Final Report

Name	Schoemann
Selection	
Host institution	Université Libre de Bruxelles
Supervisor	Prof. Jean-Louis Tison
Period covered by this report	from 08/06/2013 to 07/06/2015
Title	Marine trace metal biogeochemistry and its control on the biological carbon pump

1. Objectives of the Fellowship

Iron (Fe) is a bio-essential metal with extremely low and therefore bio-limiting concentrations in more than 30% of the oceans, including the Southern Ocean and some parts of the Arctic Ocean. It has a crucial impact on the biogeochemical cycles of carbon and other elements like nitrogen, phosphorus, silica and sulphur with ultimate influence on the Earth climate system. Other trace metals, like Mn, Zn, Co and Cu are also required for microorganisms cell metabolism and may be (co-) limiting in those areas, but are poorly studied so far.

Trace metals dusts inputs are known to be generally insignificant in Antarctica. Previous dissolved and particulate Fe concentrations data from East Antarctica and the Weddell Sea pack ice showed that Fe is 10-100 times more concentrated in the sea ice than in underlying seawater and that sea ice melt can be a significant source of Fe, delivering up to 70% of the daily Fe supply to the surface waters (Lannuzel et al. 2007, 2008, 2010). According to budget estimates, sea ice accumulated Fe in the Weddell Sea and East Antarctic pack ice would largely derive from the underlying seawater rather than from atmospheric inputs. Most of the studies on trace metals in the sea ice so far focused on Antarctic pack ice in early spring-summer. In the present project, our aim is to investigate landfast ice and pack ice in winter in Antarctica, as well as pack ice in Central Arctic.

The specific objectives of the fellowship were to:
(i) determine the distribution and the chemical and physical (particulate, colloidal, soluble) speciation of bio-essential trace metals (e.g. Fe, Mn, Zn, Co, Cu) in polar ocean waters and sea ice;
(ii) identify and quantify the sources of these bio-essential trace metals to the ocean; (iii) assess the solubility and bioavailability of the different external and internal sources of Fe and their impact on primary production, the plankton community structure and consequent impact on the biological carbon pump;
(iv) further develop the use of non-traditional isotopes (e.g. Fe, Zn, Cu) as a tool to elucidate biogeochemical processes involving biologically relevant trace metals;
(v) parameterize, using the obtained results, the major physical, chemical and biological processes describing the biogeochemistry of Fe to be incorporated into ocean biogeochemical models.

2. Methodology in a nutshell

Sampling

Sea-ice, brines, snow and underice seawater have been collected: (i) in the landfast ice environment at Cape Evans during the YROSIAE sampling program (Scott Base, McMurdo Sound, Ross Sea, Antarctica) from November 2011 to December 2011 and from August 2012 to December 2012 (ii) in the Weddell Sea during the AWECS cruise aboard RV Polarstern from June to August 2013, (iii) in Central Arctic during the IceARC cruise also aboard RV Polarstern from August to October 2013. At Rothera samples of seawater were collected from November 2013 to March 2014 in collaboration with Dr. J. Bown (NIOZ, Texel). In order to assess whether atmospheric inputs in McMurdo Sound and in Central Arctic may play a significant role in providing bio-essential trace metals, dusts samples were also collected at Cape Evans and aboard the RV Polarstern.

Methodology

Dissolved trace metals concentrations (Mn, Fe, Al, Co, Ni, Cu, Zn, Mo, Cd and Pb) are measured by a method that was developed during the first year of the project in collaboration with Ing. J. de Jong (DSTE, ULB). It combines multiple element isotope dilution (Milne et al. 2010) with preconcentration using the Nobias Chelate PA1 resin (Sohrin et al. 2008, Biller et al. 2012) and ICP-MS (Agilent Quadrupole) analysis. This method was applied to dissolved samples of snow, brines and underice seawater collected during YROSIAE and to dissolved samples of snow, sea ice, brines and seawater collected in Central Arctic. Particulate trace metals concentrations have been measured after digestion of the particulate matter as in de Jong et al. (2007).

The Fe, Zn and Cu isotopic composition will be determined according to the methodology developed by de Jong et al. 2007, with the recently acquired new Nu MC-ICPMS-MS in collaboration with Prof. N. Mattielli and Ing. J. de Jong (DSTE, ULB). We expect to reach better detection limits than with the older Nu MC-ICPMS. Due to interferences problems, which are not yet solved, the new instrument is still currently being set-up and we did not take the risk to loose our precious field samples.

