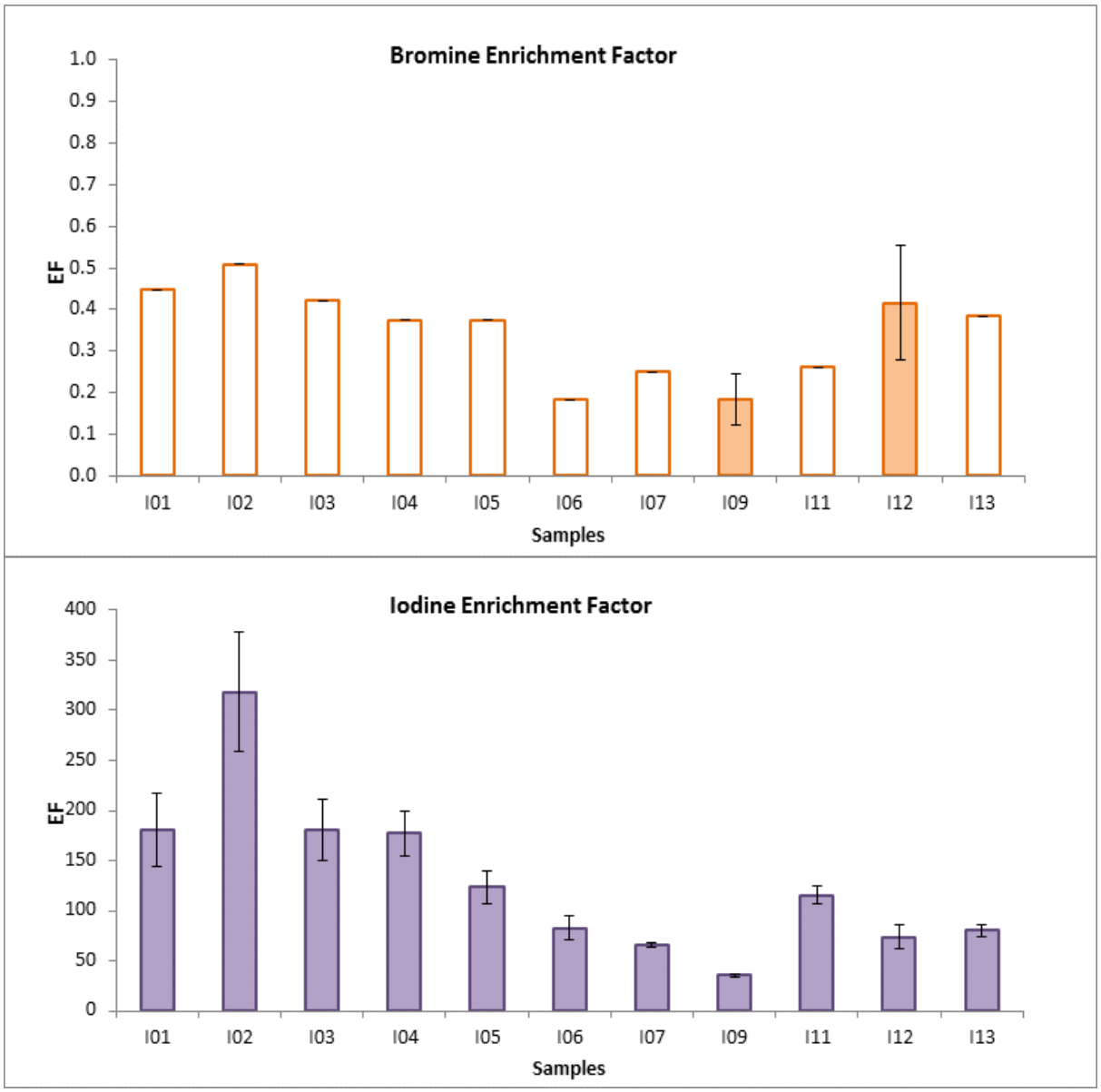


Figure 1. Enrichment factors (relative to seawater composition) for bromide and total soluble iodine. Note that unfilled bars in upper panel indicate samples for which bromide concentrations were below analytical detection limits. These bars therefore show the possible range of EF values for these samples.

In Figure 2 we show the speciation distribution of iodine between iodide, iodate and SOI in the SHIVA aerosol samples. This illustrates that all three species make significant contributions to the aerosol contribution in the region, although there is considerable sample-to-sample variability in the relative proportions of each species. Relative to samples collected from other environments, the SHIVA samples generally contain rather higher proportions of iodide and lower proportions of iodate than, for example, aerosols containing Saharan dust (Allan et al., 2009; Baker, 2005; Yodle,

unpublished data). We are continuing our efforts to understand the factors that control aerosol halogen chemistry and its impact on tropospheric ozone chemistry.

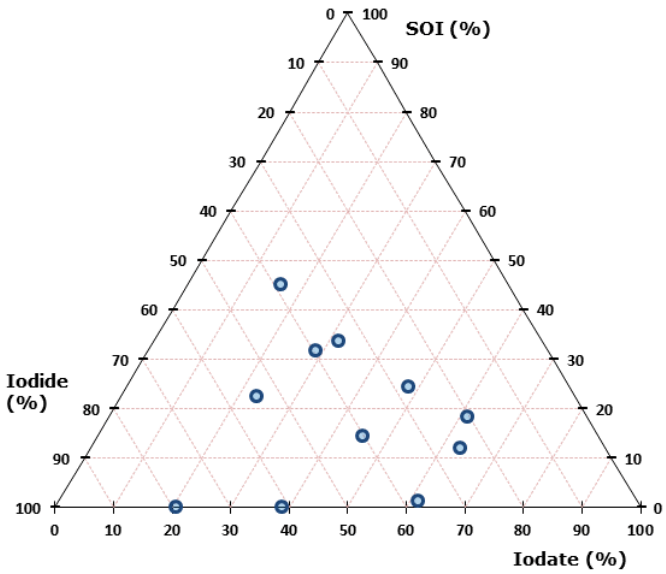


Figure 2. Ternary composition diagram for iodine species in SHIVA aerosol samples. Each axis shows the percentage of iodide, iodate and soluble organic iodine (SOI) contained in each aerosol sample.

References

Allan, J.D. et al., 2009. Composition and properties of atmospheric particles in the eastern Atlantic and impacts on gas phase uptake rates. Atmospheric Chemistry and Physics, 9: 9299-9314.

Baker, A.R., 2005. Marine aerosol iodine chemistry: The importance of soluble organic iodine. Environmental Chemistry, 2(4): 295-298.

Baker, A.R., Thompson, D., Campos, M.L.A.M., Parry, S.J. and Jickells, T.D., 2000. Iodine concentration and availability in atmospheric aerosol. Atmospheric Environment, 34(25): 4331-4336.

Duce, R.A., Woodcock, A.H. and Moyers, J.L., 1967. Variation of ion ratios with size among particles in tropical oceanic air. Tellus, 19(3): 367-379.

Lai, S.C., Hoffmann, T. and Xie, Z.Q., 2008. Iodine speciation in marine aerosols along a 30,000 km round-trip cruise path from Shanghai, China to Prydz Bay, Antarctica. Geophysical Research Letters, 35: L21803, doi:10.1029/2008GL035492.

Saiz-Lopez, A. et al., 2012. Atmospheric chemistry of iodine. Chemical Reviews, 112: 1773-1804.

Sander, R. et al., 2003. Inorganic bromine in the marine boundary layer: a critical review. Atmospheric Chemistry and Physics, 3: 1301-1336.

