

EXPEDITION PROGRAMME PS94

Polarstern

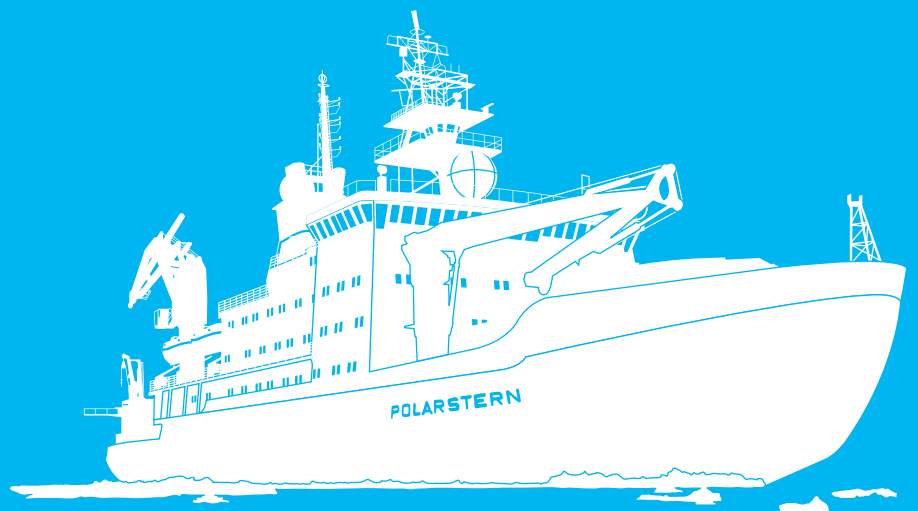
PS94

Tromsø - Bremerhaven

17 August 2015 - 15 October 2015

Coordinator: Rainer Knust

Chief Scientist: Ursula Schauer



Bremerhaven, June 2015

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1. ÜBERBLICK UND FAHRTVERLAUF

U. Schauer (AWI)

Die Expedition PS94 "TransArc II" (Trans-Arctic survey of the Arctic Ocean in transition) dient der Erfassung der physikalischen, biologischen und chemischen Veränderungen im Arktischen Ozean. Während der drastische Rückgang der arktischen Meereisausdehnung vom Satelliten aus beobachtet werden kann, müssen alle weiteren Veränderungen auf wiederholten Schiffsexpeditionen gemessen werden. Dieser Strategie folgend wird auf TransArc II acht Jahre nach dem Internationalen Polarjahr IPY 2007/2008 und vier Jahre nach der ersten „TransArc“-Expedition die nächste großskalige Aufnahme der Dicke und Beschaffenheit des Meereises, der Wassermasseneigenschaften und ihrer Zirkulation sowie chemischer und biologischer Kreisläufe durchgeführt. TransArc II ist ein Beitrag zu den internationalen Programmen GEOTRACES (www.geotraces.org/), Arctic ROOS (<http://arctic-roos.org/>), IABP (International Arctic Buoy Program) und Transdrift (www.transdrift.info), sowie zum nationalen Programm RACE (<http://race.zmaw.de/>). Darüber hinaus ist TransArc II eine Fahrt für das Infrastrukturprogramm FRAM (Frontiers in Arctic Monitoring) der Helmholtz-Gemeinschaft Deutscher Forschungszentren (HGF).

Die Reduzierung des Meereises und die Änderungen in der Ozeanzirkulation und im Wärme- und Süßwasserhaushalt sind eng verknüpft mit Änderungen im Gasaustausch sowie mit biogeochemischen Stoffumsätzen und Prozessen im Ökosystem im Eis und in der gesamten Wassersäule. Während TransArc II werden diese Zusammenhänge durch Beprobung aller Parameter an gemeinsamen Stationen entlang von Gradienten von den Eurasischen Schelfmeeren über die Rücken bis ins Amerasische Becken und vom offenen Ozean bis ins Packeis untersucht.

TransArc II beginnt am 17. August 2015 in Tromsø. *Polarstern* wird die Barentssee passieren und nördlich von Franz-Josef-Land das Arbeitsprogramm mit einem Schnitt nach Norden beginnen. Dabei wird am Kontinentalhang der warme, salzreiche Randstrom des atlantischen Einstroms aus der Framstraße beprobt und weiter nördlich am Gakkelrücken der Rückstrom atlantischen Wassers zur Framstraße. Der Schnitt wird - wie alle anderen Schnitte der Fahrt – aus einer dichten Folge von hydrographisch/biogeochemischen und biologischen Stationen, Eisstationen und Netzfängen bestehen. Die schiffsgebundenen Stationen werden durch Arbeiten vom Hubschrauber ergänzt, durch die die Dicke und weitere Eigenschaften des Meereises gemessen werden. Am nördlichen Ende des Schnittes im Amundsenbecken wird eine Verankerung mit ozeanographischen Instrumenten und biologischen Probennehmern ausgesetzt, die im Sommer 2016 auf der *Polarstern*-Expedition ICEARC II aufgenommen werden sollen.

Nach der Rückkehr zur Schelfkante der Karasee westlich von Severnaja Semlja und führt der zweite lange Schnitt wieder nach Norden, um die Konfluenz der atlantischen Einströme aus der Framstraße und über die Barentssee zu erfassen. Weiter geht es über das Nansenbecken, das Amundsenbecken und den Lomonossowrücken bis in das Makarowbecken, wo wir auf einer festgelegten Position eine Station zur Interkalibration für mehrere diesjährige GEOTRACES-Expeditionen fahren werden. Hier erreichen wir auch den pazifisch beeinflussten Teil der Arktis und die Transpolare Drift von Eis und Süßwasser. Unser Kurs führt möglicherweise über das Makarowbecken hinaus, da wir das mehrjährige Packeis beproben und dazu soweit wie möglich in dickes Eis vordringen wollen. Je nach Eissituation

werden auf dem Schnitt verteilt diverse Eisbojen ausgebracht, die einen Beitrag zum IABP und RACE liefern.

Vom westlichen Makarowbecken - oder wenn möglich vom Alpha-Mendelejew-Rücken aus - führt ein Schnitt nach Süden zur Ostsibirischen See. Dabei vermessen wir die Transpolare Drift und bewegen uns vom Packeis bis ins offene Wasser. Am Kontinentalhang wird wieder der Randstrom überquert, der hier den Einstromast ins Kanadische Becken repräsentiert. Anschließend werden wir den Lomonossowrücken kreuzen und damit in den eurasischen Teil der Arktis zurückkehren. Im Nansenbecken werden weitere Eisbojen ausgesetzt und dann werden wir in die Laptewsee fahren, wo neben der Fortsetzung des Schnittprogramms sieben Verankerungen des deutsch-russischen Programms Transdrift aufgenommen werden sollen.

Vom westlichen Rand der Laptewsee aus wird die Rückreise durch die Nordostpassage angetreten. Am 15. Oktober 2015 wird die Expedition in Bremerhaven enden.

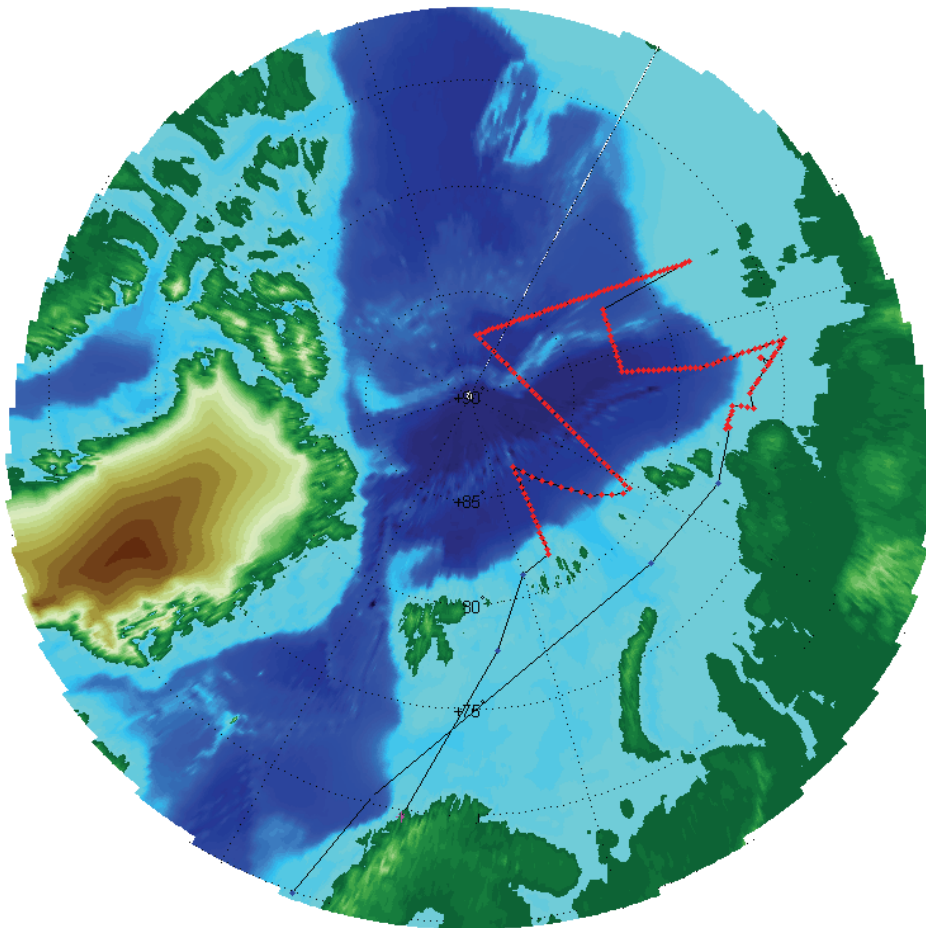


Abb. 1: Schnitte mit Stationsarbeiten (rote Punkte) und An/Abfahrtroute (schwarze Linie). Die Fahrt PS94 beginnt am 17. August 2015 in Tromsø und endet am 15. Oktober 2015 in Bremerhaven. Der genaue Verlauf der Fahrt ist abhängig von der Eissituation und der Forschungsgenehmigung für die ausschließliche russische Wirtschaftszone.

Fig. 1: Cruise track for research (red dots) and steaming (black line). The cruise PS94 will start on August 17, 2015 in Tromsø and will end on October 15, 2015 in Bremerhaven. The exact cruise track depends on the ice situation and on the clearance for the Russian exclusive economic zone.

SUMMARY AND ITINERARY

The expedition PS94 "TransArc II" (Trans-Arctic survey of the Arctic Ocean in transition) will capture the current state of the physical, biological and chemical components of the Arctic Ocean in order to assess its changes. While the drastic retreat of the sea ice can be measured through satellites, assessment of all other Arctic Ocean changes need repeat observations through ship expeditions. Following this strategy, TransArc II will, eight years after the International Polar Year 2007/2008 and four years after the first TransArc expedition, conduct the next survey of the thickness and properties of sea ice, of properties and circulation of water masses, of geochemical biogeochemical cycles and of ecosystem changes. TransArc II is a contribution to the international programs GEOTRACES (<http://www.geotraces.org/>), Arctic ROOS (<http://arctic-roos.org/>), IABP (International Arctic Buoy Program) and Transdrift (www.transdrift.info/home), as well as to the national program RACE (<http://race.zmaw.de/>). TransArc II is also a component of the strategic infrastructure program FRAM (FRontiers in Arctic Monitoring) of the Helmholtz Foundation of German Research Centers.

The reduction of sea ice and the variability of ocean circulation and its heat and fresh water budgets are tightly linked with changes in the gas exchange as well as with biogeochemical and ecosystem cycles in the sea ice and in the entire water column. During TransArc II these relations will be studied through joint observations on stations along gradients from the Eurasian shelf seas into the Amerasian Basin and from the pack ice into the open water.

TransArc II will start in Tromsø on August 17, 2015. *Polarstern* will steam through the Barents Sea and the work will begin north of Franz Josef Land with a northward section. Thereby we will cross the warm, saline boundary current of the Atlantic Water inflow through Fram Strait and further north at the Gakkel Ridge the return flow of Atlantic water towards Fram Strait. Like all other sections during this cruise, this section will consist in a dense sequence of stations containing hydrographic, biogeochemical, and biological sensing and sampling work and net hauls as well as ice stations. The shipborne measurements will be complemented by helicopter-borne observations of the thickness and other properties of sea ice. At the northern end of the section, in the Amundsen Basin, a mooring with oceanographic and biological sensing and sampling instrumentation will be deployed; the mooring will be recovered in summer 2016 during the *Polarstern* expedition ICEARC II.

After returning to the shelf edge in the Kara Sea west of Severnaya Semlja, *Polarstern* will again head northward to conduct a long section, which will capture the confluence of the branches of Atlantic water entering through Fram Strait and through the Barents Sea. The section will then cross the Nansen and Amundsen basins and the Lomonosov Ridge into the Makarov Basin. Here we will take a cast at an intercalibration position for several GEOTRACES cruises of 2015. In this region, we will cross the front towards waters of Pacific origin and the Transpolar Drift of ice and fresh water. Depending on the ice situation we will go even further to the Mendelejev Ridge because we want to extend the section as far as possible into the perennial pack ice. Along the section we will deploy various ice buoys that will contribute to IABP and to RACE.

Leaving the western Makarov Basin, we will head towards the East Siberian Sea. Along this section, we will capture large parts of the Transpolar Drift and sample from pack ice to the open ocean. We will cross once more the boundary current, which represents here the inflow

branch into the Amerasian Basin. Then we will take a second crossing of the Lomonosov Ridge. In the Nansen Basin we will deploy further ice buoys and then move on to the Laptev Sea where we will recover seven moorings for the German-Russian project Transdrift.

Research will be finished in the western Laptev Sea. From there we will get back along the Northern Sea Route and return to Bremerhaven where *Polarstern* will arrive on 15 October 2015.

2. PHYSICAL OCEANOGRAPHY

B. Rabe, R. Graupner, M. Hoppmann, M. Horn, U. Schauer (AWI), M. Korhonen (FMI), S. Pisarev (SIO), N. Villaceros Robineau, J.-P. Savy (LOCEAN)

Background and objectives

Next to the dramatic retreat of sea ice, the strongest climatic signal of the Arctic Ocean and the Nordic Seas in the past decade are changes in temperature and salinity. A strong accumulation of fresh water has been observed in the past decades in the Arctic Ocean; the waters advected from the Atlantic and the Pacific became much warmer, the Atlantic inflow became saltier. Concurrently, there is a multi-decadal positive trend in continental runoff into the Arctic and decadal changes in the atmospheric circulation.

The aim of the physical oceanography part of this cruise is to document and quantify the present state of the water mass distribution and circulation in the Eurasian and Makarov basins, and the East Siberian and the Laptev Sea. The observations will be fundamental to understand the time-mean state of the Arctic Ocean from basin-scales to individual ice floes. They will allow us, in the context of appropriate modelling, to identify variability on seasonal to decadal timescales and long-term trends.

Waters imported to the Arctic Ocean are subject to cooling, freezing and melting, altering the properties of these water masses. The warm inflow of waters of Atlantic origin occurs via two pathways: the eastern Fram Strait and the Barents Sea. These two branches are subject to transformation by surface processes and lateral mixing before and after entering the Nansen Basin. Continental runoff enters the Eurasian and Makarov basins via the extensive shelf regions north of Eurasia, before advected within the Transpolar Drift and, at times, the Beaufort Gyre. At slightly lower salinity than Atlantic Water, Pacific Water enters the Amerasian Basin via the Bering Strait and even reaches into the Eurasian Basin in particular years. This water mass is sandwiched between the warmer waters of Atlantic origin and the fresher, colder waters near the surface.

In the central Arctic, stratification due to fresh water in the mixed layer and the halocline inhibits the release of heat from underlying waters to the atmosphere. This stratification is maintained by continental runoff, and ice or meltwater. However, the variable distribution of fresh water may facilitate the release of some of this heat in certain areas; for example, the recent convergence of fresh water in the central Arctic may, for dynamical reasons, lead to a weakening of the stratification along the warm boundary current at the rim of the basins. Changes may also occur from the different wind mixing with and without ice cover, and the fact that now large areas have longer seasons without sea ice.

To address these questions we will conduct physical measurements in the Eurasian and Makarov basins. Several hydrographic sections will improve our understanding of changes in time by repeating work from earlier cruises that have been conducted since the early 1990s with the icebreakers *Polarstern* and *Oden*, and within the NABOS (Nansen-Amundsen Basin Observation System) project. These observations will be augmented by upper-water-column hydrography perpendicular to the sections to capture horizontal gradients in all directions. We will run continuous and on-station measurements of current velocity to aid the interpretation of the hydrographic data and estimate transports. To extend the observational range of the ship survey in space and time, we plan to deploy autonomous, ice-based buoys, and deploy and recover bottom-moored observatories. From sea-ice, we will use a turbulence profiler to obtain estimates of fine structure and turbulent energy dissipation in the upper water column. This will improve our understanding of vertical mixing processes in the context of large scale hydrography.

Our work is part of the Helmholtz strategic investment Frontiers in Arctic Marine Monitoring (FRAM) and contributes to several projects on a national (Bundesministerium für Bildung und Forschung, RACE and TRANSDRIFT) and international (International Arctic Buoy Program, IABP; Forum for Arctic Modeling and Observational Synthesis, FAMOS; French equipex IAOOS, <http://www.iaos-equipex.upmc.fr> and <http://iaos.ipev.fr>; EU FP7 Ice Arc project, <http://www.ice-arc.eu>).