The organic complexation of Fe in the sea ice and underice sea water was measured by voltametry (CLE-ACSV) on samples collected in the Central Arctic according to the method described in Gerringa et al. 2015.

3. Results (6-8 pages)

McMurdo Sound (YROSIAE)

Results obtained in McMurdo Sound are shown in Table 1. Dissolved trace metals concentrations in snow are one to up to five orders of magnitude higher than the concentrations previously observed in snow from East Antarctica (Lannuzel et al. 2011), showing a strong dust input of these metals in McMurdo Sound. The trace metals concentrations observed in the snow are extremely variable with highest values being 2 orders of magnitude higher than the lowest ones. Concentrations of Fe, Al, Mn and Co are much higher in the snow than in the underice seawater, whereas concentrations of Cu, Zn, Ni and Pb are similar and the concentrations of Mo and Cd are lower. Similar concentrations of dissolved Fe, Mn, Cu, Zn, Cd, Co and Al were observed in underice seawater in Nov-Dec 2011 and in Nov-Dec 2012. Dissolved Fe, Cu, Zn, concentrations were also similar Nov-Dec 2011 and 2012 in brines.

As shown in figure 1, from September to November, temperature increased from -20°C to reach ca. -2.5°C along the whole ice core. At the same time, the brine volume that was below 5% in the upper 120 cm in September-October increased to brine volumes above 10% in November-December, reflecting the interconnection between the brine pockets along the whole ice core. Those changes in the physical conditions allowed algae growth in the whole core as indicated by increased chlorophyll a concentrations in November-December. In the bottom ice, chlorophyll a (Chl a) concentration increased from 13 µg/L in September to 975 µg/L in November 2012. In 2011, it decreased from 285 to 25 µg/L. As an example, particulate (PFe) and dissolved Fe (DFe) data are shown in figure 1. Trends in particulate iron concentrations followed those in Chl a concentrations. Considering all PFe in the bottom ice to be associated to the ice algae (intracellular and extracellular Fe) and a C:Chl a ratio of 30, the estimated PFe:C ratios ranged between 6 to 27 µmoles/moles, corresponding to $Fe_{intra+extra}$:C ratios obtained for Antarctic species of microalgae grown in pure cultures (2-155 µmoles/moles, Hassler and Schoemann, 2009). This suggests that the accumulated Fe in the bottom ice is due to algae growth, which takes up dissolved Fe from underice seawater. It means sea ice accumulates Fe not only during the sea ice formation in winter but also and mainly in Spring due to the growth of bottom ice algae that allows the sea ice sequestration of Fe coming from below. Maxima in dissolved Fe were also observed in the bottom ice. Like previously observed (Becquevort et al, 2009), very high maxima of dissolved organic carbon concentrations were found in the bottom ice (up to 2732 µM, data not shown), which likely indicate high remineralization and excretion rates in the bottom ice. The high DFe concentrations could therefore result from the combined dissolution of Fe due to remineralization processes and to the organic complexation of Fe maintaining Fe in the dissolved fraction by preventing its precipitation. In the top ice, maxima in PFe and DFe were detected at the end of November 2012 and could derive from snowmelt and percolation of the Fe enriched melt into the surface layers of the land-fast sea ice in McMurdo Sound induced by the warming of the sea ice in late

Spring-summer. PFe and DFe concentrations in snow respectively ranged from 240-10906 nmoles/L and 110-2400 nmoles/L.

Table 1 Dissolved trace metals concentrations (average and range) in snow, brines and underice seawater at Cape Evans (McMurdo Sound, Antarctica).