REPORT 12: OCEANIC CIRCULATION -TRANSIENT TRACER MEASUREMENTS DURING CRUISE SONNE-218

Toste Tanhua, Anke Schneider

GEOMAR, Marine Biogeochemistry, Chemical Oceanography, Kiel, Germany

Samples for the measurements of CFC-12 and SF_6were collected at 4 stations in the central Sulu Sea, Figure 1. The samples were the first to be taken from the Rosetta, were taken in 300 ml glass ampoules and were flame sealed in the lab immediately after sampling, leaving a small head-space of pure N_2 over the water sample. The samples were measured in the lab in Kiel during 2012 using a technique that also measures the tracer content in the head-space of the ampoules.

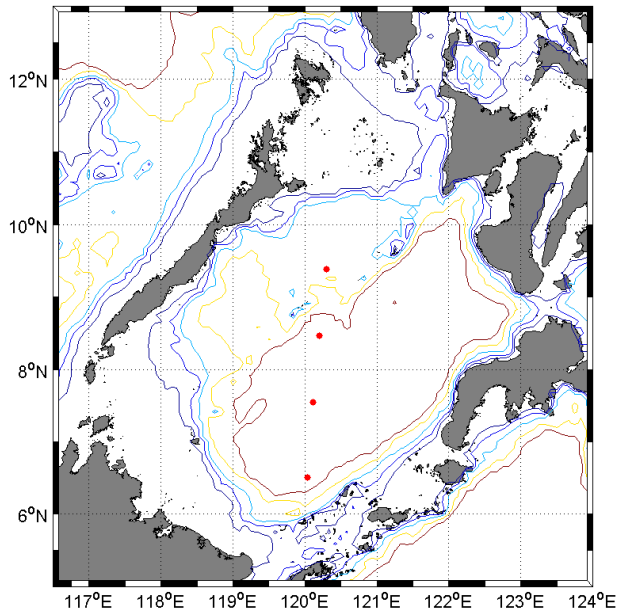


Figure 1: *Stations that were sampled for CFC-12 and SF6 measurements. These are stations 28, 29, 32 and 35.*

Preliminary results:

The CFC-12 profiles from the 4 stations are very similar to each other, indicating small horizontal variability of ventilation within the Sulu Sea. We therefore present a figure of the average profile of anthropogenic carbon and mean ages in the Sulu Sea, Figure 2. These two properties were calculated with the measured CFC-12 data, applying the transit time distribution (TTD) method. Comparison of the CFC-12 and SF_6 data suggest that an inverse Gaussian distribution (IG) of the TTD with the two parameters Δ (i.e. the "width" of the IG-TTD) and Γ (i.e. the mean of the TTD) set equal (i.e. $\Delta/\Gamma=1$) well represent the data. The profile of the anthropogenic carbon in the Sulu Sea show relatively high concentrations at the surface, which is expected due to the high temperatures, and rapidly declining concentration with depth. The mean age (i.e. the Γ of the IG-TTD) shows rapidly increasing ages towards depth, reaching about 600 years in the bottom waters, although ages over 400 years are very uncertain due to analytical difficulties in measuring CFC-12 at such low concentrations. This suggests that the Sulu Sea is slowly ventilated and implies a small inventory of anthropogenic carbon (C_{ant}).

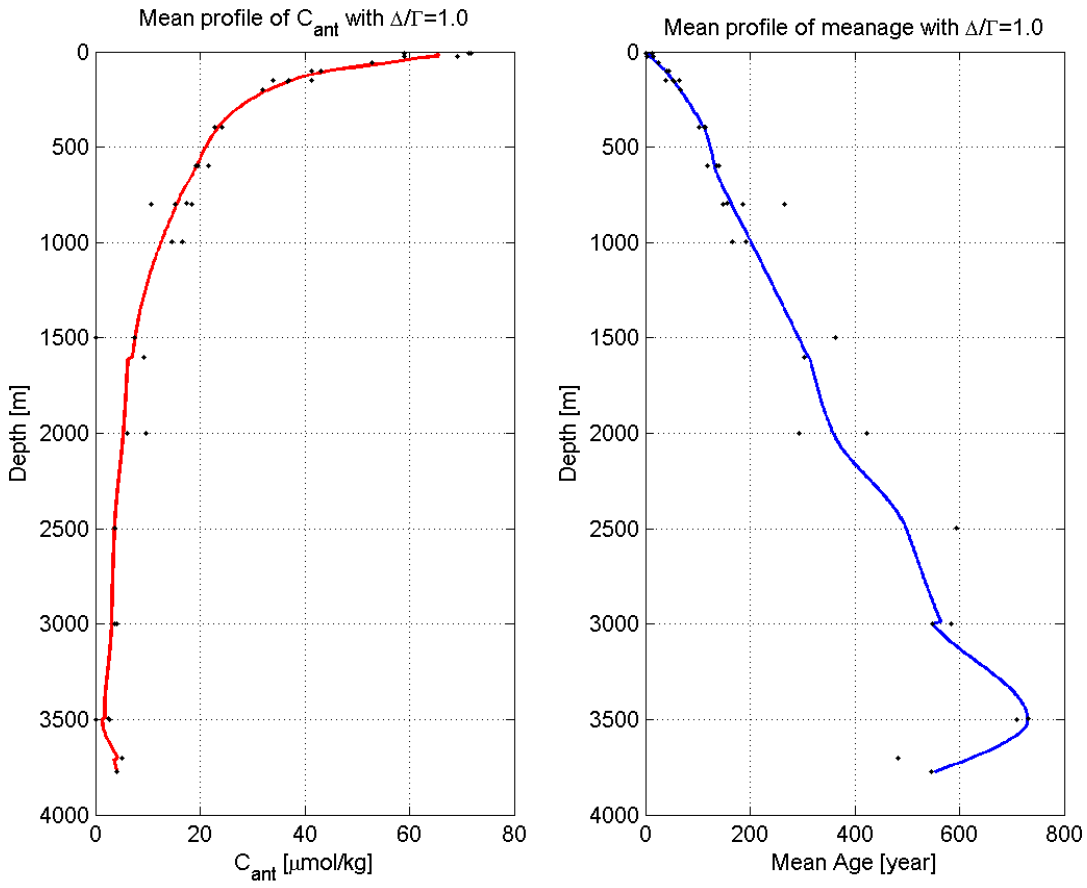


Figure 2: *Mean profiles of the anthropogenic carbon content (left panel) and the mean age (right panel) of the Sulu Sea. These values are calculated using CFC-12 data and the TTD method.*

REPORT 13A: RESULTS OF THE LOCAL BOAT DEPLOYMENTS IN KUCHING, KOTA KINA BALU, AND SEMPORNA

Felicity W.I. Kuek[1], Aazani Mujahid[2], Lim Po Teen[2], Leaw Chui Pin[3], Moritz Müller[1,] Ann Anton[4]

[1]Faculty of Engineering, Computing and Science, Swinburne University of Technology, Sarawak campus, 93350 Kuching, Sarawak, Malaysia.

[2]Department of Aquatic Science, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 93400 Kota Samarahan, Sarawak, Malaysia.