Work at sea

Profiles of salinity and temperature will be obtained using different systems with Conductivity-Temperature-Depth (CTD) sensors:

170 CTD stations are planned along the route from Frantz-Josef-Land into the Eurasian and Makarov basins, and on the way from north of the East Siberian Sea into the Laptev Sea. An SBE 9/11+ CTD system will be used in combination with an SBE 32 Carousel Water Sampler (Seabird). Two rosettes with each 24 bottles for water samples will be used: one with 12 litre, the other with 25 litre bottles. We will also use sensors for dissolved oxygen and fluorescence, to detect Chl-a and Carbonate Dissolved Organic Matter (CDOM). A custom-made ultra-clean CTD rosette system for trace metal work will be operated by the GEOTRACES group. Around 100 additional profiles, ranging from the surface to 1,100 m depth, will be obtained by an expendable CTD (XCTD) system from the moving ship and from ice floes accessible by helicopter. In the presence of sea ice, XCTD profiles will be interspersed to enhance resolution in currents near ridges or the continental slope, and additional sections perpendicular to the track of *Polarstern* will resolve the horizontal gradients in that direction. A mobile CTD-system, using a custom-made winch and an SBE 16+ CTD, and capable of measuring full-depth profiles, will be used from ice floes with helicopter assistance. This system will be used to obtain additional profiles at the end of XCTD sections, branching off the route of *Polarstern*. If no sea-ice is present, an underway CTD (UCTD) system will be used from the ship in a similar way as the XCTD system to obtain profiles from the surface to about 400 m depth.

A vessel mounted ADCP (VMADCP) will measure velocity in the upper water column, both on CTD stations and during transit between stations. A lowered ADCP (LADCP) system will be attached to the CTD rosette to measure velocities over the full water depth at CTD stations.

A turbulence profiler (MSS90L, Sea & Sun Technology) will be used from sea-ice to obtain profiles of fine-scale motion by measuring temperature, salinity, pressure, current shear and light transmission. The profiler is free-falling with a 400 m long data cable attached to an electrical winch.

Ice-tethered Profiler (ITP) systems contain a profiling CTD and a surface unit, that transmits the CTD-profiles daily to land for further processing. We are planning to deploy two ITP systems on drifting ice floes in the Transpolar Drift, far enough upstream of the Fram Strait to allow at least one or more years of observation during the drift. IAOOS (Ice Atmosphere Ocean Observing System) platforms perform profiles through the atmosphere, the ice and the ocean. The atmospheric observations are provided by a microlidar and an optical depth sensor, the snow, ice observations by an ice mass balance buoy and the ocean observations by a profiling CTD. We are planning to deploy six IAOOS systems on ice floes and in open water.

One mooring mounted on the seafloor will be deployed in the Amundsen Basin. The mooring will record temperature, salinity and currents in the whole water column while simultaneously collecting water and sediment samples in the upper water column at regular intervals throughout approximately one year. Recovery of this system is planned for 2016 during the expedition PS101. We will recover several moorings, mounted on the seafloor, with sensors for temperature, salinity, pressure, current velocity in the Markarov and Amundsen basins, as part of the NABOS/AON, and in the northern Laptev Sea, as part of TRANSDRIFT.

Data management

Data from the different CTD systems, turbulence profiler, VMADCP and LADCP, collected during PS94, will be delivered after post-cruise calibration to the PANGAEA database and to the appropriate national data centres.

ITP data will be available in near real-time on the website at Woods Hole Oceanographic Institution (<http://www.whoi.edu/itp>). IAOOS data will be made available after validation at the French Data and service centre ICARE (www.icare.univ-lille1.fr) The data recorded by the moored instrumentation will be processed after the cruise at AWI and submitted to the PANGAEA database.

3. SEA ICE PHYSICS

S. Hendricks (AWI)

Objectives

Recent evaluations of trends in Arctic sea ice extent observed by passive microwave satellite missions show a downward trend of -3.8 % per decade of total yearly averaged sea ice cover, whereat multi-year ice coverage is effected the most (-11.5 % per decade) (Comiso et al., 2014). While these are yearly averaged values, the spread in the seasonal cycle is most pronounced during the summer minimum, where the three lowest observed ice extents occurred between 2007 and 2012. The reduction of summer sea ice cover and its shift to a dominant seasonal ice type has implications on the energy balance in form as the ice-albedo feedback, but also increased absorption of solar radiation in ice covered waters (Nicolaus et al., 2012) and its function as a habitat (Boetius et al., 2012).

Except passive microwave estimations of sea-ice concentration and satellite retrieval algorithms of melt pond concentrations, most observations of the mass balance during summer and the following freeze-up period rely on airborne, ship-borne and *in-situ* observations.

We therefore aim to extend the time series of physical sea-ice observations of *Polarstern* during summer and freeze-up of 2015. Earlier observations of sea-ice thickness range back as far back as 1991 and form one of the longest time series in the central summer Arctic Ocean. Besides the continuation of the sea-ice thickness time series, we plan to use novel techniques to estimate the spatial variability of sea-ice porosity and its influence on sea-ice volume estimation. This is motivated by the earlier anecdotal findings of significant ice porosity, which might lead to a bias in ice volume estimation by means of sea-ice thickness measurements alone.

Work at sea

The planned work can be categorized in airborne surveys, on-ice field work and continuous observations from the bridge:

AEM ice thickness measurements

Thickness observations by airborne electromagnetic (AEM) induction sounding are one of the established long term sea-ice thickness time series in the central Arctic Ocean. We plan to conduct helicopter sea ice surveys using a small towed AEM system at regular intervals along the cruise track. The AEM sensor is towed by the helicopter on a 20 m long cable and operational altitude range between 40 and 500 ft. Ice thickness are derived by differences from laser ranging to the surface and EM ranging to the ice-water interface. Thickness measurements therefore include the snow depth and are referred to as total thickness. During high altitude calibrations, aerial images from a nadir looking camera inside the AEM sensor will yield estimations of melt pond concentration. Together with a GPS/INS unit and a laser altimeter, each image can be geo referenced and used for the retrieval of the floe size distribution using image analysis techniques.

Multi-frequency handheld EM

Recent advances in multi-frequency electromagnetic induction sounding with handheld devices (Hunkeler et al., 2015) show the potential of direct sea-ice porosity retrieval by proxy measurements of ice-layer DC conductivity. Porosity data from sea ice during Arctic summer is currently mostly available from analysis of ice cores, whereat systematic surveys of the floe and regional scale variability have not been accomplished yet to the knowledge of the sea ice physics group. We therefore plan to coordinate multi-frequency EM soundings with validation core measurements to assess the regional distribution of summer sea ice porosity and its impact on ice volume estimations. The work will take place during ice stations and comprise floe scale grid surveys.

Buoy deployments

We plan to support long-term monitoring programs, such as the International Arctic Buoy Program by deployments of sea-ice drifting buoys on ice stations and by helicopter several kilometres off the *Polarstern* cruise track. Types of sea ice buoys ranges from GPS drifters for ice dynamics, snow depth and ice mass balance buoys for monitoring ice growth and snow accumulation throughout the following winter as well as radiation stations for energy budget estimations. The main focus of buoy deployments lies on regions as far into the eastern marginal seas of the Arctic Ocean as possible, which are areas typically sparsely observed by autonomous systems. The deployments of sea ice buoys will be coordinated with the ocean buoy program and the FRAM project.

Routine sea ice observations

Hourly sea ice observations will be carried out by trained observers on an hourly basis from the bridge of *Polarstern* according to the ASSIST protocol (Arctic Shipborne Sea Ice

Standardization Tool). The observations will be made during normal working hours between 7 am and 9 pm.

Expected results

We expect *in-situ* measurements and regional distribution of total thickness distributions and regular observations of a broad range of physical surface parameters (thickness, ice concentration, surface roughness and melt pond concentration). Physical sea-ice data will be available from autonomous drifting stations throughout the winter after the cruise. Ice type dependent sea-ice porosity estimations are a research topic and the availability and accuracy are currently not known.

Data management

The sea ice thickness, sea ice observations from bridge, multi-frequency handheld EM data will be released following final processing after the cruise in the PANGAEA database, meereisportal.de and other international databases.

References

- Boetius A., Sebastian Albrecht, Karel Bakker, Christina Bienhold, Janine Felden, Mar Fernández-Méndez, Stefan Hendricks, Christian Katlein, Catherine Lalande, Thomas Krumpfen, Marcel Nicolaus, Ilka Peeken, Ben Rabe, Antonina Rogacheva, Elena Rybakova, Raquel Somavilla, Frank Wenzhöfer, RV Polarstern ARK-XXVIII/3-Shipboard Science Party: *Export of algal biomass from the melting Arctic sea ice*. Science 02/2013;
- Comiso, J. C. and Hall, D. K. (2014), Climate trends in the Arctic as observed from space. WIREs Clim Change, 5: 389–409. doi: 10.1002/wcc.277
- Haas, Christian, Andreas Pfaffling, Stefan Hendricks, Lasse Rabenstein, J-L Etienne, I.Rigor: *Reduced ice thickness in Arctic Transpolar Drift favors rapid ice retreat*. Geophysical Research Letters 01/2008; 35:L17501.
- Hunkeler, Priska A., Stefan Hendricks, Mario Hoppmann, Stefan Paul, Rüdiger Gerdes: *Towards an estimation of sub sea ice platelet layer volume with multi frequency electromagnetic induction sounding*. Annals of Glaciology 01/2015; 56(69).
- Nicolaus, M., Christian Katlein, James Maslanik, Stefan Hendricks: *Changes in Arctic sea ice result in increasing light transmittance and absorption*. Geophysical Research Letters 12/2012; 39(24).
- Pfaffhuber, Andreas A., Stefan Hendricks, Yme A. Kvistedal: *Progressing from 1D to 2D and 3D near-surface airborne electromagnetic mapping with a multisensor, airborne sea-ice explorer*. Geophysics 07/2012; 77(4):109.

4. PRODUCTION AND CYCLING OF CLIMATE RELEVANT TRACE GASES (METHANE AND DMS) IN SEA ICE AND SEA WATER

E. Damm, C. Uhlig, G. Dieckmann (AWI) , E. Vinogradova (SIO)

Objectives

Summer sea ice retreat alters water mass formation and convection, which may have profound effect on natural biogeochemical cycles between sea ice and seawater. Especially feedback effects to pathways of climatically relevant trace gases will loom large in the equation of change. Increasing water stratification during sea ice melting is likely to limit nutrient availability in near-surface water, which in turn hampers the enhancement of primary production. A characteristic feature of the Arctic Ocean is the distinct post-bloom nutrient

limitation found in the Atlantic-dominated and Pacific-dominated sectors. Nutrient limitation may be also a possible regulator of methane production in surface water. Methanogens form methane via various pathways commonly classified with respect to the type of carbon precursor utilized, e.g. the methylothrophic pathway indicates the intact conversion of a methyl group to methane. The contribution of methylated substrates is potentially large in sea ice, and methylothrophic methanogenesis may be a principal pathway from which methane is readily formed by microbial activity. However, the direct evidence of this role of methylated substrates in sea ice is still lacking. In this context the degradation of dimethylsulfoniopropionate (DMSP), an abundant methylated substrate in surface water and sea ice becomes pivotal. DMSP is produced by marine phytoplankton and sea ice algae. Cleavage of DMSP can be carried out by bacteria or by phytoplankton, and leads to formation of DMS (dimethylsulfide) or methanethiol. DMS, an important climate-cooling gas, partly escapes to the atmosphere where it is oxidized to sulphuric acid and methanesulfonic acid. Methanethiol is a key reactive intermediate utilized as sulphur and carbon sources for biosynthesis or energy generation. In anaerobic environments methanethiol act also as precursor for methane production. Our goal is to trace methane cycle between sea ice and sea water, to stimulate methane production in sea ice microbial communities (experiment), to distinguish the different degradation pathways of DMSP and subsequently to quantify the formation of DMS, methanethiol and methane.

Work at sea

We intend to measure dissolved gases in sea ice and surface sea water. Water samples will be collected in Niskin bottles mounted on a rosette sampler at discrete depths throughout the water column up to 200 m water depth on several stations along transects. The number of sampling depths depends of the fluorescence signal and the O₂- sensor signal. We sample one-year and multi-year sea ice and brine by taking cores with a standard corer. Sea ice cores will be sectioned and melted at 4°C. Methane concentration is measured on board by gas chromatography (GC) equipped with a flame ionization detector (FID). Gas samples will be stored for analyses of the d¹³C values of methane by mass spectrometry in the home laboratory. DMS, DMSP and methanethiol concentrations are measured on board by GC equipped with a pulsed flame photometer (PFPD) and by GC equipped by a flame photometer (FPD), respectively.

To gain a better understanding on the possible formation of methane from the substrate DMSP we will additionally conduct incubation experiments. Different treatments will be set up by adding DMSP and varying nutrient concentrations to melted sea ice or sea water collected with Niskin bottles. During the experiments DMSP, DMS, methanethiol and methane will be measured on board. Bacterial abundance and community composition (16S) as well as DMSP degradation pathways (degradation genes) will be analysed in the home laboratory. Some of the experiments will be conducted with ¹³C-labeled DMSP to track the DMSP-derived methyl groups.

Data management

All data collected during the expedition will be stored in the PANGAEA data repository at the AWI within three years after the cruise.

5. GEOTRACES

M. Rutgers van der Loeff (AWI) and the GEOTRACES scientific party (the corresponding names of the participating party are listed under the respective articles)

Objectives

GEOTRACES (www.geotraces.org) is an international programme that aims to determine global ocean distributions of selected trace elements and isotopes, including their concentration, chemical speciation and physical form, and to evaluate the sources, sinks and internal cycling of these species. This knowledge is needed to characterize more completely the physical, chemical and biological processes regulating their distributions so that the response of these cycles to global climate change can be predicted, and their impact on the carbon cycle and climate understood (Henderson et al., 2007).

Warming of Arctic terrestrial areas caused increased river discharge, which, combined with net loss of the Greenland ice-cap and melting of sea ice, resulted in a freshening of surface waters and increased stratification. These climate-induced changes are expected to change the biogeochemical cycling and therefore the distribution of many Trace Elements and Isotopes (TEI's).

Work at sea

As part of a pan-Arctic GEOTRACES effort in coordination with Canadian and US initiated research cruises in 2015, we will carry out a sampling program of TEIs including all tracers considered as key TEIs by Henderson et al. (2007). We expect to have a cross over station in the Makarov Basin with the US expedition on board USCG Healy. Samples will be collected for intercalibration programs with GEOTRACES partners, especially with our colleagues on the US and Canadian ships.

Expected results

In combination with the results of the synoptic US and Canadian studies we hope to provide maps of the distribution of TEIs in the Arctic including a full section from the Kara Sea to the Bering Strait. Comparison with previous data may allow us to determine whether distributions have changed, which could be indicative of changes in water mass circulation, primary productivity, or particle fluxes.

Data management

Data from a crossover station with the US cruise and other intercalibration results from duplicate sampling will be submitted to the GEOTRACES Standards and Intercalibration Committee for evaluation and approval.

All data and metadata will be submitted to the international GEOTRACES data management office (BODC, www.bodc.ac.uk/geotraces) under the data management scheme agreed upon in the GEOTRACES programme available at <http://www.geotraces.org>. Most data and metadata will also be submitted to the PANGAEA data base.

References

Henderson GM, Anderson RF et al. (2007) GEOTRACES - An international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chem Erde-Geochem* 67: 85-131.

5.1 Nutrients

J. van Ooijen (NIOZ)

Objective

The nutrients phosphate (Murphy & Riley, 1962), silicate (Strickland & Parsons, 1968), nitrite and nitrate (Grasshoff et al., 1983) will be measured at all GEOTRACES stations to determine its distribution in the Eurasian sector of the Arctic Ocean. The nutrients are important parameters allowing other parameters to be related to biological activity such as primary production and remineralization. Nutrients function also as tracers of water masses.

Work at sea

The nutrients will be measured in a dedicated laboratory container. Unfiltered samples will be taken from the CTD bottles.

Expected results

With the help of the nutrient data that will be available approximately within two days after sampling we will have an overview of water masses, biological activity and functioning of the sampling system. Later the nutrient data will be used for many studies related to the cruise to indicate a diversity of physical and biological processes.

Data management

See chapter 5 for details on data management.

References

- Grasshoff, K. et al., Methods of seawater analysis. Verlag Chemie GmbH, Weinheim, 1983 419 pp
- Murphy, J. & Riley, J.P., A modified single solution method for the determination of phosphate in natural waters. *Analytica chim. Acta*, 1962, 27, p31-36
- Strickland, J.D.H. and Parsons, T.R., A practical handbook of seawater analysis. first edition, Fisheries Research Board of Canada, Bulletin. No 167, 1968. p.65.