Dissolved metals	Snow	Underice seawater		Brines	
		Nov-Dec 2011	Nov-Dec 2012	Nov-Dec 2011	Nov-Dec 2012
	(n=10)	(n=6)	(n=6)	(n=4)	(n=4)
Fe (nM)	4038 (110-17751)	1.42 (0.90-2.48)	1.5 (0.92-1.98)	8.69 (4.95-16.50)	13.37 (6.22-28.74)
Ni (nM)	2.77 (0.55-5.07)	6.29 (5.69-6.50)	6.59 (6.52-6.69)	8.09 (6.62-9.28)	12.47 (10.60-14.71)
Cu (nM)	3.06 (0.47-5.09)	2.24 (1.86-3.87)	2.02 (1.74-2.26)	2.84 (2.42-3.70)	3.71 (3.26-4.37
Zn (nM)	13.93 (4.26-26.58)	7.47 (5.80-10.27)	17.14 (7.20-39.74)	11.12 (8.41-12.28)	17.93 (13.17-22.59)
Pb (pM)	373 (167-701)	92.2 (57.33-126.27)	22.02 (13.00-40.69)	315.74 (128.46-690.17)	107.47 (41.00-283.99)
Al (nM)	2044 (285-4496)	6.20 (4.47-9.14)	7.40 (4.15-9.39)	8.53 (4.91-15.47)	6.83 (4.02-13.33)
Mn (nM)	64 (6-136)	1.15 (1.03-1.35)	1.07 (1.02-1.11)	2.56 (2.07-2.98)	8.56 (6.84-11.30)
Co (pM)	847 (135-1660)	37.78 (32.39-56.04)	40.27 (34.24-51.70)	56.73 (45.35-77.19)	103.2 (89.58-118.88)
Mo (nM)	19.23 (3.77-43.61)	108.78 (106.42-114.69)	94.85 (85.59-101.92)	130.62 104.86-147.50	130.57 (110.24-158.28)
Cd (pM)	54.24 (1.44-188.97)	735.24 (668.76-797.66)	707.23 (699.63-724.88)	418.59 (298.79-507.71)	1875.37 (1561.17-2413.94)

Inventories of the trace metals in the land fast ice sea ice give insights on its role as a source of bio-essential trace metal for the fuelling of the seasonal Ross Sea bloom. As an example for Fe, we showed that entrainment of wind-blown material and sediment-derived Fe is the most important pathway for high Fe concentrations in land-fast ice in McMurdo Sound (de Jong et al. 2013). Wind-blown lithogenic material in the snow on the land-fast ice makes up for 14–68% of the total Fe inventory of the sea ice. The data suggest that the usual spring breakup of sediment-laden land-fast ice to the Ross Sea may have a significant potential fertilizing effect on the waters of the Ross Sea Polynya. According to our budget, together with pack ice melting, the land-fast ice melting could provide 84 to 90% of the supply of new dissolved Fe (Figure 2) to the Ross Sea.