[3]Institute of Biodiversity and Environmental Conservation, Universiti Malaysia Sarawak, Kota Samarahan, 94300 Sarawak, Malaysia

[4] Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu, Sabah, email: aanton@ums.edu.my

The South China Sea is a marginal sea of the western Pacific Ocean, encompassing an area from the Singapore and Malacca Straits to the Strait of Taiwan .The Celebes Sea is connected to the South China Sea through the Sulu Sea. In conjunction with European and Malaysian research partners, the SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) Western Pacific field campaign was performed in the fall of 2011. The core field campaign took place in the South China Sea and along the coastline of Peninsula Malaysia and Borneo using the German Research Vessel (RV) Sonne during a cruise leading from Singapore to Manila, Philippines (Figure 1)

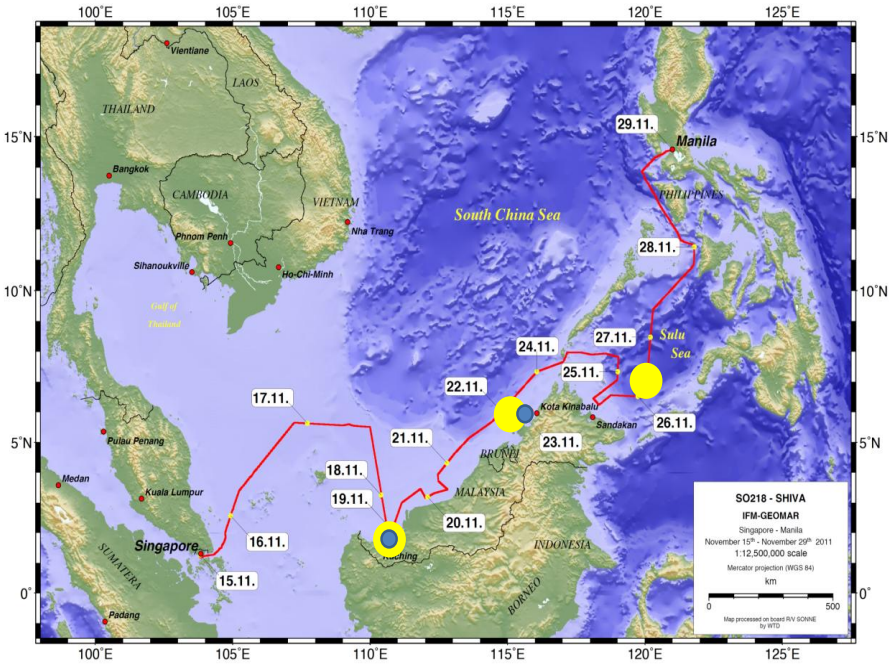


Figure 1: Cruise track of *RV Sonne*: Singapore-Manila (15-29 November 2011), including the local boat meetings at Kuching and Kota Kinabalu (blue circles) and overflights by the DLR air craft Falcon (yellow circles).

Local cruises took place in Kuching on both November 16 and 19, 2011 (see Figure 2 for sampling stations), Kota Kinabalu (November 23, 2011; see Figure 3 for sampling stations) and Semporna (November 26, 2011; see Figure 4 for sampling stations) to provide additional data from near shore locations and coastal influence.

Table 1: Locations of sampling stations at Kuching, Kota Kinabalu and Semporna.

Sampling stations	GPS coordinates			
	Kuching (1611)	**Kuching (1911)**	**Kota Kinabalu**	**Semporna**
Station 1	1°38'36.24"N, 110°30'5.28"E	1°39'28.81"N, 110°31'24.42"E	6° 3'4.56"N, 116° 5'54.60"E	4°35'15.96"N, 118°32'58.14"E
Station 2	1°39'44.82"N, 110°32'7.26"E	1°42'44.24"N, 110°33'23.46"E	6° 3'5.82"N, 116° 4'1.45"E	4°38'37.86"N, 118°20'25.44"E
Station 3	1°42'2.80"N, 110°37'12.36"E	1°45'32.93"N, 110°35'16.86"E	6° 3'4.02"N, 116° 0'2.77"E	4°42'31.68"N, 118°23'19.38"E
Station 4	1°42'46.62"N, 110°39'17.40"E	1°48'2.16"N, 110°37'51.53"E	6° 2'49.85"N, 115°57'38.26"E	4°40'42.48"N, 118°32'11.34"E
Station 5	1°45'49.07"N, 110°41'27.77"E	1°50'54.15"N, 110°40'11.26"E	6° 4'23.64"N, 115°54'36.42"E	4°37'31.26"N, 118°41'5.99"E
Station 6	N/A	N/A	N/A	4°35'56.76"N, 118°43'19.14"E
Station 7	N/A	N/A	N/A	4°35'30.66"N, 118°42'17.10"E
Station 8	N/A	N/A	N/A	4°33'17.83"N, 118°39'22.57"E

**1611 and 1911 denotes November 16 and 19, 2011 respectively.*

***N/A denotes coordinates are unavailable.*

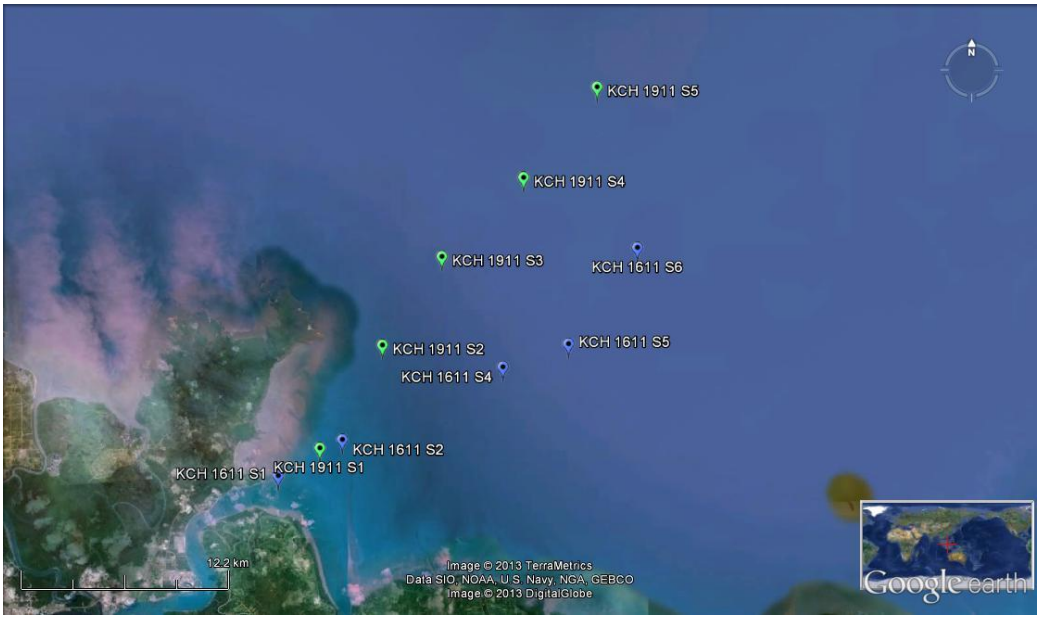


Figure 2: Locations of sampling stations in Kuching, Sarawak.