5.2 CO₂ System

E. M. Jones (NIOZ), A. Ulfsbo (UGOT),
not on board: L. G. Anderson (UGOT), H. J. W. de Baar (NIOZ)

Objectives

The overarching objective of this study is to further improve our understanding of the carbon system in the rapidly changing Arctic Ocean, with an emphasis on the spatial and temporal variability of CO₂ fluxes and NCP using novel high-resolution methods in the surface mixed layer within the central basins. More specifically, we aim at improving our understanding of the feedbacks by physical and biogeochemical processes on the Arctic Ocean carbon system within the surface mixed layer. This also includes carbon transformation on the large shelf areas and the exchange with the deep central basins, as well as likely changes in the effect by export of marine produced organic matter to the deep central Arctic Ocean when the sea-ice coverage is absent during the productive summer season. In addition, apart from hydrography, a thorough knowledge of the carbon system is essential for the understanding of the distribution of trace elements in the ocean in terms of their cycling, sources and sinks, supporting the on board GEOTRACES program.

Work at sea

Discrete water samples will be taken at the combined hydrographic and biogeochemical stations from the CTD rosette sampler at depths all through the water column, but with a bias

towards the upper layers. Total dissolved inorganic carbon (DIC; also known as TCO_2 , C_T), total alkalinity (TA; also known as A_T), and pH are determined in discrete water samples taken from the rosette sampler. Both DIC and TA are sequentially determined according to standard operating procedures (Dickson et al., 2007) with a VINDTA instrument (MARIANDA, Kiel), which combines the two measurements. DIC is determined by a coulometric titration (Johnson et al., 1985; Johnson et al., 1987; Johnson et al., 1993) and TA is determined by potentiometric titration with acid in a semi-closed cell (Dickson, 1981; Dickson et al., 2007). The seawater pH is determined spectrophotometrically (Clayton and Byrne, 1993; Carter et al., 2013) using purified m-cresol purple as indicator (Patsavas et al., 2013). The sampling and analysis work are according to the best practices for ocean CO_2 measurements (Dickson et al., 2007). The accuracy is set by internationally recognized and widely used certified reference material (CRM) obtained from Prof. A. Dickson at Scripps Institute of Oceanography (USA). In addition, underway data of surface water partial pressure of CO_2 ($p\text{CO}_2$) and biological oxygen supersaturation ($\Delta(\text{O}_2/\text{Ar})$) will be collected off the ship's seawater intake system. $p\text{CO}_2$ is obtained with a General Oceanics system with an infra-red analyzer (LI-COR), both for seawater using an water-air equilibrator and for the atmosphere, the air being pumped from the crew's nest. Biological oxygen supersaturation (Craig and Hayward, 1987; Emerson et al., 1991) is determined using Equilibrator Inlet Mass Spectrometry (Cassar et al., 2009). In addition, the on board analysts will determine dissolved oxygen concentration by Winkler titration to calibrate the oxygen sensors from the CTD.

Expected results

TransArc II is more or less a repeat survey of TransArc 2011 (PS78/ARK-XXVI/3) where all of the above mentioned parameters were determined, and there will be a unique opportunity to study the spatial and temporal changes in the seawater CO_2 system in a central Arctic Ocean in transition.

Data management

See chapter 5 for details on data management.

References

- Carter, B.R., Radich, J.A., Doyle, H.L. and Dickson, A.G., 2013. An automated system for spectrophotometric seawater pH measurements. *Limnology and Oceanography: Methods*, 11: 16-27, 10.4319/lom.2013.11.16
- Cassar, N., Barnett, B.A., Bender, M.L., Kaiser, J., Hamme, R.C. and Tilbrook, B., 2009. Continuous High-Frequency Dissolved O_2/Ar Measurements by Equilibrator Inlet Mass Spectrometry. *Analytical Chemistry*, 81(5): 1855-1864, 10.1021/ac802300u
- Clayton, T.D. and Byrne, R.H., 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep Sea Research (Part I, Oceanographic Research Papers)*, 40(10): 2115-2129, 10.1016/0967-0637(93)90048-8
- Craig, H. and Hayward, T., 1987. Oxygen Supersaturation in the Ocean: Biological Versus Physical Contributions. *Science*, 235(4785): 199-202, 10.1126/science.235.4785.199
- Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep Sea Research Part A*, 28(6): 609-623, 10.1016/0198-0149(81)90121-7
- Dickson, A.G., Sabine, C.L. and Christian, J.R., 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication. North Pacific Marine Science Organization (PICES), Sidney, British Columbia, pp. 173.
- Emerson, S., Quay, P., Stump, C., Wilbur, D. and Knox, M., 1991. O_2 , Ar, N_2 , and ^{222}Rn in surface waters of the subarctic Ocean: Net biological O_2 production. *Global Biogeochemical Cycles*, 5(1): 49-69, 10.1029/90GB02656

- Johnson, K.M., King, A.E. and Sieburth, J.M., 1985. Coulometric TCO₂ analyses for marine studies; an introduction. *Marine Chemistry*, 16(1): 61-82, 10.1016/0304-4203(85)90028-3
- Johnson, K.M., Sieburth, J.M., Williams, P.J.I. and Brändström, L., 1987. Coulometric total carbon dioxide analysis for marine studies: Automation and calibration. *Marine Chemistry*, 21(2): 117-133, 10.1016/0304-4203(87)90033-8
- Johnson, K.M., Wills, K.D., Butler, D.B., Johnson, W.K. and Wong, C.S., 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. *Marine Chemistry*, 44(2-4): 167-187, 10.1016/0304-4203(93)90201-X
- Patsavas, M.C., Byrne, R.H. and Liu, X., 2013. Purification of meta-cresol purple and cresol red by flash chromatography: Procedures for ensuring accurate spectrophotometric seawater pH measurements. *Marine Chemistry*, 150: 19-24, 10.1016/j.marchem.2013.01.004

5.3 Trace metals and clean sampling

M. Rijkenberg, J. Bown, L. Gerringa, J. van Ooijen, H. Slagter (NIOZ), L.-E. Heimbürger (UB), A Gonzales (IUEM), H. de Baar (not on board),

Objectives

During this cruise we plan to sample 40 full depth stations for dissolved Al, the suite of bio-essential trace metal elements Mn, Fe, Co, Ni, Cu, Zn, Cd and the mostly anthropogenic (pollutant and/or potentially toxic) trace metals Hg and Pb.

Work at sea

Samples will be taken with a system for ultra clean trace metal sampling consisting of an all-titanium frame with 24 sample bottles of 24 L each made of polypropylene. Sampling of the ultra clean sampling system will occur in a class 100 clean-room container (de Baar et al., 2008; Rijkenberg et al., submitted) where samples will be directly filtered under nitrogen pressure using 0.2 µm Sartobran 300 cartridges (Sartorius).

On board we will measure the nutrients, phosphate, silicate, nitrite and nitrate, dissolved Fe, the organic speciation of Fe, dissolved Co and possibly dissolved Al, reactive Hg, total Hg and dissolved gaseous Hg. At the home laboratories we will measure methylHg and inorganic Hg, using species specific isotope dilution GC-SF-ICP-MS and, using very new methodology, a suite of twelve trace metals including lead, cadmium, copper, zinc in each sample. Library samples collected during our preceding Arctic expedition in 2007 can now be measured for the same trace metals. This allows us to couple changes (2007 versus 2015/2016) in the distribution of these trace metals with climate induced changes in the Arctic Ocean. Below the separate sub-projects will be discussed in more detail.

Data management

See chapter 5 for details on data management.

References

- de Baar, H.J.W., Timmermans, K.R., Laan, P., De Porto, H.H., Ober, S., Blom, J.J., Bakker, M.C., Schilling, J., Sarthou, G., Smit, M.G., Klunder, M., 2008. Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. *Mar. Chem.*, 111(1-2): 4-21.
- Rijkenberg, M.J.A., de Baar, H.J.W. Bakker, K. Gerringa, L.J.A. Keijzer, E. Laan, M., P. Laan, R. Middag, S. Ober, J. van Ooijen, S. Ossebaar, E.M. van Weerlee, M.G. Smit: "PRISTINE", a new high volume sampler for ultraclean sampling of trace metals and isotopes (submitted to *Mar Chem*).

5.4 Dissolved Al

M. Rutgers van der Loeff (AWI), R. Middag (not on board)

Objective

Dissolved Al is a trace metal with a scavenged-type distribution and an extreme difference between the extremely low concentrations in the North Pacific and the elevated concentrations in the North Atlantic; varying by greater than two orders-of-magnitude (Orlans and Bruland, 1985). The distribution of dissolved Al in surface waters of the open ocean is influenced by atmospheric dust inputs (Measures et al., 2008) and variations in the intensity of removal by scavenging. Dissolved Al was measured in the Arctic Ocean during ARK XXII/2 by Middag et al., in 2007. Very low, concentrations in the surface layer showed that there is no or little influence from aeolian dust input in Arctic. Dissolved Al showed a nutrient-type increase with depth up to 28 nM, but large differences existed between the different deep Arctic basins.

Work at sea

Dissolved Al will be measured directly from all samples collected with the ultra-clean CTD using shipboard FIA measurements. In a continuous FIA system, the acidified pH 1.8, filtered (0.2 µm) seawater is buffered to pH 5.5. The metal is concentrated on a column, which contains the chelating material aminodiacetic acid (IDA). This material binds only transition metals and not the interfering salts. After washing of the column with ultra pure water (MQ) the column is eluted with diluted acid (0.1 M HCl). The Al is determined using Lumogallion after Brown and Bruland (2008). Lumogallion is a fluorometric agent and reacts with aluminum. The change in the fluorescence detected by a fluorometer is used as a measure for the dissolved Al concentration. In order to verify the consistency of the analysis, every day a sample was measured from a check sample that was taken in the beginning of the cruise. Also a duplicate sample was taken every cast and this sample was analysed with the samples of the next cast to further check for inter daily variation. Furthermore, a GEOTRACES seawater reference sample was analysed regularly and the values are consistent with those found previously.

If analysis on board is not possible, samples will be collected by the NIOZ trace metal party for later analysis in the home laboratory.

Data management

See chapter 5 for details on data management.

References

- Brown, M.T., Bruland, K.W., 2008. An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. *Limnology and Oceanography Methods* 6, 87-95
- Measures, C.I., Landing, W.M., Brown, M.T., Buck, C.S. 2008. High-resolution Al and Fe data from the Atlantic Ocean CLIVAR-CO2 Repeat Hydrography A16N transect: Extensive linkages between atmospheric dust and upper ocean geochemistry. *Global Biogeochemical Cycles* 22, GB1005.
- Middag, R., H.J.W. de Baar, P. Laan, K. Bakker., Dissolved aluminium and the silicon cycle in the Arctic Ocean, *Marine Chemistry* (2009), doi:[10.1016/j.marchem.2009.08.002](https://doi.org/10.1016/j.marchem.2009.08.002)
- Orlans, K.J., Bruland, K.W., 1985. Dissolved aluminum in the Central North Pacific. *Nature* 316 (6027), 427– 429.

5.5 Dissolved Fe, Mn, Zn, Ni, Cu, Cd, Pb

M. J.A. Rijkenberg (NIOZ)

Objective

In contrast to other oceans, the Arctic Ocean has high concentrations of dissolved Fe (DFe) in the surface layers, relative to lower concentrations at depth. These high surface concentrations are due to Siberian and North American rivers giving a strong lateral DFe supply into the stratified surface layers combined with relatively little vertical mixing (Klunder et al., 2012a; 2012b).

In this cruise we will focus on the exchange between the enriched surface layer and the deep water. We will investigate the forms, complexed by organic ligands, bound in colloids or as particles, in which Fe enter the Arctic Ocean. What physical and chemical changes occur in the photic zone and in the deep waters to explain the depth profiles as found by Klunder et al., 2012a and 2012b). Samples will be taken from different size fractions, a.o. unfiltered samples and filtered by different filter sizes (a.o., 0.2 μm ; 0.02 μm) and particulate material. This will be done in close cooperation with L. Gerringa and H. Slagter who will investigate the organic complexation of Fe and the resistance of organic ligands to degradation.

Much less is known about the distribution of dissolved Zn, Ni, Cu, Cd, Pb, Ga, Ti, La, Zr, Sc, V and Y in the Arctic Ocean. We will collect 0.2 μm filtered seawater samples during TransARCII (PS94) and compare these with the outcome of similar measurements on library samples collected during our preceding Arctic expedition in 2007. This allows us to couple changes (2007 versus 2015/2016) in the distribution of these trace metals with climate induced changes in the Arctic Ocean.

Work at sea

DFe concentrations will be measured directly on board by the automated Flow Injection Analysis (FIA) method (Klunder et al., 2011). Filtered and acidified (Seastar© baseline hydrochloric acid; pH 1.7) seawater will be concentrated on a column containing amino-di-acetic acid (IDA). Samples will be analysed in triplicate and standard deviations (SD) are given. The consistency of the FIA system over the course of a day will be verified by measuring the same seawater sample several times. Certified SAFe standards (Johnson et al., 2007) for the long term consistency and absolute accuracy will be measured on a regular basis. Samples will be taken for particulate trace metals. Filtered seawater samples will be taken for the measurements of dissolved Zn, Ni, Cu, Cd, Pb, Ga, Ti, La, Zr, Sc, V and Y.

Data management

See chapter 5 for details on data management.

References

- Johnson, K.S., Boyle, E., Bruland, K., Measures, C., Moffett, J., Aquilarislas, A., Barbeau, K., Cai, Y., Chase, Z., Cullen, J., Doi, T., Elrod, V., Fitzwater, S., Gordon, M., King, A., Laan, P., Laglera-Baquer, L., Landing, W., Lohan, M., Mendez, J., Milne, A., Obata, H., Ossiander, L., Plant, J., Sarthou, G., Sedwick, P., Smith G.J., Sohst, B., Tanner, S., Van Den Berg, S., Wu, J., 2007. Developing standards for dissolved iron in seawater. *Eos Trans.* 88, 131.
- Klunder, M.B., Laan, P., Middag, R., De Baar, H.J.W., van Ooijen, J.C., 2011. Dissolved Fe in the Southern Ocean (Atlantic sector). *Deep-Sea Res.* II 58, 2678-2694.
- Klunder, M.B., Bauch, D., Laan, P., De Baar, H.J.W., van Heuven, S., Ober, S., 2012a. Dissolved iron in the Arctic shelf seas and surface waters of the central Arctic Ocean: Impact of Arctic river water and ice-melt. *J. Geophys Res.* 117, , C01027, doi:10.1029/2011JC007133.

Klunder, M.B., Laan, P., Middag, R., De Baar, H.J.W., Bakker, K., 2012b. Dissolved iron in the Arctic Ocean: Important role of hydrothermal sources, shelf input and scavenging removal. *J. Geophys. Res.* 117, C04014, doi:10.1029/2011JC007135.

5.6 Organic speciation of Fe

L. J. A. Gerringa, H. A. Slagter (NIOZ)

Objective

The binding of Fe by dissolved organic ligands may play an important role in the dissolution of Fe from dust, and in keeping Fe from rivers, ice melt and hydrothermal sources in the dissolved phase. Organic complexation influences the photochemistry and bioavailability of Fe. To allow biological utilization of Fe, part of the organically complexed Fe pool must be available for phytoplankton uptake. It is still not clear which part of the organically complexed Fe pool can be directly utilized by phytoplankton and how it is taken up. With voltammetric methods the ligand concentration and binding strength of the ligand with dissolved Fe(III) can be measured (Croot and Johansson, 2000; Laglera et al., 2013; Thuróczy et al., 2011). The excess ligand concentration over Fe is an indication of the solubility of Fe in the ocean. In most oceans this excess decreases with depth, however, in the Arctic Ocean the excess increases with depth. This might be due to the input of organic matter by Canadian and Siberian rivers. According to Klunder et al., (2012) this water is spread over the surface layer of Arctic Ocean. During this cruise we want to investigate in close co-operation with M. Rijkenberg what happens with these ligands introduced by the rivers. Are these ligands also transported to deeper layers and/or are they degraded by bacterial degradation? For this we will especially sample the surface layer of the Arctic Ocean and incubate samples to detect possible changes with time.

Work at sea

~900 mL FeL samples from the ultra clean CTD systems, filtered over a 0.2 µm filter using N₂ overpressure will be analysed as soon as possible on board (within two days). Two different methods will be applied using TAC (Croot and Johansson, 2000) and DHN (van den Berg 2006; Laglera et al., 2013) as competing ligands. The complex formed between Fe and the competing ligands will be measured after equilibration (> 6 h) by cathodic stripping voltammetry (CSV). The current signal recorded with this method (nA) will be converted into a concentration (nM), then the ligand concentration and the binding strength will be estimated using the non-linear regression of the Langmuir isotherm (Gerringa et al., 2014). CLE-CSV will be performed using a two setups consisting of a µAutolab potentiostat (Metrohm Autolab B.V., formerly Ecochemie, The Netherlands), a 663 VA stand with a Hg drop electrode (Metrohm) and a 778 sample processor with ancillary pumps and dosimats (Metrohm), all controlled using a consumer laptop running Nova 1.9 (Metrohm Autolab B.V.). The VA stands will be mounted on elastic-suspended wooden platforms in aluminium frames developed at the NIOZ to minimize motion-induced noise while electrical noise and backup power was provided by Fortress 750 UPS systems for spike suppression and line noise filtering (Best Power). Sample manipulations will be performed in laminar flow cabinets. Dissolved Fe necessary for the data interpretation will be measured in separated samples taken from the bottles sampled for Fe complexation, with Flow Injection Analysis (FIA) on board by Micha Rijkenberg.

Data management

See chapter 5 for details on data management.