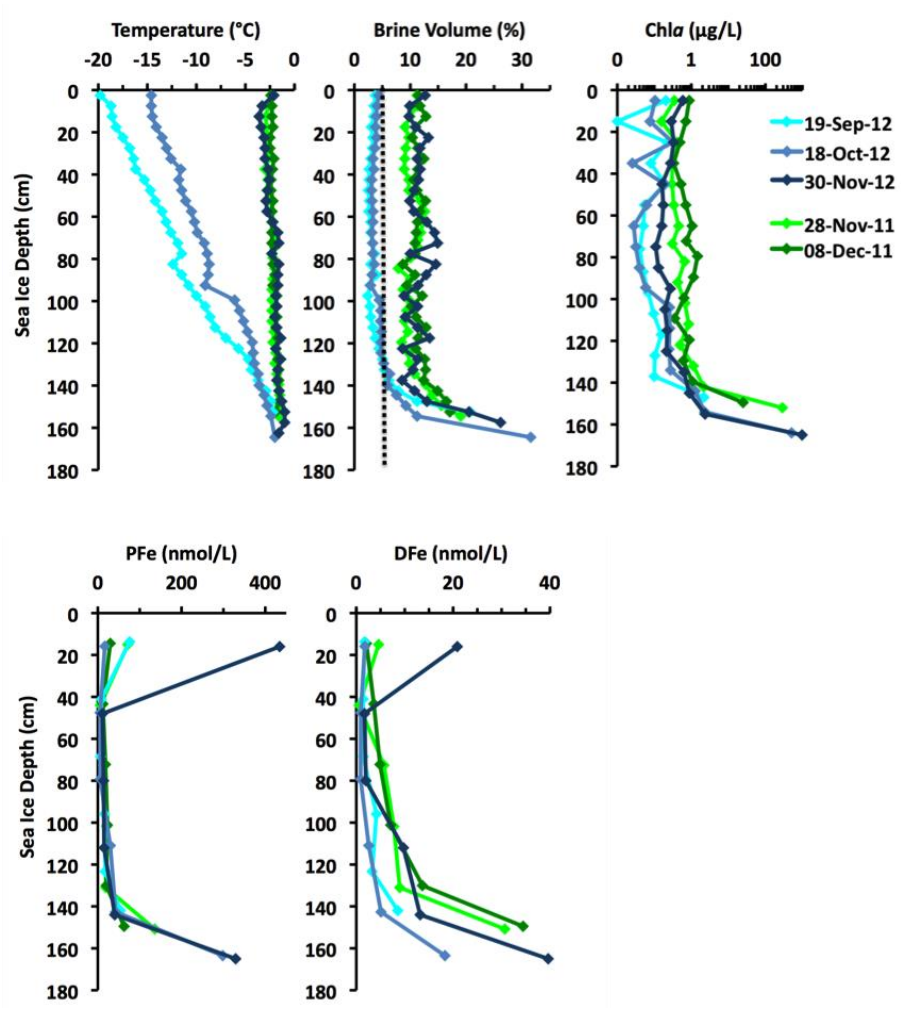


Figure 1: Seasonal evolution of temperature, brine volume, chlorophyll a, particulate Fe and dissolved Fe profiles in the sea ice.

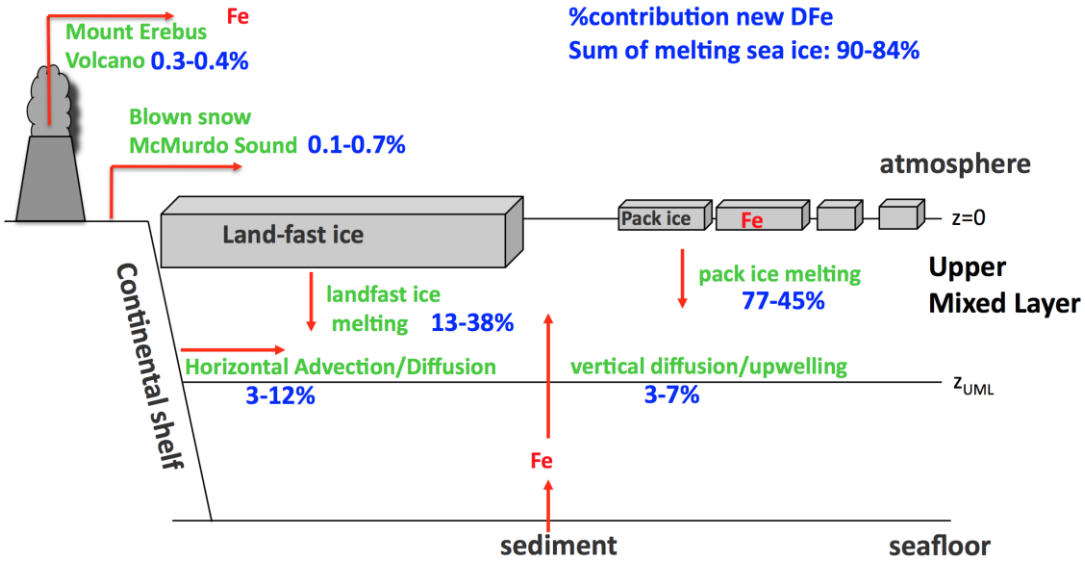


Figure 2: Fe budget for the Ross Sea

Results ANT XXVII/3 IceArc

During cruise ANT XXVII/3 'IceArc' on board of German RV Polarstern a total of 8 stations were sampled in the Eurasian Basin of the Central Arctic to investigate the concentrations of trace metals in sea ice (Figure 3). For each station, samples of snow, sea ice (plus surface scattering layer SSL), brine, under-ice seawater (0-1-30 m depth) and melt-pond water were collected.