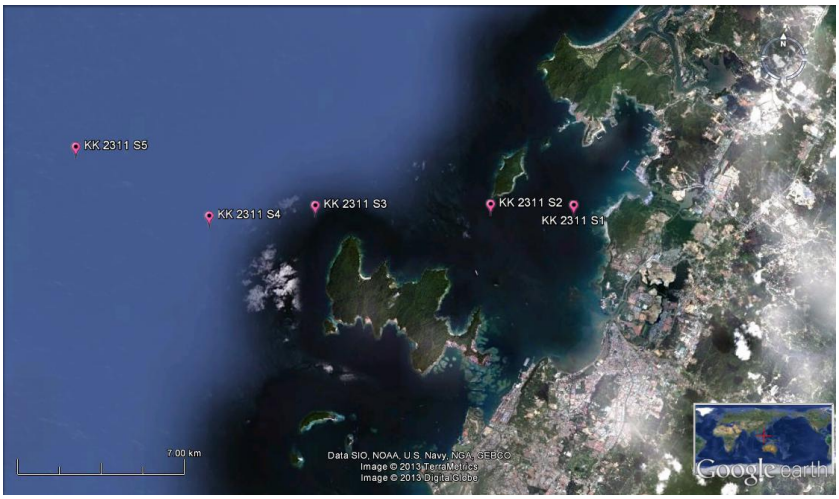


Figure 3: Locations of sampling stations in Kota Kinabalu, Sabah.

Figure 4: Locations of sampling stations in Semporna, Sabah.

Physico-chemical parameters

Basic physico-chemical parameters were recorded during sampling in Kuching (November 19, 2011) and Kota Kinabalu (see Table.2). Values for Semporna are not reported as the measuring instruments were inconsistent and not functioning properly at the time of sampling.

Table 2: Physico-chemical parameters measured from Kuching and Kota Kinabalu.

Station	Depth (m)	Temperature (°C)	pH	Salinity (ppt)	Nitrate (ppm)	Phosphate (ppm)	Nitrite (ppm)	Silicate (ppm)
KCH-1	1	29.06	7.90	28.48	9.13	0.60	1.46	23.47
	5	29.34	8.10	30.59	ND	ND	ND	ND
KCH-2	1	28.98	8.25	30.65	2.02	0.33	0.60	7.48
	5	29.11	8.25	30.89	ND	ND	ND	ND
KCH-3	1	29.05	8.33	31.18	0.85	0.15	0.03	2.97
	5	29.16	8.30	30.53	ND	ND	ND	ND
KCH-4	1	29.00	8.33	31.07	0.49	0.10	0.00	4.52
	5	29.10	8.29	30.52	ND	ND	ND	ND
KCH-5	1	29.27	8.31	31.61	0.15	0.06	0.00	5.86
	5	29.40	8.29	31.85	0.15	0.05	0.00	2.21
KCH		**29.15**	**8.24**	**30.74**	**2.13**	**0.22**	**0.35**	**7.75**

mean								
KK-1	1	29.80	8.44	31.85	1.04	0.15	ND	3.47
	5	29.90	8.37	32.04	ND	ND	ND	ND
KK-2	1	29.73	8.36	31.44	0.25	0.17	ND	3.21
	5	29.78	8.33	31.95	ND	ND	ND	ND
KK-3	1	29.55	8.34	31.88	0.23	0.11	ND	2.67
	5	29.54	8.33	31.87	ND	ND	ND	ND
KK-4	1	29.52	8.36	31.93	ND	ND	ND	ND
	5	29.45	8.34	31.91	ND	ND	ND	ND
KK-5	1	29.68	8.38	32.03	0.13	0.03	ND	2.74
	5	29.50	8.37	31.92	0.15	0.02	ND	2.79
KK mean		**29.65**	**8.36**	**31.88**	**0.36**	**0.10**	**ND**	**2.98**

**KCH denotes Kuching; KK denotes Kota Kinabalu.*

***ND denotes values are not detactable.*

Sampling stations at Kota Kinabalu stretched further away from the coastline and displayed average values of salinity at 31.88 ppt, pH of 8.36 and temperature of 29.65 °C (see Table 3.2), The first sampling station at Kuching (KCH-1) was closer to the river mouth of the Sarawak river and displayed a visible influence by riverine water with its surface water displaying a salinity of 28.48 ppt and pH of 7.90 (see Table 2). The salt and minerals in sea water made it denser than fresh water thus at the mouth of the river where it meets the sea, the fresh water flows downstream across the surface and the sea flows upstream at the bottom, resulting in an increasing trend from low to high salinity as it goes deeper (salinity at depth is 2 units higher; Table 2). The pH values at KCH-1 also showed an increase from pH 7.90 at 1 m depth to pH 8.10 at 5 m depth.. Subsequent stations were however more representative of ocean waters with pH around 8.3 and salinity around 31ppt (Table 3.2). Temperatures at Kuching and Kota Kinabalu are consistent at both 1 and 5 m depth (mean temperature of 29.15 and 29.65 °C respectively; see Table 2).

The riverine input at Kuching was also visible with significantly higher nitrate, phosphate, nitrite, and silicate values closer to the river mouth (KCH-1 and KCH-2; see Table 2). Nutrient levels in Kuching were also generally higher than in Kota Kinabalu. To assess differences in distribution in the upper surface layers, samples were also taken from 5 m depth (KCH-5 and KK-5; see Table 2). Interestingly, the samples for Kota Kinabalu show ‘identical’ values, however, for Kuching, the silicate drops from 5.86 ppm to 2.21 ppm within the first 5 metres (Table 2).

REPORT 13 B: RESULTS OF THE LOCAL BOAT DEPLOYMENT KUCHING

Moritz Müller[1], Aazani Mujahid[2], Felicity W.I. Kuek[1], Hong-Chang Lim[2], Sing-Tung Teng[3], Chui-Pin Leaw[3], Ann Anton[4], Lim Po Teen[2]

[1]*Faculty of Engineering, Computing and Science, Swinburne University of Technology, Sarawak campus, 93350 Kuching, Sarawak, Malaysia.*
[2]*Department of Aquatic Science, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 93400 Kota Samarahan, Sarawak, Malaysia.*
[3]Institute of Biodiversity and Environmental Conservation, *Universiti Malaysia Sarawak, 93400 Kota Samarahan, Sarawak, Malaysia.*
[4]*Borneo Marine Research Institute, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia.*

Corresponding email: ptlim@frst.unimas.my

As part of complementary three-part series of local boat deployments, two transects were organised in Kuching on the 16th and 19th November 2011 respectively. Air and water samples were collected at 5 stations with intervals of 5 km, along transects at 1 to 20 km off the Kuching coasts (see Figure 1 below).