References

- Croot P.L., Johanson M. (2000). Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-Thiazolylazo)-p-cresol (TAC). *Electroanalysis*. 12, No.8, 565-576.
- Gerringa, L.J.A. Rijkenberg, M.J.A., Thuróczy, C-E, Maas, L.R.M., 2014. A critical look at the calculation of the binding characteristics and concentration of iron complexing ligands in seawater with suggested improvements. *Environmental Chemistry*, 11, 114-136. <http://dx.doi.org/10.1071/EN13072>
- Klunder, M.B., Laan, P., Middag, R., De Baar, H.J.W., Bakker, K., 2012b. Dissolved iron in the Arctic Ocean: Important role of hydrothermal sources, shelf input and scavenging removal. *J. Geophys. Res.* 117, C04014, doi:10.1029/2011JC007135.
- Laglera, L.M., Santos-Echandia, J., Caprara, S., Monticelli, D., 2013. Quantification of Iron in Seawater at the Low Picomolar Range Based on Optimization of Bromate / Ammonia / Dihydroxynaphthalene System by Catalytic Adsorptive Cathodic Stripping Voltammetry. *Anal. Chem.*, 85, 2486-2492.
- Thuróczy, C.-E., L.J.A. Gerringa, M. Klunder, P. Laan, M. le Guitton, H.J.W. de Baar, 2011. Distinct trends in the speciation of iron between the shelf seas and the deep basins of the Arctic Ocean. *Oceans J. Geophys. Res.*, VOL. 116, C10009, doi:10.1029/2010JC006835.
- Van Den Berg, C.M.G., 2006. Chemical Speciation of Iron in Seawater by Cathodic Stripping Voltammetry with Dihydroxynaphthalene. *Analytical Chemistry*, 78, 156-163.

5.7 Co biogeochemical cycle

J. Bown (NIOZ)

Objectives

Cobalt (Co), is present in oceanic waters at extremely low concentrations (10^{-12} mol.l⁻¹) but is nevertheless involved in important biological functions for phytoplankton growth, such as B₁₂ vitamin and carbonic anhydrase enzyme (Morel et al., 2004). Cobalt can also limit growth of key photosynthetic organisms like cyanobacteria, most abundant in oligotrophic regions (Saito et al., 2002), or affect the growth of *Phaeocystis Antarctica*, an alga that is able to grow underneath or in sea-ice in Antarctica (Saito et al., 2008). Because of the harsh climatic conditions, very little research has been conducted in the Arctic Ocean, however, a recent study depicted massive phytoplankton blooms underneath sea-ice (Arrigo et al., 2012). The key role of Co within critical biological functions and the specific Co requirements of different phytoplankton species suggest that Co could be a key factor for primary production and the composition of phytoplankton communities in the Arctic Ocean.

For the first time Co concentrations will be measured for the whole water column in contrasted regions of the Arctic Ocean in order to identify and quantify physical and biogeochemical processes that control Co vertical distributions.

Work at sea

The work onboard will mainly consist of ultraclean sampling for trace elements and isotopes and of dissolved cobalt measurements by flow injection analysis (Bown et al., 2011). Samples for studying cobalt organic speciation will also be collected and measured back in the laboratory by voltammetry (Bown et al., 2012).

Data management

See chapter 5 for details on data management.

References

- Arrigo, K. R., D. K. Perovich, R. S. Pickart, Z. W. Brown, G. L. van Dijken, K. E. Lowry, M. M. Mills, M. A. Palmer, W. M. Balch, F. Bahr, N. R. Bates, C. Benitez-Nelson, B. Bowler, E. Brownlee, J. K. Ehn, K. E. Frey, R. Garley, S. R. Laney, L. Lubelczyk, J. Mathis, A. Matsuoka, B. G. Mitchell, G. W. K. Moore, E. Ortega-Retuerta, S. Pal, C. M. Polashenski, R. A. Reynolds, B. Scheiber, H. M. Sosik, M. Stephens, J. H. Swift, (2012). Massive phytoplankton blooms under Arctic sea ice, *Science*.
- Bown, J., Boye, M., Baker, A., Duvieilbourg, E., Lacan, F., Le Moigne, F., Planchon, F., Speich, S. and Nelson D. M., (2011), The biogeochemical cycle of dissolved cobalt in the Atlantic and the Southern Ocean south off the coast of South Africa, *Marine Chemistry*, 126(1-4).
- Bown, J., Boye, M., & Nelson, D. M. (2012). New insights on the role of organic speciation in the biogeochemical cycle of dissolved cobalt in the southeastern Atlantic and the Southern Ocean. *Biogeosciences*, 9, 2719-2736.
- Morel, F. M.M., Milligan, A.J., Saito, M.A., Heinrich, D.H., and Karl, K.T., (2003), Marine Bioinorganic Chemistry: The Role of Trace Metals in the Oceanic Cycles of Major Nutrients, *Treatise on Geochemistry*, Pergamon, Oxford, 113–143.
- Saito, M.A., Moffett, J.W., Chisholm, S.W., and Waterbury, J.B., (2002), Cobalt limitation and uptake in *Prochlorococcus*, *Limnology & Oceanography*, 47, 1629–1636, 2002.
- Saito, M. A. and Goepfert, T.J. (2008), Zinc-cobalt colimitation of *Phaeocystis antarctica*, *Limnology & Oceanography*, 53, 266–275.

5.8 Hg

L.-E. Heimbürger (UB)

Objectives

Mercury levels in Arctic biota are among the highest in aquatic ecosystems and impact the health of Arctic wildlife and human populations (AMAP 2011). The idea has taken hold that the Arctic is a global mercury sink and that its main entry route is *via* the atmosphere (AMAP 2011). A recent three-dimensional GEOS-Chem model run by Fisher et al. (2013) puts both ideas into question and argues that the Arctic Ocean is net source and boreal rivers to be the major input (Sonke and Heimbürger 2012). Their findings shift current paradigms of the Arctic mercury research that has focused for the past 20 years on atmospheric phenomena and cycling (e.g. atmospheric mercury depletion events). It has been shown for the Arctic (Beattie et al. 2014) and for Antarctica (Cossa et al. 2011) that sea ice, in particular brine formation is a major player in polar Hg budgets. Yet, the Arctic Ocean itself remains under-sampled. No central Arctic Ocean mercury profiles have been published thus far. This is why the following key questions remain to be answered:

- Is the Arctic Ocean a global sink or a source for mercury?
- What is the cause for the high mercury concentrations in Arctic marine biota: anthropogenic Hg emissions or is that a “normal natural” phenomenon?
- What is the impact of boreal rivers: how much of the dissolved and particulate mercury is transported to the central Arctic Ocean?
- How much of the rapidly deposited mercury during atmospheric mercury depletion events is re-emitted to the atmosphere and which portion of it is bioavailable (bio-amplified along the marine food chain)?
- What is the overall impact of warming climate to the Arctic Mercury cycle? Will warming climate shift Hg’s biogeochemical cycle and the functioning of the Arctic ecosystems in a way that we should expect even higher methylmercury levels in marine biota?

Our few preliminary results from the 2011 *Polarstern* Arctic cruise show that:

- Methylmercury concentrations in the Arctic Ocean are highest in the marginal sea ice zone and just below the halocline (~200 m-depth)
- Methylmercury concentrations are among the highest observed (together with the Mediterranean Sea (Heimbürger et al. 2010) and the Southern Ocean (Cossa et al. 2011)) in the Global Ocean
- Total mercury concentrations of the Central Arctic Ocean are suggest anthropogenic enrichments (Lamborg et al. 2014)

Work at sea

- High resolution sampling for mercury species (including methylmercury), with particular focus on halocline and gradient along the sea ice edge
- At ice stations we will measure Hg in the sea ice, snow cover, brine and in the water column directly below the sea ice
- Atmospheric Hg sampling
- Analysis on board: reactive mercury Hg_R, total mercury (Hg_T) and dissolved gaseous mercury (DGM)
- Analysis at home lab: MeHg and inorganic Hg
- Applications of new tracer: mercury stable isotopes to track sources and processes that govern Arctic Mercury cycling (large volumes required at 2 or 3 selected stations)
- 2015 GEOTRACES Hg species in sea water intercalibration at crossover station with US

Expected results

Alarming rise in Hg levels of Arctic marine biota has been attributed to increased anthropogenic Hg emissions. However, the Hg species that accumulates along the trophic chain is MeHg. MeHg is produced in the oceanic water column during the remineralization of organic matter. This process seems to be independent from atmospheric Hg deposition. The basis of the food web structure determines the amount of MeHg that is produced *in-situ*. We will measure the first high resolution transect for MeHg in the central Arctic Ocean. This is critical to understand marine MeHg production and to predict the impact of ongoing global warming on the Arctic Hg cycles.

- Attempt to include marine inorganic Hg and methylHg species in an Arctic Hg mass balance model
- Determine the role of sea ice in controlling Hg species dynamics
- Exploring the role of the Arctic Ocean in the global mercury cycle

Data management

See chapter 5 for details on data management.

References

- AMAP (2011). AMAP Assessment 2011: Mercury in the Arctic. Oslo, Norway.
- Beattie, S. A., D. Armstrong, A. Chaulk, J. Comte, M. Gosselin and F. Wang (2014). "Total and Methylated Mercury in Arctic Multiyear Sea Ice." *Environmental Science & Technology* 48(10): 5575-5582.
- Cossa, D., L. E. Heimbürger, D. Lannuzel, S. R. Rintoul, E. C. V. Butler, A. R. Bowie, B. Averty, R. J. Watson and T. Remenyi (2011). "Mercury in the Southern Ocean." *Geochimica Et Cosmochimica Acta* 75(14): 4037-4052.

- Fisher, J. A., D. J. Jacob, A. L. Soerensen, H. M. Amos, E. S. Corbitt, D. G. Streets, Q. Wang, R. M. Yantosca and E. M. Sunderland (2013). "Factors driving mercury variability in the Arctic atmosphere and ocean over the past 30 years." *Global Biogeochemical Cycles*: 2013GB004689.
- Heimbürger, L. E., D. Cossa, J.-C. Marty, C. Migon, B. Averty, A. Dufour and J. Ras (2010). "Methylmercury distributions in relation to the presence of nano- and picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean)." *Geochimica Et Cosmochimica Acta* 74(19): 5549-5559.
- Lamborg, C. H., C. R. Hammerschmidt, K. L. Bowman, G. J. Swarr, K. M. Munson, D. C. Ohnemus, P. J. Lam, L. E. Heimbürger, M. J. A. Rijkenberg and M. A. Saito (2014). "A global ocean inventory of anthropogenic mercury based on water column measurements." *Nature* 512(7512): 65-68.
- Sonke, J. E. and L. E. Heimbürger (2012). "Environmental science: Mercury in flux." *Nature Geosci* 5(7): 447-448.

5.9 Fe Isotopic composition

M. Staubwasser (UNIK)

Objectives

The objectives are: 1) To sample depth profiles across the Transpolar drift and the Siberian shelf to analyze the Fe isotope composition of dissolved Fe and particulate Fe and map the Fe isotope distribution in the Arctic Sea. 2) To trace a potential Fe-isotopic signature in the water column from sedimentary diagenetic Fe reflux and/or resuspension from shelf sediments. 3) To study the impact of isotopic exchange between dissolved Fe and particle surface-bound Fe on marine particles in order to clarify to what extent the isotopic composition of dissolved Fe can be considered conservative – which is a requirement for using Fe isotopes as a source tracer.

Work at sea

Objectives 1) and 2) require ultra clean filtration of up to 4L of seawater from depth profiles for lab based isotope analysis. Objective 3) is essentially a first attempt to sample the exchangeable surface-bound Fe from suspended particles by two different approaches. One is to attempt chemical leaching of surface-bound Fe from suspended particles collected on cartridge filters from large volumes of seawater. The other is to collect suspended particles from large volumes by ultrafiltration and performing exchange reactions with a ⁵⁸Fe enriched isotope in bottle experiments on board.

Expected outcome

Based on a study on dissolved Fe by Klunder et al. (2012) in the Arctic Ocean, who showed unusually high surface / near-surface concentrations of well above 1 nM within the Transpolar Drift, and low concentrations outside the Drift as well as in the deep open ocean, I expect to find an isotopic contrast that may reveal information about the source of Fe inside the Drift. The same study showed high concentration in shelf bottom waters and in surface waters close to arctic river estuaries. This may indicate two potential sources of dissolved Fe in the Transpolar Drift. One source may be directly related to discharge from rivers with high Fe concentration – responsible for high surface concentrations near estuaries – while another is indirectly related to particle deposition and high rates of diagenetic reflux or resuspension rates from the shelf bottom near river mouths. The two sources should carry different isotopic composition due to different dissolution mechanisms (Anbar & Rouxel 2007). However, solution-particle exchange on oxidative reprecipitation of diagenetic reflux Fe (e.g. Staubwasser et al., 2013a) and/or subsequent exchange with mineral surface-bound Fe – which is the main control in sediment pore space (Staubwasser et al., 2013b) – may alter the isotopic composition of dissolved Fe on transport off the shelf region. The initial

experiments to be conducted (objective 3) should reveal whether this aspect has to be considered when using mass balancing approaches to calculate Fe fluxes from isotope measurements within the GEOTRACES studies (e.g. Convoy et al., 2014).

Data management

See chapter 5 for details on data management.

References

- Anbar & Rouxel (2007). *Ann. Rev. Earth Planet. Sci.* 2007. 35:717–46
- Convoy & John (2014). *Nature* 511, 212–215
- Klunder, Bauch, Laan, de Baar, van Heuven and Ober (2012). *J. Geophys. Res.* 117, C01027, doi:10.1029/2011JC007133
- Staubwasser, Schoenberg, von Blanckenburg, Krüger and Pohl (2013a). *Biogeosciences*, 10, 233–245
- Staubwasser, Henkel, Kasten, and Poulton, (2013b). *Mineralogical Magazine - S: Goldschmidt Abstracts 2013*, 77 (5), p. 2253 . doi: 10.1180/minmag.2013.077.5.19

5.10 Neodymium isotopes, rare earth element concentrations and long-lived natural radionuclides

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Objectives

The unique conditions in the Arctic of input, removal, and exchange processes in relation to particle composition, particle fluxes, and circulation are acting on trace element and isotope distributions in the Arctic Ocean. These distributions are sensitive to the environmental changes already taking place in the Arctic. We propose, that the processes in this region can be ideally addressed by a combined study of Nd isotopes ($^{143}\text{Nd}/^{144}\text{Nd}$, ϵ_{Nd}), rare earth elements (REE), Th isotopes and ^{231}Pa , and that the results will add important insights into trace element and isotope biogeochemistry in the Arctic. Moreover, the simultaneous analysis of the other GEOTRACES key parameters on the same cruise and on all cruises of our international partners (US, Canada) will provide a solid basis for the evaluation and modelling of biogeochemical processes in the Arctic.

Our study will test the following overriding hypothesis:

The exceptional conditions in the Arctic Ocean of high continental inputs and extended shelf areas, contrasting with low particle fluxes and low opal production in the deep basins uniquely affect the distribution and budgets of ϵ_{Nd} , REE, Th isotopes, and ^{231}Pa . A detailed study of these tracers will help to understand their behaviour in the Arctic Ocean, with relevance for the processes controlling these and other trace element and isotope distributions globally.

Specific objectives of the proposed work to test this hypothesis include:

- Investigation of the effect of particles on the distribution of ϵ_{Nd} , REEs, Th isotopes, and ^{231}Pa (and by extension, on other TEIs) in the water column with a particular focus on particle composition (opal-rich vs. opal-poor), particle fluxes, and terrigenous input.
- Investigation of exchange processes at the margins with exceptionally large shelf areas (ϵ_{Nd} for margin-seawater exchange, Th and Pa isotopes for boundary scavenging) and provenance of particles supplied to the Arctic by rivers and ice.

- Determination of whether changes in the circulation of the Beaufort Gyre have led to further changes in the distribution of dissolved ^{230}Th , ^{231}Pa , REE, and Nd isotopes in comparison to the situation in 1991-2001.
- Investigation of the REE and Nd isotopic composition of the contributions of Siberian rivers and Pacific water to the Arctic.
- Determination of the influence of hydrothermal activity at Gakkel Ridge on seawater ϵ_{Nd} , REE, and Th, Pa isotopes.

In more detail, we want to exploit the unique boundary conditions in the Arctic and their strong contrast to those in other ocean basins, particularly those in the Southern Ocean, to improve our understanding of biogeochemical processes in the ocean in general and the Arctic in particular and to develop a common interpretation of these tracers. We particularly hope to see to what extent the large continental inputs in the Arctic (river, shelf, dirty ice) affect ϵ_{Nd} and REE in the water column and how the low opal content in the Arctic compared to the large range in opal concentrations in the Southern Ocean influences the vertical REE distribution and contributes to a less efficient separation between ^{231}Pa and ^{230}Th in the Arctic. Terrigenous particles are transported to the central Arctic both in suspension in river water and ice rafted in “dirty ice”. The combined analysis of Nd and Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) on terrigenous river and dirty ice particles will provide insight into the provenance of particles as well as particle-seawater interactions and lateral transport of particles. In turn, this will afford insight into the potential impact of future changes on these distributions.