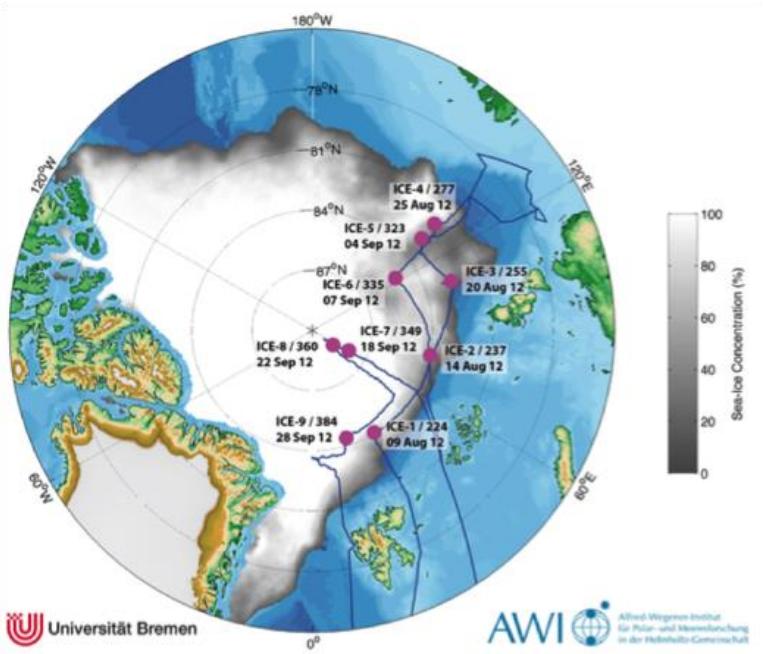


Figure 3. Map of the Arctic Ocean with cruise track, station indication and sea ice cover.

Based on the dissolved trace metal (TM) results (see summary Table 2) we can distinguish three types of sea ice stations: multi-year ice (St 360) and two contrasting groups of first year ice (St 277-323-335 versus St 224-237-255-348). Higher TM concentrations (Fe, Mn, Al) were observed in sea ice and under-ice seawater (Fe, Mn, Al, Cu, Co) at St 277-323-335, when compared to St 224-237-255-348 (Figure 4). Multi-year ice of St 360, which was sampled close to first year ice of St 348, exhibited high Fe, Mn and Co in the lower part of the ice core. The high seawater Fe, Mn Al, Cu and Co concentrations at St 277-323-335, together with the shape of their profiles (enhanced near the sea ice) suggest input of these metals from the melting sea ice. This is supported by the salinity profiles (Figure 5), which show the presence of fresher water under the sea ice, with the freshest water at the sea ice – seawater interface.

The higher Fe-Mn-Al concentrations in the sea ice at these stations may be indicative of a continental shelf provenance of this sea ice, possibly the Eurasian inner continental shelf, which also receives terrestrial input of trace metals via the Lena River. The sea ice was later transported into the research area through the Transpolar Drift.

Snow concentrations were especially high for Fe, Al and Pb, rather low for Mn and Zn, and very low for Ni, Cu and Cd, suggesting an atmospheric dust origin of these metals. The highest Fe and Al concentrations in the snow were observed at those stations closest to the Eurasian continental landmass (notably St 224-255-277), whereas the more remote stations closer to the North Pole (St 323-335-360) exhibited much lower Fe and Al concentrations.