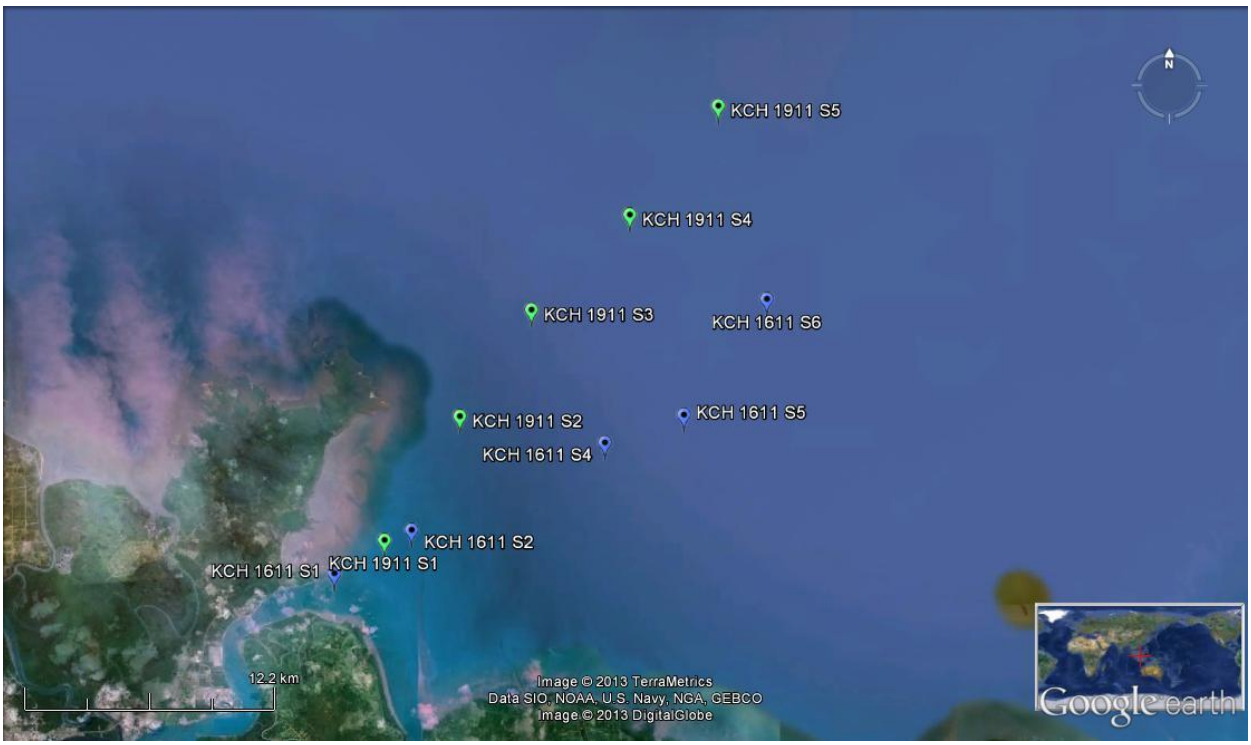


Figure 1: Locations of sampling stations in Kuching, Sarawak.

The main aims of the local boat deployments were two-fold: (i) to obtain coastal samples to complement open ocean samples made by RV Sonne, Falcon aircraft and satellites; (ii) to enable the exchange of samples collected at the coasts (e.g. VSLS and nutrients) to be taken onboard RV Sonne for further analyses, and those collected onboard RV Sonne (sensitive biological samples) to be taken back to UNIMAS and Swinburne labs for storage and further analyses. The rendezvous station was at the RV Sonne diurnal station on the 19th November 2011. Measured parameters include VSLS in seawater and air (UEA, UM), plankton biological sampling (UNIMAS, UMS), and selected surface and subsurface water parameters (UNIMAS, SUTS). Also collected were samples for baseline

information on bacterial communities in Kuching (SUTS), for further comparisons to bacterial communities at other local boat deployment sites (Kota Kinabalu, Semporna), and with regards to *in situ* physico-chemical parameters. The first sampling station at Kuching was close to the river mouth of the Sarawak river and displayed a visible influence by riverine water with its surface water displaying a salinity of 28.48 ppt and pH of 7.90 (data not shown). The riverine input at Kuching was also visible with significantly higher nitrate, phosphate, nitrite, and silicate values closer to the river mouth (data not shown). Nutrient levels in Kuching were also generally higher than in Kota Kinabalu. To assess differences in distribution in the upper surface layers, samples were also taken from 5 m depth (data not shown). Interestingly, the samples for Kota Kinabalu show 'identical' values, however, for Kuching, the silicate drops from 5.86 ppm to 2.21 ppm within the first 5 metres (data not shown), indicative of an active biological pump. From Kuching waters, 89 bacterial isolates were obtained over the two sampling periods (November 16 and 19, 2011). The total bacterial assemblage had representatives within the *Alpha-*, *Beta-* and *Gammaproteobacteria*, as well as *Firmicutes*, however, the diversity and distribution were depth dependent. Bacteria isolated from Kuching displayed the highest abundance of both DMSP degrading genes (36%) compared to communities isolated from Kota Kinabalu and Semporna with 13 and 19 %, respectively. Our findings indicate that the community structure of *Gammaproteobacteria* in the area could be tightly linked to the local sulphur and also possibly the nitrogen cycle. The community structure of *Pseudo-nitzschia* species was also identified based on genetic information by using the automated ribosomal intergenic spacer analysis (ARISA). Amplification was carried out on a total of 75 surface water samples (collected during local and SHIVA cruise), and the amplicons were analyzed by fragment analysis using DNA analyzer. Total of 50 ribotypes were detected. Community structure of *Pseudo-nitzschia* along the eastern SCS was characterized. Clustering analysis revealed a degree of community structuring in *Pseudo-nitzschia*. The results showed two linkages, one cluster with locations being dominated by *P. caciantha* ribotype 2; and the other with locations where *P. caciantha* is absent. However, no significant variation was found between samples collected from coastal water or Open Ocean.

REPORT 13 C: RESULTS OF THE LOCAL BOAT DEPLOYMENT KOTA KINABALU,

Ann Anton

Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu, Sabah, email: aanton@ums.edu.my

During the Kota Kinabalu (KK) local ship cruise on 23 November 2011, selected water parameters (light, temperature, salinity, pH, demand oxygen (DO)) were measured at 5 sampling stations to support the SHIVA program.

The range of temperature (^{o} C), pH, salinity (psu), DO) (mg/L) during this sampling was 29.49 ±0.14 ^{o} C, 8.33 ±0.02, 32.09± 0.05 psu, 3.44 ±0.16 mg/L, respectively. Salinity at water surface was increasing while temperature, DO, pH and light were decreasing with water depth. Horizontal and vertical fluctuation of the parameters were mainly due to change of weather condition. For example, light value at water surface were slightly low at St1 where field measurement was conducted around 5:50am and increased at St 4 (-11 am) where sky is clear from cloud cover. Higher water temperature and salinity at St 5 when sampling were conducted near noon time and far away from mainland, respectively.