We will further investigate the relative contributions of Pacific and Atlantic waters in the Arctic using their distinct ϵ_{Nd} signatures, and investigate whether the recently reported circulation changes and freshwater input to the Arctic over the past decade (Karcher et al., 2012) have also impacted the trace element and isotope distributions in the Arctic since the first studies were carried out (samples collected in 2000-2001: ^{230}Th , ^{231}Pa by Bacon et al. (1989) Scholten et al. (1995), Edmonds et al. (2004), and ourselves (unpublished results), obtained in the years 1983, 1991, 1994, 2007: ϵ_{Nd} and REE from (Andersson et al., 2008; Porcelli et al., 2009; Zimmermann et al., 2009).

The study of REE, Nd and Th isotopes and ^{231}Pa in the water column and particles in the Arctic (this cruise, and US and Canadian cruises) will provide a baseline of their distributions for the evaluation of expected future changes in this rapidly changing environment.

Work at sea

Water column sampling at 16 stations (up to 16 depths per station) for dissolved REE, Nd and Th isotopes and ^{231}Pa will be realized by direct filtration of seawater from Niskin bottles using AcroPak500 cartridges (0.8/0.45 μm pore size, Supor[®] pleated membrane). For dissolved isotope samples we require 15-25L per sample, for REE concentrations we will collect 100 ml. All samples will be acidified to pH = 3.5 to 2 using 6N ultra-clean hydrochloric or nitric acid. Samples for Nd isotopes will be preconcentrated onboard using C18 cartridges (Waters Inc.) filled with a complexing agent. Suspended particles will be sampled from up to 13 depths per station at up to 12 stations using *in-situ* pumps. The filters will be prepared, cut, and stored in plastic sample bags onboard under a laminar flow hood with HEPA filter.

We plan to collect dirty ice (2-30L, depending on particle concentration) using stainless steel tools at 10 stations. The dirty ice will be allowed to melt and we will collect the particles by filtration over the same filter type used for suspended particles (Supor[®]-0.8 μm).

If available, we will also collect surface sediments (1-2g dry weight) for Nd isotope, $^{231}\text{Pa}/^{230}\text{Th}$ and REE analyses on the lithogenic and authigenic phases for the determination

of sediment provenance and direct comparison of authigenic ϵ_{Nd} with the overlying bottom water, respectively.

Expected results

The results will provide an unprecedented spatial and vertical resolution of dissolved and particulate REE, Nd and Th isotope and ^{231}Pa distributions in the Central Arctic. The results are expected to provide insight into the terrigenous sources to the Arctic, their impact on the dissolved trace element and isotope distributions, and the influence of rivers and Pacific and Atlantic waters on these distributions. Additionally, we expect to be able to evaluate the results with respect to data collected on previous expeditions (1991-2001).

Data management

See chapter 5 for details on data management.

References

- Andersson, P.S., Porcelli, D., Frank, M., Björk, G., Dahlqvist, R., Gustafsson, Ö., 2008. Neodymium isotopes in seawater from the Barents Sea and Fram Strait Arctic-Atlantic gateways. *Geochim. Cosmochim. Acta* 72, 2854-2867.
- Bacon, M.P., Huh, C.-A., Moore, R.M., 1989. Vertical profiles of some natural radionuclides over the Alpha Ridge, Arctic Ocean. *Earth Planet. Sci. Lett.* 95, 15-22.
- Edmonds, H.N., Moran, S.B., Cheng, H., Edwards, R.L., 2004. ^{230}Th and ^{231}Pa in the Arctic Ocean: implications for particle fluxes and basin-scale Th/Pa fractionation. *Earth Planet. Sci. Lett.* 227, 155-167.
- Karcher, M., Smith, J.N., Kauker, F., Gerdes, R., Smethie, W.M., 2012. Recent changes in Arctic Ocean circulation revealed by iodine-129 observations and modeling. *J. Geophys. Res.* 117, C08007.
- Porcelli, D., Andersson, P.S., Baskaran, M., Frank, M., Björk, G., Semiletov, I., 2009. The distribution of neodymium isotopes in Arctic Ocean basins. *Geochim. Cosmochim. Acta* 73, 2645-2659.
- Scholten, J.C., Rutgers van der Loeff, M.M., Michel, A., 1995. Distribution of ^{230}Th and ^{231}Pa in the water column in relation to the ventilation of the deep Arctic basins. *Deep Sea Res. II* 42, 1519-1531.
- Zimmermann, B., Porcelli, D., Frank, M., Andersson, P.S., Baskaran, M., Lee, D., Halliday, A.N., 2009. Hafnium isotopes in Arctic Ocean water. *Geochim. Cosmochim. Acta* 73, 3118-3233.

5.11 Natural radionuclides – short lived

V. Puigcorbé (UAB), N. Casacuberta (LIP), M. Rutgers van der Loeff (AWI), P. Masqué (not on board)

^{234}Th and ^{210}Po as tracers of export production of POC

Objectives

Part of the carbon dioxide fixed in photosynthesis is transferred to the interior of the ocean, mainly by gravitational settling of particulate organic carbon (POC). Quantifying this export is essential for determining the efficiency of the biological carbon pump, which is a key component of the marine and global carbon cycle. Besides carbon, the vertical drawdown of particles connects the ocean surface with the deep waters, affecting the distribution of nutrients and biominerals and it represents an important food source for pelagic but also for benthic organisms (Smith et al., 2008), making the study of the particle cycling of broad interest for a variety of research fields.

The natural pairs of radionuclides $^{234}Th/^{238}U$ and $^{210}Po/^{210}Pb$ have been frequently used to provide information on particle export and export production (Benitez-Nelson and Moore, 2006; Buesseler et al., 1992; Verdeny et al., 2009). In a closed system, a radioactive isotope

should be in secular equilibrium with its progeny. In the oceanic water column, a deficit of the decay product with respect to the concentration of the parent is found when its particle affinity is larger, due to removal by uptake by particles. Disequilibria among the activities of these tracer pairs indicate exportation to deeper waters, and it can be used to derive the flux of particles that are removed from the surface layer on time scales of weeks (half life of ^{234}Th = 24 days) to months (half life of ^{210}Po = 138 days), becoming a powerful tool for tracing export events occurring on similar time scales such as phytoplankton blooms.

Our objective is to quantify the POC export flux by measuring the depletion of these radionuclides with respect to their parents in the upper water column. Different ice coverage conditions will be sampled in order to better assess the influence of ice thickness and the timing of the ice melting on particle export. In order to convert the radionuclide fluxes to a POC export fluxes, $\text{POC}/^{234}\text{Th}$ and $\text{POC}/^{210}\text{Po}$ ratios will be determined in sinking particles (e.g. Buesseler et al., 2006).

Work at sea

During this cruise we plan to collect about 300 water samples to analyze total ^{234}Th and total ^{210}Po . In addition, at some stations, triplicates of deep samples (2500 m) will be collected for calibration purposes. Total ^{234}Th concentrations will be determined from 4L of seawater collected at 12 depths along the upper 400 m. Deeper profiles might also be obtained at specific stations to examine particle dynamics in near-bottom and margins areas, driven by sediment resuspension and scavenging by hydrothermal vents. Total ^{210}Po and ^{210}Pb concentrations will be determined from 10L samples collected in parallel with the ^{234}Th samples.

The ^{234}Th samples will be processed according to the MnO_2 co-precipitation technique (Benitez-Nelson et al., 2001; Pike et al., 2005) and counted on board using low background beta counters (Risø National Laboratories). Due to the conservative behavior of uranium in seawater, its activity is typically derived from salinity (Owens et al., 2011). However, additional seawater samples will be collected at some stations to measure ^{238}U by inductively coupled plasma mass spectrometry (ICP-MS) to confirm the U-Salinity relationship.

The ^{210}Po and ^{210}Pb samples will be processed according to the Co-APDC chelate co-precipitation technique, adapted from Boyle and Edmond (1975). During the cruise only the precipitation and filtration steps will be carried out. The rest of the radiochemical procedure will be done in the home laboratory, as well as the measurements by alpha spectrometry (Rigaud et al., 2013).

Particulate samples will be collected using *in-situ* Challenger filtration pumps deployed below the euphotic zone and at a greater depth (100 m below the euphotic zone). Additional particulate samples will be collected from the CTD rosette bottles in order to complement the *in-situ* pump samples. An attempt to obtain size-fractionated samples (1-53 μm and >53 μm) will be done by using a two filter support head for the *in-situ* pump. ^{234}Th particulate samples will be counted on board on low background beta counters whereas particulate samples to analyze ^{210}Po , C and N will be processed and measured at the home laboratory.

Expected results

Results obtained from these samples are expected to provide insights into particle export in the central Arctic. This area is known to have low export production (Cai et al., 2010; Lalande et al., 2014) but the rapid reduction in sea ice cover might alter the phytoplankton community and increase primary productivity (Arrigo et al., 2008; Frey et al., 2014), therefore affecting POC export and other elements' biogeochemical budgets (Boetius et al., 2013). Additionally, the data covering the entire water column down to the sea-bed might bring to light features

related to particle dynamics in intermediate and deep waters that have been previously undersampled.

Data management

See chapter 5 for details on data management.

References

- Arrigo, K.R., van Dijken, G., Pabi, S., 2008. Impact of a shrinking Arctic ice cover on marine primary production. *Geophys. Res. Lett.* 35, L19603.
- Benitez-Nelson, C., Buesseler, K.O., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G., Charette, M.A., 2001. Testing a new small-volume technique for determining ^{234}Th in seawater. *J. Radioanal. Nucl. Chem.* 248, 795–799.
- Benitez-Nelson, C.R., Moore, W.S., 2006. Future applications of ^{234}Th in aquatic ecosystems. *Mar. Chem.* 100, 163–165.
- Boetius, A., Albrecht, S., Bakker, K., Bienhold, C., Felden, J., Fernández-Méndez, M., Hendricks, S., Katlein, C., Lalande, C., Krumpen, T., 2013. Export of algal biomass from the melting Arctic sea ice. *Science* 339, 1430–1432.
- Boyle, E.A., Edmond, J.M., 1975. Determination of trace metals in aqueous solution by APDC chelate co-precipitation. *Anal. methods Oceanogr.* 44.
- Buesseler, K.O., Bacon, M.P., Kirk Cochran, J., Livingston, H.D., 1992. Carbon and nitrogen export during the JGOFS North Atlantic Bloom Experiment estimated from ^{234}Th : ^{238}U disequilibria. *Deep Sea Res. Part A. Oceanographic Res. Pap.* 39, 1115–1137.
- Buesseler, K.O., Benitez-Nelson, C.R., Moran, S.B., Burd, A., Charette, M., Cochran, J.K., Coppola, L., Fisher, N.S., Fowler, S.W., Gardner, W.D., 2006. An assessment of particulate organic carbon to thorium-234 ratios in the ocean and their impact on the application of ^{234}Th as a POC flux proxy. *Mar. Chem.* 100, 213–233.
- Cai, P., Rutgers van der Loeff, M., Stimac, I., Nöthig, E.M., Lepore, K., Moran, S.B., 2010. Low export flux of particulate organic carbon in the central Arctic Ocean as revealed by ^{234}Th : ^{238}U disequilibrium. *J. Geophys. Res.* 115, C10037.
- Frey, K.E., Comiso, J.C., Cooper, L.W., Gradinger, R.R., Grebmeier, J.M., Saitoh, S.-I., Tremblay, J.-É., 2014. Arctic Ocean Primary Productivity [in Arctic Report Card 2014], Arctic Report Card 2014.
- Lalande, C., Nöthig, E.-M., Somavilla, R., Bauerfeind, E., Shevchenko, V., Okolodkov, Y., 2014. Variability in under-ice export fluxes of biogenic matter in the Arctic Ocean. *Global Biogeochem. Cycles* 2013GB004735.
- Owens, S.A., Buesseler, K.O., Sims, K.W.W., 2011. Re-evaluating the ^{238}U -salinity relationship in seawater: Implications for the ^{238}U - ^{234}Th disequilibrium method. *Mar. Chem.* 127, 31–39.
- Pike, S.M., Buesseler, K.O., Andrews, J., Savoye, N., 2005. Quantification of Th-234 recovery in small volume seawater samples by inductively coupled plasma-mass spectrometry. *J. Radioanal. Nucl. Chem.* 263, 355–360.
- Rigaud, S., Puigcorbé, V., Cámara-Mor, P., Casacuberta, N., Roca-Martí, M., Garcia-Orellana, J., Benitez-Nelson, C.R., Masqué, P., Church, T., 2013. A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of ^{210}Po and ^{210}Pb activities in seawater. *Limnol. Ocean. Methods* 11, 561–571.
- Smith, C.R., Leo, F.C. De, Bernardino, A.F., Sweetman, A.K., Arbizu, P.M., 2008. Abyssal food limitation, ecosystem structure and climate change. *Trends Ecol. Evol.* 23, 518–528.
- Verdeny, E., Masqué, P., Garcia-Orellana, J., Hanfland, C., Kirk Cochran, J., Stewart, G.M., 2009. POC export from ocean surface waters by means of ^{234}Th / ^{238}U and ^{210}Po / ^{210}Pb disequilibria: A review of the use of two radiotracer pairs. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 56, 1502–1518.

5.12 Radium isotopes

Objectives

Four natural isotopes of radium (the radium quartet) occur in the ocean. ^{228}Ra (half life 5.8y) is a known tracer for shelf waters. It is strongly enriched in the Arctic shelves and in the Transpolar Drift waters that originate in the Siberian shelves (Rutgers van der Loeff et al., 1995). ^{223}Ra and ^{224}Ra are short lived (11.4 and 3.7 d half life, respectively). They can trace near-shore processes (Kadko et al., 2005) but can also be used as indirect tracer of the distribution of their parent nuclides, ^{228}Th (Rutgers van der Loeff et al., 2012) and ^{227}Ac (Geibert et al., 2008). The fourth isotope, ^{226}Ra (half life 1600yr), is stable on the time scale of mixing of the Arctic Ocean and can be used as yield tracer for the analysis of other isotopes. Since Pacific and Atlantic source waters have distinct ^{226}Ra activities, the isotope can serve as tracer for the origin of water masses. In previous expeditions we have studied the distribution of the radium quartet in surface waters, we now want to include measurements of depth profiles of these isotopes in the water column for the study of exchange rates between shelf/slope and open ocean.

Work at sea

Whenever *in-situ* pumps (ISP) are deployed for the collection of suspended particles, we will mount MnO_2 -coated acrylic cartridges in the pumps to collect dissolved radium and thorium isotopes by adsorption on the MnO_2 . The activities of ^{223}Ra , ^{224}Ra and ^{228}Th will be determined by repeated counting of the radon emanation of the fibers in a delayed coincidence counting system (RaDeCC; Moore and Arnold, 1996). The $^{228}\text{Ra}/^{226}\text{Ra}$ ratio will be determined later in the home laboratory using gamma spectrometry, whereas absolute ^{226}Ra will be quantified by coprecipitation of radium in discrete water samples as BaSO_4 and subsequent analysis with gamma spectrometry.

Expected results

From the distribution of radium isotopes we hope to derive exchange rates of the shelf and slope with the open ocean at various depths. These exchange rates are needed in models describing the distribution of other tracers like ^{230}Th and ^{231}Pa .

Data management

See chapter 5 for details on data management.

References

- Geibert, W., Charette, M., Kim, G., Moore, W.S., Street, J., Young, M., Paytan, A., 2008. The release of dissolved actinium to the ocean: A global comparison of different end-members. *Marine Chemistry* 109, 409.
- Kadko, D., Muench, R., 2005. Evaluation of shelf-basin interaction in the western Arctic by use of short-lived radium isotopes: The importance of mesoscale processes. *Deep Sea Research Part II: Topical Studies in Oceanography* 52, 3227.
- Moore, W.S., Arnold, R., 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. *J. Geophys. Res.* 101, 1321-1329.
- Rutgers van der Loeff, M.M., Key, R.M., Scholten, J.C., Bauch, D., Michel, A., 1995. ^{228}Ra as a tracer for shelf water in the Arctic Ocean. *Deep-Sea Res. II* 42, 1533-1553.
- Rutgers van der Loeff, M.M., Cai, P., Stimac, I., Bauch, D., Hanfland, C., Roeske, T., Bradley Moran, S., 2012. Shelf-basin exchange times of Arctic surface waters estimated from $^{228}\text{Th}/^{228}\text{Ra}$ disequilibrium. *Journal of Geophysical Research - Oceans* 117, C03024.

5.13 Artificial radionuclides as tracers of water masses

M. Rutgers van der Loeff (AWI), N. Casacuberta (LIP), V. Puigcorb  (UAB)
not on board: M. Christl, P. Masqu , T. Kenna

Objectives

Artificial radionuclides have been widely used as oceanic tracers to study watermass circulation. Radioactive tracers (^{99}Tc , ^{90}Sr , ^{137}Cs and ^{129}I) dispersed from European nuclear fuel reprocessing plants located at Sellafield (formerly Windscale) in the UK and La Hague in France (Kershaw & Baxter, 1995) have proved particularly powerful to that aim. The discharged radioactive waste in coastal waters of northwest Europe has been used to track the water movement through the North Sea (Kershaw & Baxter, 1995), the Norwegian Coastal Current (Alfimov et al., 2004b), the Arctic Ocean Karcher et al., 2012; Smith et al., 1999; Smith et al., 2011) and the Nordic Seas (Alfimov et al., 2004a). The atmospheric weapon tests performed in the 1950's and 1960's have been another source of artificial radionuclides to the marine environment Povinec et al., 2005).