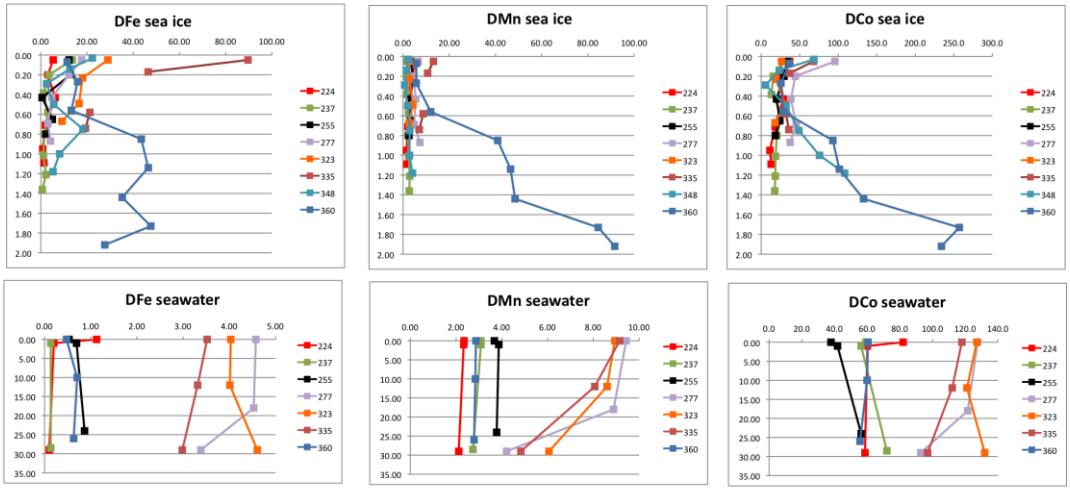


Figure 4. Sea ice and under-ice seawater profiles for dissolved Fe, Mn and Co. Fe and Mn in nM, Co in pM, vertical axis in m.

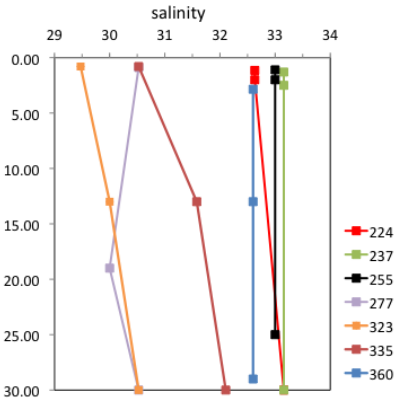


Figure 5. Under-ice seawater profiles for salinity.

The melt ponds that were sampled fall in two distinct groups, based on the salinity in the melt water: fresh water in the melt ponds of St 255-277-335 with high Fe, Mn and Al concentrations and saline water at St 348-360 with low Fe, Mn and Al, indicating that in the latter case the melt ponds were in open connection with the underlying seawater and had drained their TM content through the brine channel system. This is supported by the seawater signature of the other TM concentrations in the drained melt ponds. This observation of melt pond drainage in combination with high brine concentrations, which also drain in the underlying seawater, strongly suggest the role of Arctic sea ice in fertilizing the ocean, where Fe concentrations can be potentially limiting (Klunder et al., 2012). These results highlight the role of sea ice as a vector for transporting bio-active trace metals into depleted ocean regions.

In the sea ice, organic Fe complexing ligands ([L_T]) ranged from 1.3 to 47.2 nM in the sea ice, from 2.0 to 5.3 nM in the seawater and from 2.3 to 13.8 in the melt ponds. Organic ligands were almost saturated with Fe in all media, with a positive linear relationship observed between [DFe] and [LT]: [LT] = 0.89 [DFe] + 0.75 (r^2=0.88, n=22). Our results suggest that the organic ligands produced by sea ice algae and bacteria help to maintain Fe in the dissolved fraction, therefore enhancing its bioavailability for the sea ice algal and phytoplankton communities.

Table 2. Overview of dissolved trace metal concentrations (average and range) during cruise ANT XVII/3 IceArc.