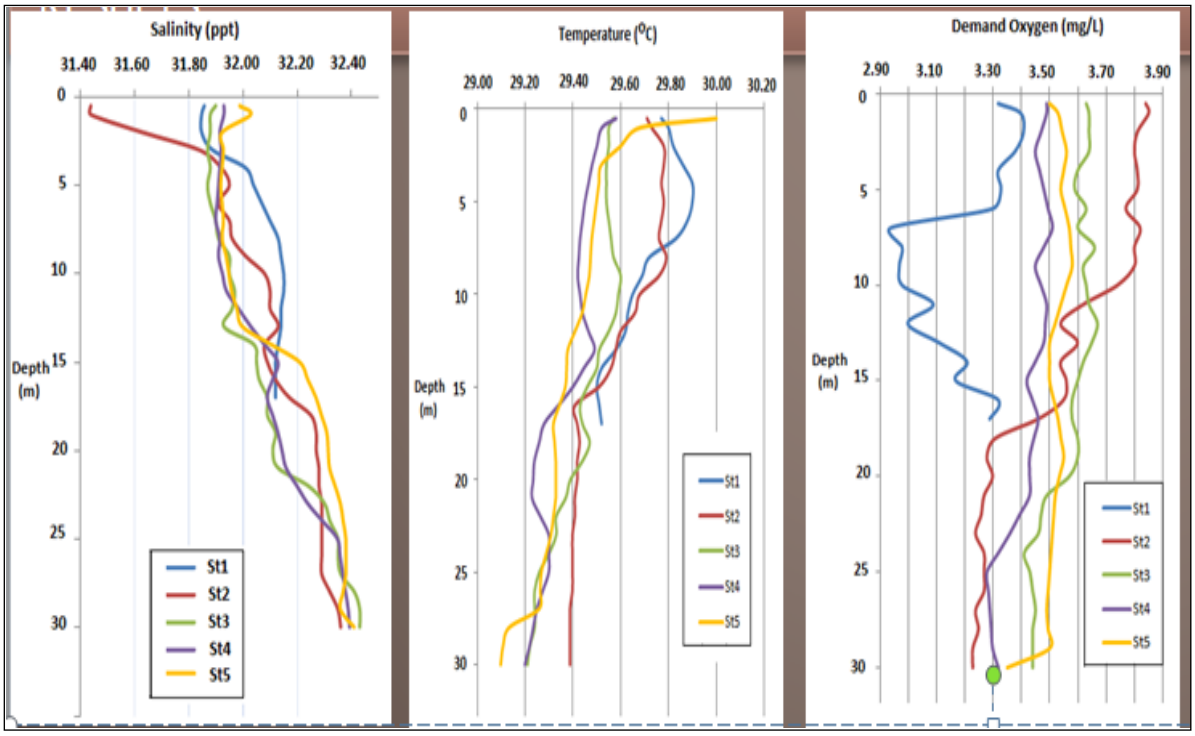


Figure 1: Physico-chemical parameters (salinity, temperature, oxygen demand)at the five stations off the coast of Sabah during the local ship cruise at Kota Kinabalu on 23rd November 2011.

The local boat cruise in KK characterized the microbial, phytoplankton and zooplankton communities which are potential biogenic sources of halogenated compounds.

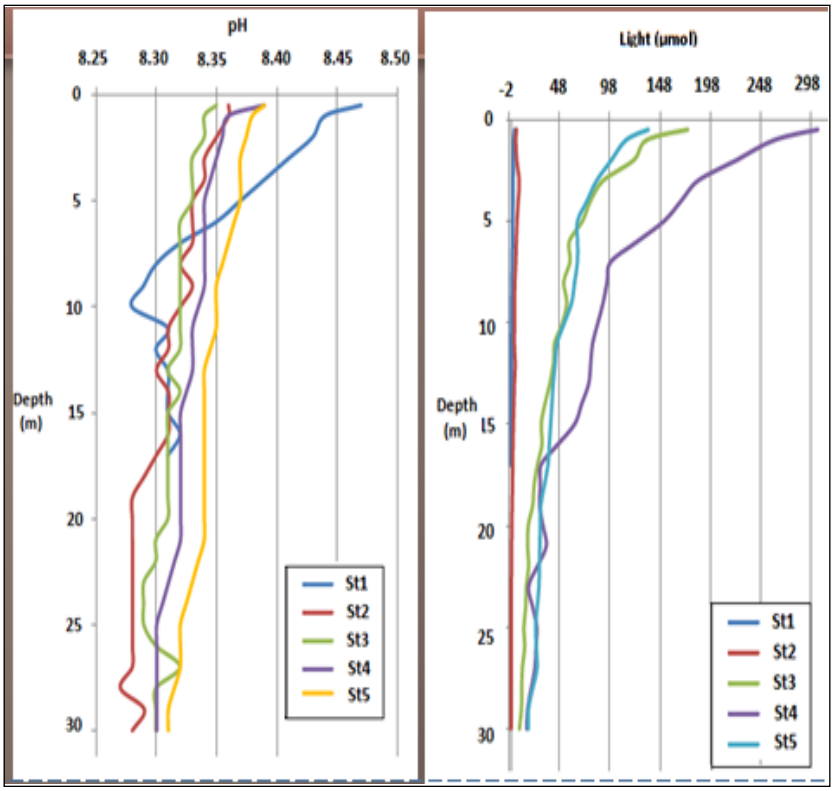


Figure 2: Physico-chemical parameters (pH, Light) at the five stations off the coast of Sabah during the local ship cruise at Kota Kinabalu on 23rd November 2011.

In particular the cruise was conducted in an region infested with harmful algal blooms of the high-growth biomass microalgae Cochlodium polykrikoides (Figure 3).

Figure 3 : Harmful microalgae blooms of C. polykrikoides in KK coastal waters

Results showed a high diversity and abundance of species in the coastal areas (stations 1-2) compared to the offshore stations (3-5)

This can be related to similar trends in bromoform concentrations which decreased from 100pmol/L at station 1 to 30 pmol/L at station 5 (Shi , 2013, Report 1a).

Phytoplankton species identification and fluorometer measurements during the coastal cruise can be used to calibrate against the satellite imagery data for chlorophyll a.

REPORT 14: THE CONTRIBUTION OF OCEANIC HALOCARBONS TO THE STRATOSPHERIC HALOGEN LOADING

Susann Tegtmeier, Kirstin Krüger, Birgit Quack

[1]GEOMAR, Maritime Meteorology, Chemical Oceanography, Kiel, Germany.

We investigate the contribution of oceanic halocarbons to the stratospheric halogen budget. Based on $CHBr_3$ and CH_3I measurements during the SHIVA ship campaign and Lagrangian transport calculations we provide a detailed analysis of halocarbon transport from the ocean surface to the cold point in the upper tropical tropopause layer (TTL). The level above which no significant washout is expected is particularly important for stratospheric halogen chemistry, since all $CHBr_3$ and CH_3I which reaches this level before being chemically destroyed can be expected to contribute to the stratospheric halogen budget. While the exact altitude of the 'no-washout level' is still under debate we have chosen the cold point altitude at approximately 17 km as an upper estimate since no dehydration is expected to occur above.

The atmospheric transport of $CHBr_3$ and CH_3I from the oceanic surface into the upper troposphere and TTL is simulated with the Lagrangian particle dispersion model FLEXPART. This model includes parameterizations for moist convection, turbulence in the boundary layer and free troposphere, dry deposition and in-cloud as well as below-cloud scavenging, and the simulation of chemical decay. In order to describe the transport, dispersion and convection of $CHBr_3$ and CH_3I, we simulate trajectories of a multitude of air parcels. For each data point of the observed sea-to-air flux a separate FLEXPART run is launched where 10000 air parcels were released over one hour from a 0.0002° x 0.0002° grid box (~500 m^2) at the ocean surface centered at the measurement location. The total amount of $CHBr_3$ and CH_3I emitted from this grid box over one hour is calculated based on the observation-derived flux and uniformly distributed over the 10000 air parcels. The FLEXPART runs are driven by the 6-hourly fields of horizontal and vertical wind, temperature, specific humidity, and precipitation from the ECMWF reanalysis product ERA-Interim. Trajectories were terminated after 3 months for $CHBr_3$ and after 7 days for CH_3I according to their atmospheric life times.

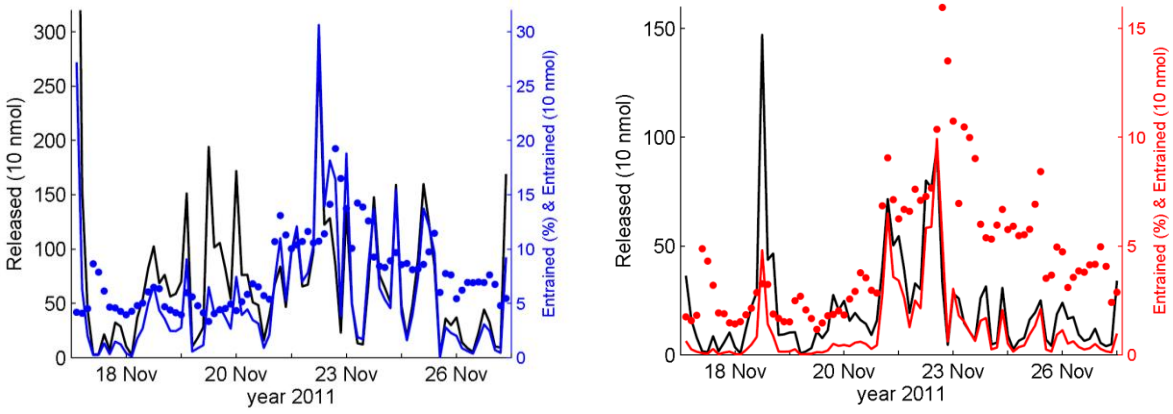


Figure1. Emissions (black line), as well as the relative (colored dots) and total (colored line) amount of $CHBr_3$ (left panel) and CH_3I (right panel) entrained above 17 km are displayed as a function of time along the cruise track. Emissions are calculated from the observed flux for a time period of one hour and an area of 500 m^2 for each observation.