Other than ^{137}Cs , ^{90}Sr , ^{99}Tc , ^{129}I , etc., in recent years, several studies have measured the anthropogenic occurrence of ^{236}U ($T_{1/2}=23$ My) in the ocean and pointed out its potential to become a new oceanographic tracer Christl et al., 2012; Eigl et al., 2013; Sakaguchi et al., 2012; Steier et al., 2008. Its conservative behavior in seawater and the fact that has it not yet reached steady state in the oceans, together with new developments in Accelerator Mass Spectrometry, proved that the $^{236}\text{U}/^{238}\text{U}$ atomic ratio can be used as a marker of water masses, particularly in the Arctic and Atlantic Oceans Casacuberta et al., 2014.

Atom ratios between different artificial radionuclides can be used to identify the sources of radionuclides in the marine environment (i.e. $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{90}\text{Sr}/^{137}\text{Cs}$) and track the water masses circulation (i.e. $^{129}\text{I}/^{137}\text{Cs}$). For example, $^{129}\text{I}/^{137}\text{Cs}$ tracer measurements are used in simple mixing/advection models to estimate transit times from the North Sea to the Arctic Ocean. Similarly, and due to the different input functions of ^{129}I and ^{236}U from European reprocessing plants, the $^{129}\text{I}/^{236}\text{U}$ could become a potential tool in tagging the water masses in the North Atlantic and Arctic Oceans (Christl et al., 2012).

The objective of our work during the PS94 cruise is to obtain a comprehensive dataset of artificial radionuclides in the Arctic Ocean to: i) constrain the sources of artificial radionuclides to the Arctic Ocean (i.e. global fallout, reprocessing plants, rivers); ii) use the $^{236}\text{U}/^{238}\text{U}$ atom ratio and $^{129}\text{I}/^{236}\text{U}$ to identify water masses in the Arctic Ocean; iii) use the $^{129}\text{I}/^{137}\text{Cs}$ and $^{129}\text{I}/^{236}\text{U}$ to constrain the transit times of waters from the North Sea to the Arctic Ocean; and iv) use them as tracers of the water circulation in the Arctic Ocean.

Work at sea

We plan to collect about 100 water samples to analyze ^{236}U , ^{129}I , ^{137}Cs and Pu-isotopes. Surface samples will be collected along the cruise track and 7 depth profiles will be taken in *super stations*. Some samples will be only collected and stored for further analysis, and others will be processed onboard. Volumes of samples, specific treatment onboard as well as the laboratory where samples will be further analyzed are described in Table 5.1.

Tab. 5.1: Description of volume of water, pretreatment onboard and final laboratory of analysis for each of the artificial radionuclides collected during the PS94 cruise

Radio-nuclide	Volume of water (L)	Pretreatment onboard	Laboratory of analysis
^{236}U	3 L <i>Surface (0-500 m)</i> 5 L <i>Mid depths (500-2,000 m)</i> 10 – 20 L <i>Deep (>2,000 m)</i>	Acidify, spike and pre-concentrate (with $\text{Fe}(\text{OH})_3$).	LIP, ETH Zürich
^{129}I	0.2 L <i>Surface (0-500 m)</i> 0.4 L <i>Mid depths (500-2000 m)</i> 0.5 L <i>Deep (>2000 m)</i>	All radiochemistry based on Michel et al. (2007)	LIP, ETH Zürich
^{137}Cs and Pu-isotopes	5 L	Store	LDEO

Samples for the ^{236}U analysis will be acidified with HNO_3 suprapure and spiked with about 3 pg of a ^{233}U reference material (IRMM-051). After 24 hours of equilibration, U is pre-concentrated by Fe-hydroxide co-precipitation. Precipitates will be stored in 250 ml bottles for further analysis at ETH Zurich.

The ^{129}I samples will be processed based on the method by Michel et al. (2007). Briefly, Woodward iodine is added to the pre-weighted sample and all iodine species were oxidized with $\text{Ca}(\text{ClO})_2$ to iodate. After 15 minutes, iodate species are reduced with NH_3OHCl and NaHSO_3 to iodide. After 45 minutes, pH was raised to 5-6 before going through the separation step. This step consisted in an ion exchange separation using a BioRad® 1x8 analytical grade resins. Resins are pre-conditioned with 0.5 KNO_3 in order to increase the selectivity of the ion exchange resin. After the sample has gone through the resin, and the ion exchange columns rinsed with 0.5 M KNO_3 , the iodine is eluted with concentrated potassium nitrate solution (2.25 M). Finally, iodine is precipitated as AgI, ready for AMS measurement at ETH AMS Tandy.

Expected results

Results obtained from these samples are expected to provide insights in the general water circulation in the Arctic Ocean. In particular, we will increase the ^{236}U dataset in the oceans, in order to better constrain the main input sources (i.e. European reprocessing plants and global fallout) and identify other potential sources. Recent studies pointed to Arctic rivers as another source of both ^{236}U and ^{129}I , and investigating the $^{129}\text{I}/^{236}\text{U}$ atom ratio shall be very useful in identifying this contribution. Results on the different concentrations of artificial radionuclides will be gathered together with those obtained during US GEOTRACES and GEOTRACES Canada cruises performed simultaneously in the Arctic Ocean, in order to obtain a quasi-synoptic and comprehensive data set.

Data management

See chapter 5 for details on data management.

References

Alfimov, V., A. Aldahan, G. Possnert, A. Kekli, and M. Meili (2004a), Concentrations of ^{129}I along a transect from the North Atlantic to the Baltic Sea, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 223–224(0), 446-450.

- Alfimov, V., A. Aldahan, G. Possnert, and P. Winsor (2004b), Anthropogenic iodine-129 in seawater along a transect from the Norwegian coastal current to the North Pole, *Marine Pollution Bulletin*, 49(11–12), 1097–1104.
- Casacuberta, N., M. Christl, J. Lachner, M. Rutgers van der Loeff, P. Masqué, and H. A. Synal (2014), A first transect of U-236 in the North Atlantic Ocean, *Geochim Cosmochim Acta*, 133, 34–46.
- Christl, M., et al. Status of ^{236}U analyses at ETH Zurich and the distribution of ^{236}U and ^{129}I in the North Sea in 2009, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*(0), doi:10.1016/j.nimb.2015.01.005.
- Christl, M., J. Lachner, C. Vockenhuber, O. Lechtenfeld, I. Stimac, M. Rutgers van der Loeff, and H.-A. Synal (2012), A depth profile of uranium-236 in the Atlantic Ocean, *Geochim Cosmochim Acta*, 77(0), 98–107.
- Eigl, R., M. Srncik, P. Steier, and G. Wallner (2013), $^{236}\text{U}/^{238}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratios in small (2 L) sea and river water samples, *Journal of Environmental Radioactivity*, 116(0), 54–58.
- Karcher, M., J. N. Smith, F. Kauker, R. Gerdes, and W. M. Smethie (2012), Recent changes in Arctic Ocean circulation revealed by iodine-129 observations and modeling, *Journal of Geophysical Research: Oceans*, 117(C8), C08007, doi:10.1029/2011JC007513.
- Kershaw, P., and A. Baxter (1995), The transfer of reprocessing wastes from north-west Europe to the Arctic, *Deep Sea Research Part II: Topical Studies in Oceanography*, 42(6), 1413–1448.
- Povinec, P. P., et al. (2005), ^{90}Sr , ^{137}Cs and $^{239,240}\text{Pu}$ concentration surface water time series in the Pacific and Indian Oceans – WOMARS results, *Journal of Environmental Radioactivity*, 81(1), 63–87.
- Sakaguchi, A., A. Kadokura, P. Steier, Y. Takahashi, K. Shizuma, M. Hoshi, T. Nakakuki, and M. Yamamoto (2012), Uranium-236 as a new oceanic tracer: A first depth profile in the Japan Sea and comparison with caesium-137, *Earth and Planetary Science Letters*, 333–334(0), 165–170.
- Smith, J. N., K. M. Ellis, and T. Boyd (1999), Circulation features in the central Arctic Ocean revealed by nuclear fuel reprocessing tracers from Scientific Ice Expeditions 1995 and 1996, *Journal of Geophysical Research: Oceans*, 104(C12), 29663–29677.
- Smith, J. N., F. A. McLaughlin, W. M. Smethie, S. B. Moran, and K. Lepore (2011), Iodine-129, ^{137}Cs , and CFC-11 tracer transit time distributions in the Arctic Ocean, *Journal of Geophysical Research: Oceans*, 116(C4), C04024, doi:10.1029/2010JC006471.
- Steier, P., et al. (2008), Natural and anthropogenic ^{236}U in environmental samples, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 266(10), 2246–2250.

5.14 Biogeochemical cycling of silicon – stable isotopes

C. Ehlert (ICBM), K. Pahnke (not on board)

Objectives

In most oceanic regions, the silicon isotope composition ($\delta^{30}\text{Si}$) of water masses varies as a function of input from land, diatom primary production in surface waters and diatom silica dissolution at greater depth, together with physical water mass circulation and mixing. Therefore, the oceanic $\delta^{30}\text{Si}$ distribution bears information on the dominant pathways and processes by which silicon is cycled within the ocean (e.g. de Souza et al., 2012a). However, often the interpretation is difficult because the $\delta^{30}\text{Si}$ always represents a mixed signal of the numerous pathways and processes. The Arctic Ocean is a unique system to study the silicon cycle, because here the diatom primary productivity and silicic acid utilization in the water column is very low and quasi restricted to a short season in the year. Therefore, seawater $\delta^{30}\text{Si}$ signatures in the Arctic will mainly represent the input of terrestrial dissolved and particulate silicon via rivers, which both have a lighter $\delta^{30}\text{Si}$ signature than the surrounding seawater, and subsequent dissolution of the particles and physical water mass mixing. With our applied methods we will be able to analyse separately and therefore distinguish the

silicon isotope composition of the lithogenic (terrestrial derived) particles from the *in-situ* produced diatom biogenic silica. Both particle types should have distinctly different silicon isotope compositions (higher $\delta^{30}\text{Si}$ for biogenic particles and low $\delta^{30}\text{Si}$ for lithogenic particles, respectively). This allows us to study the terrestrial input and its influence on the seawater $\delta^{30}\text{Si}$ composition without or very little influence from biological fractionation, thus improving our understanding of the biogeochemistry of silicon in the ocean. We will then further compare the results with data from the Canadian and US GEOTRACES cruises (M. Brzezinski, D. Varela, pers. communication), the Atlantic (de Souza et al., 2012a), the Pacific (e.g., De Souza et al., 2012b; Grasse et al., 2013) and in particular the Southern Ocean (e.g. Varela et al., 2004, Fripiat et al., 2007) to evaluate and contrast the processes affecting silicon biogeochemistry. We will investigate the effects of enhanced river input and extended shelf areas in the Arctic *versus* no river discharge and restricted shelf extent in the Southern Ocean as well as the different circulation regimes, upwelling (Southern Ocean, Equatorial Pacific) *versus* no upwelling (Arctic), and the different particle compositions of opal-rich (Southern Ocean, Equatorial Pacific) *versus* opal-poor (Arctic).

Although production and subsequent burial of diatom silica is very low in the Arctic, the combination of a short growth season before and during the time of the cruise and the sampling of suspended particles together with sediment samples will provide unique information about the transfer of the surface water utilization signal, possibly with a very strong fractionation by sea ice diatoms, through the water column to the deep ocean and will therefore provide important general information on the applicability of diatom $\delta^{30}\text{Si}$ as a paleo proxy in the global ocean.

Currently, the silicon cycle in the Arctic region is not yet influenced by anthropogenic disturbances. However, this will likely change in the future. A future temperature increase and an associated decrease in permafrost may cause an increase in depth of the weathering active soil layer, land plant biomass, atmospheric precipitation, and river discharge, which may also increase the river silicon flux and stimulate future diatom growth in the Arctic and therefore influence the global silicon as well as carbon cycle (Tréguer and De La Rocha, 2013). With this project we will provide a baseline study on the present day silicon isotope distribution in the Arctic Ocean for future evaluation of the impact of climate change on the silicon cycle. This project will contribute the first $\delta^{30}\text{Si}$ data from the central and eastern Arctic Ocean. Our results will provide information about the main input sources of dissolved silicon via the major Siberian rivers by investigating the dissolved as well as particulate (suspended particles) $\delta^{30}\text{Si}$ signatures along the wide eastern Arctic shelf regions and the Arctic basin.

Work at sea

The work at sea will be conducted by Ronja Paffrath and includes mainly seawater sampling for dissolved silicon isotopes at 16 stations (up to 16 depths per station) from the conventional (not trace metal clean) rosette and additional surface water samples taken with the ships intake system upon leaving each station. The sample volume required per analysis is 1-2 L from the rosette (1 L at depth, 2 L in the lower-concentrated upper water column) and 5 L from the ships intake (for the highly depleted surface waters). Seawater will be filtered through AcroPak filter cartridges (0.8/0.45 μm pore size, Supor[®] pleated membrane) directly from the Niskin bottles (same sampling as for Nd isotopes and REEs). Afterwards no further onboard treatment is necessary and samples will be stored in plastic boxes for the transport to the home laboratory in Oldenburg.

In addition to seawater samples the planned project requires filtered material from throughout the water column taken with the *in-situ* pumps and, if possible, sample aliquots from the sediment sampling for the determination of sedimentary biogenic and lithogenic silicon isotope composition.

Expected results

The results will provide unique information about silicon biogeochemical cycling under the conditions of high terrestrial input, extensive shelf area and low diatom productivity not found in other ocean regions. We will study the input of the terrigenous sources to the Arctic and mixing with Atlantic and Pacific seawater, trace the transformation processes (formation and remineralization) of particulate silicon in the water column and the transfer to the underlying sediments.

Data management

See chapter 5 for details on data management.

References

- De Souza, G. F., Reynolds, B. C., Rickli, J., Frank, M., Saito, M. A., Gerringa, L. J. A., & Bourdon, B. (2012a). Southern Ocean control of silicon stable isotope distribution in the deep Atlantic Ocean. *Global Biogeochemical Cycles*, 26(GB2035). doi:10.1029/2011GB004141
- De Souza, G. F., Reynolds, B. C., Johnson, G. C., Bullister, J. L., & Bourdon, B. (2012b). Silicon stable isotope distribution traces Southern Ocean export of Si to the eastern South Pacific thermocline. *Biogeosciences*, 9, 4199–4213. doi:10.5194/bg-9-4199-2012
- Fripiat, F., Cardinal, D., Tison, J.-L., Worby, A., & André, L. (2007). Diatom-induced silicon isotopic fractionation in Antarctic sea ice. *Journal of Geophysical Research*, 112(G02001). doi:10.1029/2006JG000244
- Grasse, P., Ehlert, C., & Frank, M. (2013). The influence of water mass mixing on the dissolved Si isotope composition in the Eastern Equatorial Pacific. *Earth and Planetary Science Letters*, 380, 60–71. doi:10.1016/j.epsl.2013.07.033
- Varela, D. E., Pride, C. J., & Brzezinski, M. A. (2004). Biological fractionation of silicon isotopes in Southern Ocean surface waters. *Global Biogeochemical Cycles*, 18(GB1047). doi:10.1029/2003GB002140
- Tréguer, P. J., & De La Rocha, C. L. (2013). The world ocean silica cycle. *Annual Review of Marine Science*, 5, 477–501. doi:10.1146/annurev-marine-121211-172346

5.15 Stable N & O isotope of nitrate

R. S. Ganeshram (not onboard)

Objectives

To collect water sample for combined O and N stable isotopes of nitrate and where possible to collect suspended particles for C and N stable isotopes on glass fibre filters (collaboration with Ilka Peeken and Eva-Maria Noethig).

Work at sea

Pre-filtered water samples will be collected from Rosette. Detailed sampling protocol at end.

Expected results

The broad scientific aim is to understand what controls N balance in the Arctic and the Arctic through flow. Arctic through flow into the North Atlantic is depleted in N relative to P. This has significant influence on (1) preformed N contents and N:P ratios of North Atlantic Deep water and the excess P also drives N-fixation in the Atlantic. By using stable N and O isotopes of nitrate, nutrient and water mass information I wish to evaluate whether N balance of the Arctic is controlled by (1) Relative proportions of Atlantic and Pacific water masses entering the Arctic; or (2) due to terrestrial nutrients sources to the Arctic; or (3) nutrient recycling processes within the Arctic Ocean. We will use isotope data along with nutrients and water mass information in our interpretations.

Data management

See chapter 5 for details on data management.

Reference

Yamamoto-Kawai et al., Nature, 443, 43, 2006

5.16 Trace metals isotopes

S. Galer (not on board)

Objectives

A Multi-Trace Metal Isotope Study of the Arctic Ocean - Cycling and isotope fractionation of Cd, Cr and Pb in the Arctic Ocean

Several studies have now documented that the Cd isotope composition of seawater exhibits significant variability (Ripperger et al., 2007; Abouchami et al., 2011, 2014; Gault-Ringold et al., 2012; Yang et al., 2012; Xue et al., 2013; Conway and John, 2015). Our Cd isotope results from the Southern Ocean, Northwest Atlantic and Southwest Atlantic have shown that Cd isotopic variations in Cd-depleted surface waters track changes in biological productivity while deep waters show relatively uniform isotopic composition despite increasing Cd concentrations along the great conveyor (Abouchami et al., 2011, 2014, Xie et al. 2013, Janssen et al., 2014). By contrast, the few Cd isotope data available for the Arctic Ocean show limited isotopic fractionation in the surface layer compared to deeper waters despite being Cd-depleted (Ripperger et al., 2007).