Dissolved metals	Snow	Melting ponds		Multi-year sea ice	First year sea ice		SSL	Brines		Under-ice seawater	
IceArc	(n=7)	St 255-277-335 (n=6)	St 348-360 (n=2)	St 360 (n=8)	St 224-237-255-348 (n=26)	St 277-323-335 (n=14)	St 348 (n=1)	St 224-237-255 (n=5)	St 277-335 (n=2)	St 224-237-255-360 (n=12)	St 277-323-335 (n=9)
Fe (nM)	140	13	0.63	30	4.7	22	22	9.4	22	0.51	3.3
	(8.9-394)	(10-16)	(0.42-0.83)	(11-48)	(0.59-18)	(3.1-90)		(2.4-18)	(14-30)	(0.10-1.13)	(0.34-4.6)
Ni (nM)	0.58	0.52	4.1	0.76	1.8	1.5	15	0.98	1.3	3.7	4.5
	(0.26-1.00)	(0.27-0.70)	(3.9-4.3)	(0.28-1.6)	(0.16-5.4)	(0.53-5.3)		(0.39-1.5)	(0.90-1.8)	(3.2-4.4)	(0.50-5.4)
Cu (nM)	0.34	0.56	3.2	0.74	1.4	0.73	3.8	0.78	1.1	1.9	3.6
	(0.04-0.71)	(0.26-1.1)	(2.7-3.6)	(0.32-1.5)	(0.17-4.8)	(0.43-1.1)		(0.36-1.1)	(0.54-1.7)	(1.1-3.1)	(0.84-4.8)
Zn (nM)	6.3	1.8	0.44	8.5	24	26	74	7.24	2.3	1.1	1.0
	(1.4-16.5)	(1.3-3.5)	(0.42-0.46)	(3.3-19)	(0.37-199)	(8.1-52)		(2.9-10)	(0.67-3.9)	(0.29-3.3)	(0.37-1.6)
Pb (pM)	250	82	7.0	50	61	62	603	101	23	10	4
	(7-673)	(29-215)	(6.6-7.4)	(14-102)	(1-233)	(15-123)		(36-206)	(6-40)	(2.4-33)	(1.0-9.6)
Al (nM)	169	16	2.9	24	16	58	57	19	24	1.1	2.5
	(19-496)	(10-25)	(0.68-5.1)	(11-35)	(0.9-83)	(17-124)		(8-27)	(21-28)	(0.19-3.2)	(0.95-4.8)
Mn (nM)	2.5	21	6.8	42	3.6	6.2	2.3	6.4	19	3.0	6.5
	(0.1-6.1)	(11-44)	(2.4-11)	(5.7-92)	(0.57-9.4)	(2.6-13)		(2.5-12)	(18-20)	(2.1-3.9)	(0.57-9.4)
Co (pM)	74	71	67	114	46	41	68	50	73	58	102
	(10-199)	(51-105)	(52-83)	(26-257)	(5.7-132)	(18-96)		(34-58)	(71-76)	(38-82)	(12-132)
Mo (nM)	0.2	4.2	68	5.3	19	2.8	15	13	14	87	67
	(0-0.8)	(0.4-8.9)	(50-85)	(1.4-8.0)	(0.5-104)	(0.5-6.2)		(4.4-20)	(4.7-22)	(40-109)	(21-104)
Cd (pM)	17	23	28	24	51	16	26	24	22	41	64
	(0.5-52)	(18-26)	(25-32)	(4.6-88)	(6.5-295)	(7.6-31)		(11-33)	(20-23)	(15-72)	(18-99)

Results ANT XXIX/6 AWECS (Antarctic Winter Ecology and Climate Study)

During cruise ANT XXIX/6 'AWECS' on board of German RV Polarstern in the Weddell Sea during austral winter 2013 (Figure 6), the following trace metal samples were collected:

- Pancake ice: stations 486, 488, 489
- Young ice: station 500
- Slush: station 500
- Frost flowers: station 503
- Sea ice: 17 ice cores at 11 stations
- Snow, brine, seawater: 49 TD-Me samples, 126 DMe samples, 134 PMe filters.
- CTD stations: stations 509-510-511-512-514-516-517, depths between 244 m and 2475 m.

The AWECS cruise was a unique opportunity to study sea ice trace metal biogeochemistry and dynamics in the earliest stages of sea ice formation during mid winter. The analytical work is still in progress, but the following important conclusions can be drawn already from the preliminary results.

1. Sea ice

Comparing very young sea ice in the form of pancake ice (St 486) and young ice formed in a lead at St 500 (Table 3), we can see that in function of increasing ice thickness the trace metal concentrations in the ice increases also. This demonstrates the capacity of sea ice to scavenge and preconcentrate trace metals from the seawater from which it is formed. This is confirmed in an ice growth experiment that was conducted at St 517 (see below).

We also note the presence of slush (mix of melted snow and seawater) at St 500 due to flooding of the ice floe with seawater. The snow cover consisted of surface layer of 20 cm dry snow, 10 cm wet snow, followed by 14 cm of slush. Trace metal concentrations were generally low in the slush layer, probably due to the mixing of low TM snow with low TM seawater at this remote position in the Weddell Sea (i.e., far away from terrestrial sources of atmospheric dust and sedimentary input).