Figure 1 shows the oceanic emission rates (black lines) of $CHBr_3$ and CH_3I as observed during the SHIVA ship campaign. The emission strength along the cruise track demonstrates the large variability

of air–sea fluxes during the campaign with the measurement locations often about less than 100 km apart from each other. The contribution of $CHBr_3$ (CH_3I) to the stratospheric halogen loading is based on the amount of the gas entrained above 17 km, calculated as the sum of $CHBr_3$ (CH_3I) carried by all the computational particles across this altitude. For $CHBr_3$, about 5-10% of the emitted gas is entrained above 17 km during most of the cruise. Stronger vertical transport with 10-15% entrainment is taking place during 22-23 November 2011. Atmospheric $CHBr_3$ abundance at 17 km averaged over the whole campaign amounts to 0.38 ppt, while maximum abundances of 1.8 ppt are associated with strong vertical transport and large emissions on 22 November. For the much shorter lived CH_3I, only about 2-3% of the oceanic emissions are transported above 17 km. Events of very efficient vertical transport are again predicted for the section 22-23 November 2011. Here, the model estimates 0.6 ppt CH_3I at 17 km which is much larger than any values reported by high reaching aircraft measurements so far. The campaign average mixing ratio at 17 km is somewhat lower amounting to 0.07 ppt.

Compared to other oceanic regions (i.e., the tropical Atlantic) an overall stronger vertical transport is estimated for the SHIVA campaign which took place in the coastal regions of the maritime continent an area well known for deep cumulus convection and heavy precipitation systems during boreal winter. Figure 2 shows the campaign averaged mixing ratios at 17 km estimated for the SHIVA ship campaign as well as for the Sonne TransBrom ship campaign in the open ocean West Pacific in October 2009 and the DRIVE ship campaign in North East Atlantic in May/June 2010. Additionally, global estimates based on measurements of high reaching aircrafts are displayed. For both gases, estimates based on the SHIVA campaign are much larger than estimates based on other campaigns or on aircraft observations demonstrating the importance of the coastal regions of the maritime continent as a source region for stratospheric halogens. For $CHBr_3$, the SHIVA based estimate is about 0.38 ppt while the estimates from the two other campaigns and the aircraft observations range between 0.06 and 0.09 ppt. For CH_3I, the emissions reported during SHIVA result in 0.07 ppt at 17 km, while the other two ship campaigns as well as aircraft observations give 0.01 – 0.02 ppt. Note that the aircraft campaigns are located in the tropical East Pacific and can be expected to differ from West Pacific abundances.

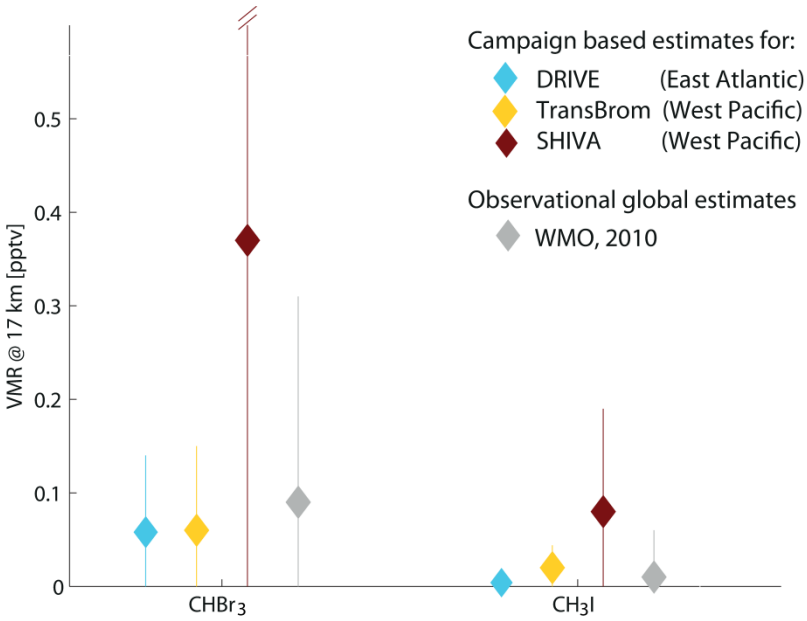


Figure2. $CHBr_3$ and CH_3I mixing ratios at 17 km estimated for three tropical campaigns and based on aircraft measurements.

For both gases the largest total entrainment takes place on 22-23 November 2011 (Figure 1) and is based on large emissions during times of maximum efficiency of vertical transport. Individual sections of the SHIVA ship campaign cruise with high correlations between emission and vertical transport have been identified. The analysis of the meteorological conditions during the campaign leads to the hypothesis that the horizontal surface winds act as a connecting link between emission and transport. On the one hand, horizontal wind strength directly determines the emission strength by diluting $CHBr_3$ or CH_3I rich air and thereby controlling the uptake capacities of the atmosphere. On the other hand, horizontal wind variations depend on the meteorological conditions such as convective systems or storm events. In particular, strong horizontal winds associated with tropical cyclones (i.e., typhoons) can indicate efficient vertical uplift possibly penetrating the stratosphere and thereby complete the line of argument connecting emission strength and troposphere-stratosphere transport.

In order to analyze whether the relatively large mixing ratios estimated for the West Pacific emissions are isolated cases strongly deviating from otherwise low CH_3I abundances or if they occur frequently enough to impact global CH_3I in the upper TTL, we analyze global model runs in addition to campaign based estimates. We quantify the global contribution of CH_3I to the stratospheric halogen budget from FLEXPART model runs using a global emission climatology provided by Ziska et al. (2013) as input data. We compare modeled CH_3I abundances to available aircraft measurements in the free troposphere and TTL region. A special focus is on the model-measurement comparison in the upper TTL and on the question whether the here available aircraft measurements are representative of existing global estimates. In a first step coincident data points for observations and model output are identified if they are less than 12 hours apart and if their distance is less than 0.5° horizontally and less than 0.5 km vertically. Profile comparisons are determined for each campaign by taking the mean and standard deviation over all coincidences identified for the particular campaign data and for the corresponding model output.

The profile comparison for three aircraft campaigns, which provide data in the free troposphere and lower UTLS, show in general a good agreement between the observations and the model results with the latter being consistently lower (not shown here). For the SHIVA aircraft campaign, observed and modeled profiles show a very similar shape with FLEXPART results being slightly smaller consistently over the whole altitude range. The largest differences are found around 11 km. For some individual flights convective outflow leads to observations of enhanced CH_3I between 10 and 12 km resulting in a ‘’C-shape’’ profile a characteristic which is well captured by the model results (not shown here).