Our objective is to investigate in detail the stable Cd isotope fractionation in the Arctic Ocean by acquiring concentration and isotope data at high resolution along the cruise track and in the water column. Surface waters and several depth profiles at key stations will allow us to assess the degree of isotope variability in view of the contributions from various sources – river runoff, precipitation, evaporation, sea-ice and exchanges with the North Pacific and Atlantic – to the Arctic Ocean’s freshwater budget.

Chromium (Cr), in contrast to Cd, is a redox sensitive element - with two oxidation states Cr(VI) and Cr(III) - whose isotopic fractionation has up until now mainly been used to trace the oxygenation levels of the past oceans (Frei et al., 2009). In oxic seawater, Cr(VI) is highly soluble while Cr(III) is particle reactive and forms insoluble hydroxide compounds. While concentration data are abundant and of nanomolar level in seawater (1-7 nM), Cr isotope data are restricted to a single profile (5 samples) in the Argentine Basin and show isotopically “heavier” values than average continental crust (Bonnand et al., 2013). Our aim is to obtain the first measurements of the Cr isotopic composition of Arctic seawater and establish a mass balance of the Cr budget of the Arctic Ocean.

Lead isotope measurements will be performed to document the distribution and cycling of Pb in the water column, identify anthropogenic (shallow) and natural (deep) sources of Pb in the Arctic Ocean basin, assess ventilation rates and mixing in the surface gyres. Important goals are to investigate the extent of downward penetration of anthropogenic lead in the thermocline and particle reactive behaviour in the Siberian shelf and, evaluate the influence of hydrothermal lead inputs in the deeper Arctic Ocean (near the Gakkel Ridge).

Work at sea

Seawater volumes varying between 20 L for surface waters, 4 L for intermediate depth and 1 L for deep waters will be sampled using the Ultraclean Titan frame (de Baar et al., 2008), filtered and acidified at pH of 1, using ultra-clean Seastar HCl (low level Cd blank). If the FISH is deployed, we aim to collect a continuous transect of surface waters along the cruise track. Vertical profiles distributed along the transect path, each consisting of 8 to 11 depths

will be collected by our NIOZ colleagues using the Ultraclean Titan frame. Samples will be analysed upon return in the Max-Planck Institute laboratories in Mainz (Germany) by Thermal-Ionization Mass Spectrometry using the double spike technology already established for Pb, Cd and Cr isotopes.

Expected results

The isotope and concentration results may also shed light on the effect of the increase of the Arctic Ocean's freshwater content over the past few decades, predominantly in the west, on the trace metal budget of the Arctic Ocean.

Data management

See chapter 5 for details on data management.

References

- Abouchami W., Galer S.J.G., de Baar H.J.W., Alderkamp A.C., Middag R., Laan P., Feldmann H., Andreae M.O. (2011) Modulation of the Southern Ocean cadmium isotope signature by ocean circulation and primary productivity. *Earth Planet. Sci. Lett.*, 305, 83-91.
- Abouchami W., Galer S. J. G., de Baar H. J. W., R. Middag, D. Vance, Y. Zhao, M. Klunder, K. Mezger, H. Feldmann, Andreae M. O. (2011) Biogeochemical cycling of cadmium isotopes in the Southern Ocean along the Zero Meridian. *Geochim. Cosmochim. Acta* 127, 348–367.
- Bonnand et al. (2013) The chromium isotopic composition of seawater and marine carbonates. *Earth Planet. Sci. Lett.* 382, 10-20.
- Conway, T.M. and John, S.G. (2015) Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. *Geochim. Cosmochim. Acta*, 148, 269-283.
- De Baar, H.J. et al. (2008) Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. *Mar. Chem.*, 11, 4-21.
- Frei, R., Gaucher C. , Poulton, S.W., Canfield, D.E. (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461, 250–253.
- Galer, S. J. G., Abouchami, W., Xie, R. C., Janssen, D. J., Rickenberg, M., Gerringa, L., Cullen, J. T., de Baar, H. J. W. (2014) Global oceanic cadmium isotope distribution. *Goldschmidt Conference*, Sacramento.
- Gault-Ringold M., Adu T., Stirling C. H., Frew R. D. and Hunter K. A. (2012) Anomalous biogeochemical behavior of cadmium in subantarctic surface waters: mechanistic constraints from cadmium isotopes. *Earth Planet. Sci. Lett.* 341–344, 94–103.
- Janssen, D.J. et al. (2014) Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. *Proceedings of the National Academy of Sciences*, 11, 6888-6893
- Janssen D. J., Cullen J. T., Abouchami W., Galer, S. J. G., de Baar, H. J. W. (2014) Cadmium Isotopes along the Line-P transect in the Northeast Subarctic Pacific. *Goldschmidt Conference*, Sacramento.
- Ripperger S., Rehkämper M., Porcelli D. and Halliday A. N.(2007) Cadmium isotope fractionation in seawater – a signature of biological activity. *Earth Planet. Sci. Lett.* 261, 670–684.
- Xue Z., Rehkämper M., Horner T. J., Abouchami W., Middag R., van de Flierdt T. and de Baar H. J. W. (2013) Cadmium isotope fractionation in the Southern Ocean. *Earth Planet. Sci. Lett.* 382, 161–172.
- Xie, R. C., Galer, S. J. G., Abouchami, W., Rijkenberg, Micha., de Jong, J. (2014) Cadmium isotope distribution along the western boundary of the South Atlantic. *Ocean Sciences Meeting*, Honolulu.
- Yang S. C., Lee D. C. and Ho T. Y. (2012) The isotopic composition of cadmium in the water column of the South China Sea. *Geochim. Cosmochim. Acta* 98, 66–77.

5.17 Aerosol sampling

A. Baker, J.B. Stuut, (not on board)

Objective

Dust forms an important form of transport of nutrients and trace metals from a terrestrial environment to the open ocean (Jickells et al. 2005). In the central Arctic dust is either deposited on ice (in winter) or directly into the ocean (Cámara-Mor et al. 2011). The dust deposited on the ice will enter the surface ocean in a relatively short time periods upon melting of the ice and may coincide with a burst in biological activity (Melnikov, 1991). However, there is little known about how much dust enters the Arctic Ocean, where it comes from, and how much nutrients and trace metals this dust contains and how much solubilizes upon entering the ocean.

Work at sea

Aerosols will be collected using three high volume aerosol samplers. One aerosol sampler will collect samples for measurement of major ions, one for sampler will collect aerosols for measurements of trace metals and one aerosol collector will collect samples to determine the dust's mineralogy. On board filters will be changed daily and more often when we encounter a dust event.

Expected results

The results will help us to get an idea about the amount and frequency of dust events in the central Arctic. Measurement of major ions and determination of the mineralogy will show us where the dust comes from (Stuut et al. 2005). Aerosol nutrient and trace metal measurements will show us if dust is or is not important for their transport to the central Arctic surface ocean (Baker et al. 2010). Leaching procedures will show how much nutrients and trace metals we expect to solubilize in the ocean (Baker et al. 2006).

Data management

See chapter 5 for details on data management.

References

- Baker, A.R., Jickells, T.D., Witt, M., Linge, K.L., 2006. Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean. *Mar. Chem.* 98, 43-58.
- Baker, A.R., Lesworth, T., Adams, C., Jickells, T.D., Ganzeveld, L., 2010. Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50 degrees N to 50 degrees S based on large-scale field sampling: Fixed nitrogen and dry deposition of phosphorus. *Global Biogeochemical Cycles* 24, 16.
- Cámara-Mor, P., Masque, P., Garcia-Orellana, J., Kern, S., Cochran, J.K., Hanfland, C., 2011. Interception of atmospheric fluxes by Arctic sea ice: Evidence from cosmogenic ⁷Be. *J. Geophys. Res.* 116, C12041.
- Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308, 67-71.
- Melnikov, S. A. (1991), Report on heavy metals, in *State of the Arctic Environment Reports*, vol. 2, pp. 82–153, *Arct. Cent.*, Univ. of Lapland, Rovaniemi, Finland.
- Stuut, J.B., Zabel, M., Ratmeyer, V., Helmke, P., Schefuss, E., Lavik, G., Schneider, R., 2005. Provenance of present-day eolian dust collected off NW Africa. *J. Geophys. Res.-Atmos.* 110, D04202.

6. PLANKTON ECOLOGY AND BIOGEOCHEMISTRY (PEBCAO)

N. Hildebrandt (AWI), V. Köhler (AWI), K. Kosobokova (IORAS), I. Petersen (AWI), J. Riedel (AWI), K. Metfies, E.-M. Nöthig, B. Niehoff (not on board)

Objectives

The Arctic Ocean is strongly affected by climate change, which in turn will have large impact on the carbon cycle and sequestering in the pelagic ecosystems. Long-term observations of all plankton size classes, from pico- to large zooplankton, as well as experiments with key species are thus required to understand and predict future ecosystem functioning. Shifts in species composition are expected: For example, at the base of the food web smallest algae may become more important. At higher trophic levels, copepods then have to cope with changes in food supply and, thus, have to adjust their species-specific patterns in population dynamics, depth distribution, and feeding biology. In addition to increasing temperatures and shrinking sea-ice, recent changes in the circulation (shift of the boundary between Atlantic and Pacific water masses) may also alter the pelagic system. In addition, the increasing advection of warmer Atlantic water masses inhabited by boreal species could favour the distribution of Atlantic communities, which could finally replace the Arctic fauna.

Since the nineties, ecological investigations of phyto- and zooplankton biomass, species composition, productivity, sedimentation and biochemical parameters (i.e. chlorophyll *a*, particulate organic carbon & nitrogen, carbonate and biogenic silica) have been carried out in Arctic waters of the central Arctic Ocean with *Polarstern* (1993, 1995, 1996, 2007, 2011, 2012, 2014). Plankton biomass and carbon flux during summer close to and beneath the sea ice do not yet appear to have increased, however, marginal ice zones have moved closer to the pole. Thus, former ice covered regions are ice-free for a longer period and allow a different summer population to develop. In addition, earlier investigations in the Eurasian Basin demonstrated that the composition and distribution of protists and the pelagic fauna in the Arctic Ocean is strongly affected at regional and even basin scales by the inflow of Atlantic water that enters via the Fram Strait and from the Barents Sea shelf into the Eurasian Basin. The ecological niches, e.g. preferences and tolerances, of advected zooplankton species then determine their success in inhabiting the Arctic basins.

During the last 20 years we have monitored biomass, species composition of phyto- and zooplankton and sedimentation of particles and since 2011 the PEBCAO group studies plankton and biogeochemical parameters relevant for the Arctic Ocean in greater detail. Molecular biological investigations on biodiversity, HPLC and flow cytometry reveal strong gradients of higher to low biomass and of diatoms to picoplankton-dominated communities from the Atlantic to the Pacific sector.

Our work on planktonic protists and biogeochemical fluxes will also focus on monitoring species and biomass distribution, on biogeochemical parameters and on the vertical particle flux of organic matter in relation to sea ice cover, nutrient distribution and water circulation patterns. Our aim is to determine the vertical particle flux in the Arctic Ocean and to follow the changes therein. Specific hypotheses we intend to test are:

- (1) Less sea ice in summer will promote higher production followed by higher sedimentation in regions that have been totally ice covered before.

- (2) Shifts in species compositions on different trophic levels will change trophic interactions and change fluxes and export of organic matter.
- (3) Changes in the circulation like the stronger influence of Atlantic water masses may also alter the pelagic system and export fluxes.

Zooplankton will be collected in the deep Eurasian and Canadian basins using multiple opening and closing plankton nets with a mesh size of 150 µm, sampling standardized depth strata over the entire water column. Our sampling protocol will follow standard procedures as applied during previous *Polarstern* cruises (1993-2012). The comparison of data obtained during PS94 with our historical data can then be used for assessing changes in the Arctic pelagic biota related to ongoing climate change and the entire data set can also be considered as a starting point for the first zooplankton time series in the history of the investigation of the Arctic. In parallel to net sampling, we will use a zooplankton imaging and analyzing system to determine the small-scale distribution of the organisms. This system - LOKI (= Lightframe On-sight Key species Investigation) - is equipped with a high-resolution digital camera and sensors measuring temperature, salinity, density and fluorescence as a proxy for algal abundance. The distribution patterns of the zooplankton organisms can thus directly be related to the hydrography. Combining both approaches will allow to analyze and to better understand changes in the zooplankton communities under changing environmental conditions.

The work of the zooplankton team will focus on

- (1) relating composition, abundance, biomass and spatial distribution of zooplankton communities across the basins and ridges to water circulation patterns and primary productivity and protist composition.
- (2) relating the reproductive state of dominant copepod species to environmental factors, including the continued biochemical analyses (i.e. carbon and nitrogen content, stable isotope ratios, lipid content and enzyme activities) to understand life strategies of and trophodynamic relationships among species.
- (3) building the DNA sequence library needed for molecular approaches to assess community structure and identifying regional and basin-scale population patterns within the Arctic using molecular markers.

All results will be compared to earlier cruises to improve projections of future status or change.

Work at sea

Biogeochemical & biological parameters from rosette samples

We will sample seawater with a CTD/rosette sampler at 5 - 8 depths. Additionally we will sample Arctic seawater approx. every 1° (longitude / latitude) using a newly developed automated filtration device that is coupled to the ships pump. All samples except those for phytoplankton & protozooplankton counts will be filtered and preserved or frozen at -20 °C and partly at -80 °C for further analyses. At the home laboratory at AWI we will determine the following parameters to describe the biogeochemistry and the abundance and distribution of protists:

- Chlorophyll *a* concentration
- HPLC pigments
- Particulate organic carbon (POC)
- Particulate biogenic silica (PbSi)
- Phytoplankton & protozooplankton abundance (traditional microscopy, with clonal cultures, molecular-biological assessments of protist communities)

Sediment trap deployment

Sediment traps (2) will be deployed in mooring systems. This work is part of the AWI FRAM project and will be carried out together with oceanographers and sea ice physicists. Traps will be exchanged every year from 2015 – 2019. Together with previous flux studies this will yield in a time series studying sedimentation events in the Arctic Ocean. Long-term trap deployments in the Arctic Ocean will also be carried out in cooperation with scientists from other nations, e.g. Canada.

Zooplankton sampling

- Quantitative sampling of zooplankton will be carried out with a Multinet Type Maxi (0.5 m² mouth opening, 150 µm mesh size). The entire water column (0 m - bottom) will be sampled with the following sampling intervals: bottom-2000-1000-500-300-200-100-50-25-0 m.
- LOKI will be deployed at the stations of Multinet sampling. The system will be towed vertically from 1,000 m depth to the surface, while continuously taking pictures for zooplankton analyses and measuring temperature, salinity, density and fluorescence.
- The material for biochemical analyses will be collected with Bongo net hauls (100 or 200 and 500 µm mesh size). This material will be used for the analyses of stable isotope signatures, lipid content and development of molecular-based identification systems based on DNA-barcoding of rare zooplankton species.

Preliminary (expected) result

We expect similar results including trends like we observed during the other years of our time-series investigations. Results will strongly depend on the physical and chemical environmental settings in the field.

Data management

We sample a large variety of interconnected parameters. Many of the samples (i.e. pigment analyses, particulate matter in the water column, etc.) will be analysed at AWI within about two years after the cruise. We plan that the full data set will be available about three years after the cruise by the latest. Most of species samples and samples which will not be analysed immediately but will be stored at AWI and will be available to other colleagues. Data will be made available to the public via PANGAEA after publishing (depending on how many comparisons will be made, long-term study 2 to 5 years after the cruise).

7. ART - ARCTIC IN RAPID TRANSITION -

D. Bauch (GEOMAR), I. Kryukova (SIO), H. Reader (DTU), E. Allhusen (AWI), A. Krell (KoWi), I. Peeken, R. Amon, D. Hansell, C. A. Stedmon, C. Wegner, K. Werner (not on board)

Objectives

ART (Arctic in rapid transition) is an interdisciplinary, international network, with pan-arctic scope to study sea ice transitions, land-ocean interactions, the biogeochemistry and marine ecosystems in the changing Arctic. During TransArc II the team consist of four sub-projects working on sea ice biology and biogeochemistry (SIB), the impact of dissolved organic matter (DOM) and suspended organic matter (SPM) and the studies of the water mass origin (WMO).

SIB: Sea ice associated communities play a major role in the cryo-benthic and cryo-pelagic coupling of the Arctic Ocean. The rapid transition from multiyear ice (MYI) to first year ice (FYI) and its implications on the sea ice and associated ecosystem are not well understood. We therefore want to investigate the sea ice and under ice algae communities in the Atlantic and the Pacific sector of the Central Arctic and compare these observations with historic data to reveal long term changes in these habitats. Special emphasis will be taken to study the recent changes observed in the melt pond associated communities and their respective role for the arctic carbon budget. The impact of DOM and SPM on the optical properties of sea ice will be determined and related to the ice algae biomass. The measurement of water mass tracers in the sea ice will help to understand the history of the sampled ice floes. To understand the seeding processes of the sea ice algae, the biodiversity of new ice, particularly from the Laptev Sea will be determined and compared to sea ice communities sampled along the transpolar drift in the framework of the Transdrift project.

DOM: The export of turbid waters from rivers and coastal regions could enhance the delivery of nutrients to micro algal populations, but could also impair photosynthesis by scattering and absorbing sunlight. We therefore want to contribute to mapping the distribution and characteristics of dissolved organic matter (DOM) in the Arctic Ocean. One of the goals is to trace the distribution and mixing of DOM originating from Siberian Rivers, in the surface layers of the Arctic Ocean, and compare these to other water mass tracers and Arctic time series data. The sampling of dissolved organic carbon (DOC) will contribute to the Canadian and US sampling program and provide a unique Trans Arctic dataset. Another goal is to obtain the first detailed vertical profiles of lignin (a terrestrial biomarker) concentrations in the Arctic and their role as ligands.

SPM: The overall goal is to study the particle flux along a shelf-to-basin transect along the Laptev Sea to improve our understanding of the pathways of suspended particulate matter (SPM), which is critical in order to draw the connection between sediment dynamics, optical properties and ecosystem dynamics under a changing climate on the one hand. Furthermore quantifying the abundance and composition of SPM, and comparing these to sea ice and surface sediment samples is required to understand the significance of large-scale lateral transport, and how this may affect the reconstruction of ice conditions in the geologic past.

WMO: The overall purpose of the stable oxygen isotope analysis ($\delta^{18}\text{O}$) and stable carbon isotopes of the total dissolved organic carbon ($\delta^{13}\text{CDIC}$) is to provide an assessment of water mass signatures and freshwater composition within the central Arctic Ocean and the Transpolar Drift. Neodymium behaves independently of any fractionation processes in the oceans and is a reliable tracer of water masses. The measurement of water mass tracers in the water column as well as in sea ice will help to understand the freshwater composition and origin within the central Arctic Ocean and the Transpolar Drift. A comparison between CDOM and $\delta^{18}\text{O}$ derived results are an important aspect of the project. Results will be compared with data from the Laptev Sea and the Fram Strait taken in the framework of the Transdrift project. Especially the data from the Laptev shelf-to-basin transect will be compared with SPM.

Work at sea

SIB: Various sea ice types from multiyear ice (MYI) to first year ice (FYI) will be investigated in the Atlantic and Pacific sector of the Central Arctic. Regular sea ice sampling involves the collection of ice-core sections, under-ice water and melt pond water. The depth of the sampling under the ice will be based on the profiles of the CTD and fluorescence probe which will be conducted prior to the water sampling. We will measure environmental parameters as sea ice temperature, snow depth, free board and ice thickness. Sea ice cores for the determination of Nd and $\delta^{18}\text{O}$ will be collected and stored at -20°C . In co-operation

with the sea ice physics team hyperspectral radiometer will be used to measure the spectral composition of the light under the ice for distinguishing the ice-algae biomass. Point measurements with this type of sensor will be carried out in drill holes for a direct validation of the hyperspectral estimates of ice-algae concentrations with pigment measurements from ice cores and further optical properties as particle absorption and coloured dissolved organic matter (CDOM) from entire sea ice cores. The melt pond, water and ice core samples will be transported back to the ship, where the ice samples for biological variables will be melted in 0,2 mm filtered sea water. From all habitats the following variables will be determined: salinity, nutrients, dissolved organic matter (DOC), coloured dissolved organic matter (CDOM), particle absorption, algae biomass and composition (determined by size-fractionated chlorophyll, marker pigments, DNA and microscopic cell counts). Additional biogenic silicate, particulate organic carbon and nitrogen (POC, PON) and the isotopic composition of POC and PON ($\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PON}}$) will be determined.

DOM: Samples will be collected from all water depths, coordinated with the sampling for inorganic nutrients and stable oxygen isotopes of water. The aim is to sample as much of the water column structure as possible. There will also be sampling for DOM in sea ice. Standard sampling will include water for the measurement of dissolved organic carbon (DOC; Hansell, 100 mL) and the UV-Visible absorption and fluorescence characteristics of DOM (coloured DOM, CDOM; Stedmon, 100 mL). Sample will be filtered in-line directly from the Niskin bottles and the volumes indicated include estimates rinsing sample bottles. At selected stations samples will be collected for dissolved lignin measurements (no filtration steps) using a newly developed small sample volume technique (Amon, 250 mL). Lignin is a biomarker of terrestrial organic matter. CDOM measurements will be carried out on board using a Perkin Elmer spectrophotometer (installed from Bremerhaven) and the AWI AQUALOG fluorimeter (according to agreement with Dr A. Bracher).

SPM: SPM concentration in the water column will be derived by direct measurements (water samples) and indirect determination via a transmissometer. In order to calibrate the transmissometer signal for SPM concentration, water samples from defined water depths will be taken, filtered through pre-weighed HVLP filters by MILLIPORE (0.45 microns), and washed carefully with distilled water after filtration.

WMO: Water samples for stable oxygen isotope analysis ($\delta^{18}\text{O}$) will be taken in parallel to CTD measurements and hydrochemical sampling. Sampling will also be coordinated with SPM and CDOM. Sampling of water for $\delta^{13}\text{C}_{\text{DIC}}$ will be performed only at selected stations. Sampling is planned within the halocline and the intermediate waters down to a depth of about 1,000 m. Sampling within the Deep and Bottom waters is planned for a selection of stations. We will take 50 ml of water for each ^{18}O sample from the CTD-Rosette. No water is needed for flushing. For $\delta^{13}\text{C}_{\text{DIC}}$ flushing is needed and 100 ml samples have to be drawn without "bubbling". With flushing about 200 ml are needed. Samples are poisoned with 0.2 ml of saturated HgCl_2 .

Expected results

SIB: The aim of this study is to understand the variability of the sea ice associated and under ice pelagic biomass with respect to the sea ice conditions and nutrient availability to access the role of sea-ice biota for the cryo-pelagic, cryo-benthic coupling in the changing Arctic. Special emphasis will be given to understand the role of melt ponds in the carbon cycling of the Arctic Ocean. These data can be used for modelling approaches to access the role of climate change on the carbon cycle of the Arctic Ocean.

DOM: The DOC measurements will provide a unique basin scale mapping of distributions and contribute to the global sampling effort coordinated by Hansell (University of Miami). The CDOM and lignin measurements will allow us to develop our understanding of how the

quantity and quality of Arctic riverine DOM changes during mixing in shelf seas and are transport across the Arctic in the halocline layer.

SPM: All transmissometer measurements will be correlated with corresponding *in-situ* water samples to obtain accuracy by taking the effects of different mineralogy, varying particle darkness, and salinity of ambient water on the response of the turbidity meter into account. The expected results will improve our understanding of the pathways of suspended particulate matter (SPM), which is critical in order to draw the connection between sediment dynamics, optical properties and ecosystem dynamics under a changing sea ice condition and add to the quantification of the environmental preconditions for productivity.

WMO: Based on hydrological data and stable oxygen isotope analysis ($\delta^{18}\text{O}$) the influence of mainly shelf-derived meteoric waters and modification by sea-ice processes (melting or formation) can be quantified. Together with nutrient data (NO_x , PO_4 and O_2) also the Atlantic and Pacific-derived components can be quantified within the halocline. With the planned work on TransArc II we expect to learn more about the origin of freshwater within the different layers of the Arctic Ocean halocline as well as in the intermediate, deep and bottom waters. With the ongoing changes in sea-ice coverage in the Arctic Ocean it can be expected that the contribution from different freshwater sources will change and with our methods we hope to learn more about the relative changes and the connected processes accordingly.

Data management

Samples

SIB: Except for the microscopic samples, all other variables taken during the cruise will be processed during or after the cruise (1 year). Leftovers of the microscopic samples and the DNA will be stored at the Polar Biological Oceanography at the AWI for approximately 10 years.

DOM: Storage: DOC samples will be stored frozen for measurement in Miami. DOC samples from sea-ice will be measured by the DTU group. Water samples for lignin analyses will be stored frozen and shipped to Texas A&M, USA. All samples will be analysed within one year.

SPM: All filters will be analysed in GEOMAR, Kiel (concentration, grain size) within one year.

WMO: Samples for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}_{\text{DIC}}$ analysis will be transported to Kiel. Analysis will be conducted at the Leibniz Laboratory at Kiel University, Kiel, Germany and at the Stable Isotope Facility at CEOAS at Oregon State University, Oregon, USA within one year.

Data

The entire data set will be submitted to PANGAEA within 1-2 years. Data will be made public subsequent to combination with the inorganic nutrient and hydrography data and after publication. The unrestricted availability from PANGAEA will depend on the progress of the PhD thesis based on the data.

8. BENTHOS INVESTIGATIONS

K. von Juterzenka, J. Kiesel, D. Piepenburg (not on board)

Objectives

Current environmental changes that are being observed in the Arctic region will likely lead to the regime shifts of the polar marine ecosystem. Large-scale and long-term observations are required to expand our current state of knowledge on the future ecological changes in the

Arctic.. During *Polarstern* expedition PS94 Benthic studies that had been started on the Laptev Sea shelf during the TRANSDRIFT expeditions in 2013 and 2014 as part of the joint Russian-German research project „Laptev Sea System" will continue the investigation of processes in response to the continuing climate change. Of special interest are the relationships between benthic community structure, food supply and boundary fluxes in response to sea-ice dynamics. Benthic processes include the rates of degradation of organic matter and associated remineralization of carbon and inorganic nutrients, which may indicate changes in benthic ecosystem functioning.

Our special focus will be to investigate benthic remineralisation and nutrient fluxes on the Laptev Sea continental slope, shelf and adjacent areas of oceanographic interest. Furthermore, oxygen profiles and sediment samples for comparative biogeochemical analysis will be taken. In adjacent deep-sea areas, the microbial community structure as well as the macrofaunal community will be sampled and analysed in collaboration with the HGF-MPG Joint Research Group on Deep-Sea Ecology and Technology.

Work at sea

To investigate benthic remineralisation, samples will be taken by means of a video-controlled multicorer (MUC). The sediment cores with inhabiting microbial, meio- and macrofaunal communities and overlying boundary water will be incubated in a temperature-controlled environment to quantify respiration as well as remineralisation rates of carbon and nutrients (silicic acid, nitrate, ammonia and phosphate). Oxygen values will be determined by non-invasive oxygen sensors.

After incubation, the oxygen profiles in the sediment are measured by optical microsensors (sediment-penetrating oxygen optodes). The same sediment cores are passed through a 0.5 mm mesh sieve under slow running seawater. The sieve residues are preserved in a 4 % seawater-formaldehyde solution for later analyses of macrofaunal species diversity and abundance under a dissection microscope. As far as possible, nutrient samples will be analysed on board. Otherwise, nutrient samples as well as sediment samples for pigments, carbon content and microbial investigations are frozen for later analysis in the home labs. We intend to take samples of up to five sediment-core replicates at the stations of oceanographic interest.

Further sediment samples by multicorer and box corer serve for quantitative investigations of biogeochemical and sedimentological parameters, benthic micro- and macro-fauna. Samples for microbial biomass and composition are frozen for analysis in the home labs. Macrofauna is retrieved by sieving through a 0.5 mm mesh and preserved in a 4 % seawater-formaldehyde solution for further investigations of benthic community composition and taxonomical studies.

Expected results

During incubation experiments, oxygen values will be determined by non-invasive oxygen sensors on board of *Polarstern*. Expected first results are overall benthic oxygen uptake rates. Vertical oxygen profiles in the sediment cores are obtained by sediment-penetrating oxygen optode measurements. Community respiration and nutrient flux rates will be calculated after the cruise and contribute to the data sets taken since 2013.

Remaining nutrient samples, macrofaunal samples, as well as sediment taken for pigment and biogeochemical parameters will be analysed in the home laboratories in the frame of "Laptev Sea System" collaborations. Oxygen profiles and deep-sea bacterial as well as macrofaunal communities will be further investigated in collaboration with the HGF-MPG Joint Research Group on Deep-Sea Ecology and Technology. Results will increase the

current knowledge about structure and functioning of deep benthic communities in the high Arctic and serve to further standardize benthic measurements.

Overall results will contribute to our understanding of ecological consequences of climate change in key areas of the Transpolar drift system and the central Arctic.

Data management

Most data will be obtained through laboratory analyses after the cruise. Processed data will be uploaded to the database PANGAEA.

9. BETEILIGTE INSTITUTE / PARTICIPATING INSTITUTES

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DTU	Technical University of Denmark National Institute of Aquatic Resources (AQUA) Kavalergården 6, 2920 Charlottenlund, Denmark
DWD	Deutscher Wetterdienst, Seeschiffahrtsberatung Bernhard-Nocht Strasse 76 20359 Hamburg, Germany
FMI	Finnish Meteorological Institute PL 503 00101 Helsinki, Finland
GEOMAR	GEOMAR Helmholtz Centre for Ocean Research Kiel Wischhofstr. 1-3 D-24148 Kiel, Germany
HeliService	HeliService International GmbH Gorch-Fock-Straße 103 26721 Emden, Germany
ICBM	Max Planck Research Group for Marine Isotope Geochemistry Institute for Chemistry and Biology of the Marine Environment University of Oldenburg Carl-von-Ossietzky-Straße Oldenburg, Germany
IUEM	LabexMer – LEMAR, Technopole Brest Iroise Place Nicolas Copernic F - 29280 Plouzane, France

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LOCEAN	Université Pierre et Marie Curie) Tour 45-46 5E 4 place Jussieu 75005 Paris, France
NIOZ	Royal Netherlands Institute for Sea Research 't Horntje Texel, the Netherlands
SIO	P.P. Shirshov Institute of Oceanology, Nakhimovskiy prospekt, 36, Moscow, 117997, Russia
SMNH	Swedish Museum of Natural History, Department of Geosciences Frescativägen 40 Stockholm, Sweden
UAB	Universitat Autònoma de Barcelona, Institut de Ciència i Tecnologia Ambientals & Department of Physics 08193-Cerdanyola del Vallès, Spain
UB	University of Bremen, Geochemistry and Hydrogeology, Department of Geosciences, Klagenfurter Straße 28359 Bremen, Germany
UGOT	Department of Chemistry & Molecular Biology, University of Gothenburg Medicinaregatan 9 c 40530 Göteborg, Sweden
UNIK	Institute of Geology and Mineralogy, University of Cologne Greinstrasse 4-6 Köln, Germany

10. TEILNEHMER / PARTICIPANTS

Name/ Last name	Vorname/ First name	Institut/ Institute	Beruf/ Profession
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Bauch	Dorothea	GEOMAR	Scientist, Geochemistry
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Korhonen (Ms)	Meri	FMI	Scientist, Phys. Oceanography
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Reader	Heather	DTU	Scientist, Biology
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Rutgers van der Loeff	Michiel	AWI	Scientist, Geochemistry
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Scholz	Daniel	AWI	Scientist, Marine BioGeoScience
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Slagter	Hans	NIOZ	PhD Student, Geochemistry
Staubwasser	Michael	UNIK	Scientist, Geochemistry
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Vinogradova	Elena	SIO	Scientist, Biogeochemistry
NN		HeliService	Pilot
NN		HeliService	Pilot
NN		HeliService	Technician
NN		HeliService	Technician

11. SCHIFFSBESATZUNG / SHIP'S CREW

No.	Name	Rank
01.	Schwarze, Stefan	Master
02.	Langhinrichs, Moritz	1.Offc.
03.	Farysch, Bernd	Ch. Eng.
04.	Lauber, Felix	2. Offc.
05.	Hering, Igor	2.Offc.
06.	Peine, Lutz	2.Offc.
07.	Pohl, Klaus	Doctor
08.	Fröb, Martin	Comm.Offc.
09.	Grafe, Jens	2.Eng.
10.	NN	2.Eng.
11.	Holst, Wolfgang	3. Eng.
12.	Redmer, Jens	Elec.Tech.
13.	Christian, Boris	Electron.
14.	Hüttebräucker, Olaf	Electron.
15.	Nasis, Ilias	Electron.
16.	Himmel, Frank	Electron
17.	Loidl, Reiner	Boatsw.
18.	Reise, Lutz	Carpenter
19.	Michaels, Jürgen-Dieter	A.B.
20.	Brickmann, Peter	A.B.
21.	Winkler, Michael	A.B.
22.	Hagemann, Manfred	A.B.
23.	Scheel, Sebastian	A.B.
24.	Brück, Sebastian	A.B.
25.	Wende, Uwe	A.B.
26.	Bäcker, Andreas	A.B.
27.	Preußner, Jörg	Storek.
28.	Teichert, Uwe	Mot-man
29.	Rhau, Lars-Peter	Mot-man
30.	Lamm, Gerd	Mot-man
31.	Schünemann, Mario	Mot-man
32.	Pinske, Lutz	Mot-man
33.	Redmer, Klaus-Peter	Cook
34.	Silinski, Frank	Cooksmate
35.	Martens, Michael	Cooksmate
36.	Czyborra, Bärbel	1.Stwdess
37.	Wöckener, Martina	Stwdss/KS

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No.	Name	Rank
38.	Dibenau, Torsten	2.Steward
39.	Silinski, Carmen	2.Stwdess
40.	Arendt, Rene	2.Steward
41.	Möller, Wolfgang	2.Steward
42.	Sun, Yong Shen	2.Steward
43.	Yu, Kwok Yuen	Laundrym.

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