Model-measurement comparisons for four campaigns conducted with the high altitude aircraft sampling in the upper TTL and lower stratosphere give an overall good agreement above 10 km. The aircraft campaign based mixing ratios in the upper TTL are below 0.1 ppt with the exception of the strongly enhanced mixing ratios at 16 km during ACCENT over Central America in 1999, which are reported by the observations and the model results. Largest discrepancies are found for the TC4-WB57 campaign over Central America in 2007, where basically no CH_3I was observed above 15 km while FLEXPART simulates mixing ratios around 0.1 ppt for the levels 13-17 km. Only below 10 and above 17 km the model output agrees well with the TC4-WB57 observations.

A summary of the model-measurement comparison in the upper TTL is displayed in Figure 3 where the observed profiles averaged over all four campaigns are displayed (grey squares). Additionally, the modeled CH_3I abundance in the aircraft campaign region is shown (black line). FLEXPART slightly overestimates the amount of CH_3I observed at 17 km (0.01 ppt) simulating a too strong CH_3I entrainment. However, the model results underestimate CH_3I at 19 km which is suggested to be around 0.02 ppt according to observations. The overall comparison of the 17-19 km region gives a good

agreement between observations (0.011-0.019 ppt) and model results (0.006 – 0.032 ppt). It is of interest to estimate CH_3I abundances in regions where no in-situ measurements in the upper TTL are available. The West Pacific region is of particular importance for the troposphere-stratosphere transport, and we will evaluate how the FLEXPART results in this area compare to the model results and observations in the East Pacific. Such a comparison will allow speculations of how representative existing aircraft measurements are of global estimates. Figure 3 shows in addition to the observations and FLEXPART results in the East Pacific, the model estimates averaged over the whole tropical belt (30°N - 30°S) and the tropical West Pacific. While for the West Pacific and the tropical belt the 2009 annual mean is displayed the East Pacific average is based on the months when aircraft measurements are available in order to allow for a comparison of the model East Pacific mean values with the in-situ observations. The observations and model results for the East Pacific agree quite well, as discussed above for the comparisons based coincidences. While observations suggest 0.01 ppt CH_3I at 17 km the modeled profile shows slightly larger values of 0.02 ppt. Overall, the comparison indicates that the available in-situ measurements provide representative estimates of the mean CH_3I abundance in the East Pacific region. FLEXPART results for the West Pacific region show considerable larger mixing ratios especially between 14 and 18 km with 0.08 ppt CH_3I at 17 km. The geographical distribution of the mixing ratios is displayed on Figure 3 (right panel) indicating that the West Pacific region between 100°W and 150°E shows the largest CH_3I abundances. Our model does not take into account terrestrial CH_3I emissions and therefore the very-short lived CH_3I is projected to reach the cold point and enter the stratosphere mostly above the oceans.

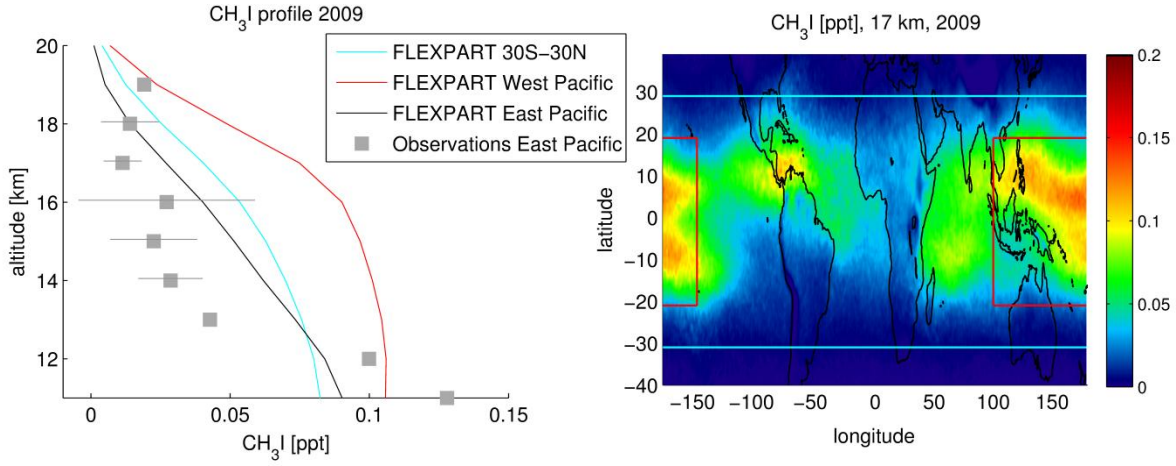


Figure 3. Comparison between observed and modeled vertical profiles of CH_3I in the upper troposphere and TTL are shown in the left panel. Observations are based on aircraft measurements and model output is averaged over the tropics (blue, 30°S-30°N) and the West Pacific (red, 100°W-150°E, 20°S-20°N) for 2009 and the East Pacific aircraft campaign region (green, 70°E-130°E, 6°S-30°N) for the months of available measurements. The modeled tropical distribution of CH_3I at 17 km for 2009 is shown in the right panel.

Reference

Ziska, F., Quack, B., Abrahamsson, K., Archer, S., Atlas, E., Bell, T., Butler, J., Carpenter, L., Jones, C., Harris, N., Hepach, H., Heumann, K., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R.M., Orlikowska, A., Raimund, S., Reeves, C., Reifenhaeuser, W., Robinson, A., Schall, C., Tanhua, T., Tegtmeier, S., S. Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., Yokouchi, Y., Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmos. Chem. Phys. Discuss., 13, 5601-5648, doi:10.5194/acpd-13-5601-2013, 2013.

ACKNOWLEDGEMENTS

We thank all scientific team members on board for their extra-ordinary hard work during the two weeks on SO218, which yielded a great and unique data set. Those who have looked after several measurement and sampling devices and those who worked day and night to get a sample every 3 hours and those who did minutes sleeps in the lab, or those who only worked at night - we thank especially that despite the hard work and occasional tensions, all managed to keep a professional and pleasant working atmosphere. It has been a rapid successful cruise during only 15 days time, where we measured a lot of gases and other parameters in ocean and atmosphere with instrumental deployments from CTD- casts, continuous running instruments over various chemical sampling systems for sea water and atmospheric measurements, biological sampling devices to soundings of atmospheric sensors and the exclusive installation of a newly built 10 " container on the forecastle deck of the ship. We managed to set everything up quickly, supported by the expertise of the professional ship's crew, who was always there, when we faced technical problems, which could all be overcome in the first days. The ships' crew was kind and helpful and we had the best cook on board, ever. His meals tasted fantastic and he did a great job in also satisfying our Muslim and vegan guests' taste. The intranet was operating well and we like to thank especially the WTD for their support in all instrumental problems we faced during the cruise, and can only repeat the words of a Malaysian technician who helped setting up the equipment in Singapore, that we had a magician on board. Pump- and CTD break down were rapidly repaired, so that we didn't lose valuable sampling time. Special thanks also to the decks fitter and electrician, who rapidly repaired all breakdowns with insight and care. Thanks to the decks crew for all helping hands and friendly support of our activities and the machinery for the smooth maintenance of all technical details of this fine ship. It has been a short, busy cruise with diurnal stations, local boat contacts and meetings with the research air craft Falcon, and despite careful preparation unforeseen circumstances happen and they were handled nicely with patience and responsive flexibility. The work has already succeeded in a lot of presentations and publications, and we are looking forward to more cooperative work.

We are grateful for the financial support given to the SHIVA- Sonne cruise SO218 project from various sources, in particular from the European Union (EU) (grant number 226224) and from the German BMBF (grant numbers: 03SO480, 03G0218A).