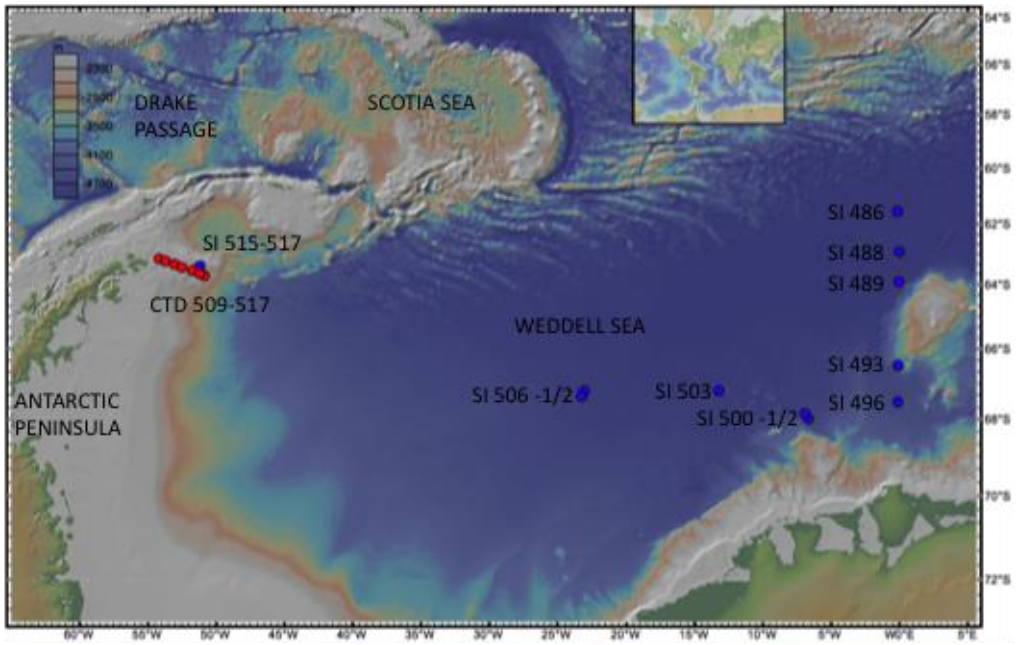


Figure 6. AWECS sea ice stations (blue) and CTD stations (red) which were sampled for trace metals, superimposed on a bathymetric map. Station 486 at the ice edge, the other stations in dense pack ice.

Table 3. Sea ice results AWECS

Unfiltered and dissolved trace metals			Fe	Fe	Ni	Ni	Cu	Cu	Zn	Zn	Mo	Mo	Cd	Cd	Pb	Pb	Al	Al	Mn	Mn	Co	Co
Sea ice	AWECS	Ice thickness	nM	nM	nM	nM	nM	nM	nM	nM	nM	nM	pM	pM	pM	pM	nM	nM	nM	nM	pM	pM
		cm	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF
486-SI	Pan cake ice	15	3.5	(841)	4.7	6.4	4.5	13.9	52.3	82.7	74	76	410	437	899	(3081)	43.3	(286)	1.3	5.4	44	(250)
500-YSI1	Young sea ice	6	0.9	10.2	2.6	2.6	1.0	1.3	7.4	8.3	46	46	300	300	56	67	9.6	18.9	0.4	0.5	17	19
500-YSI2	Young sea ice	6	2.1	10.7	3.0	2.8	1.4	1.9	12.1	11.7	52	47	375	327	133	134	30.2	105.2	1.0	1.0	20	20
500-SL	Slush		0.2	2.0	4.0	4.1	1.1	1.2	3.2	3.2	73	74	439	433	13	15	0.6	7.7	0.2	0.2	19	18
503-FF1	Frost flowers		0.4	5.9	11.8	11.9	4.2	4.3	7.5	16.3	117	204	1135	1126	119	108	9.5	15.8	0.5	0.6	50	57
503-FF2	Frost flowers		0.4	6.5	12.5	12.6	4.0	4.2	6.8	8.7	127	176	1210	1205	(104)	72	2.6	7.6	0.6	0.6	52	58

We also report the first TM data for frost flowers. Frost flowers are ice crystals commonly found growing on young sea ice in cold, calm conditions. The ice crystals are similar to hoar frost, and are commonly seen to grow in patches around 3–4 cm in diameter. Frost flowers growing on sea ice have extremely high salinities and concentrations of volatile seawater chemicals and, because of their high surface area, are efficient releasers of these chemicals into the atmosphere. The TM concentrations in frost flowers are comparable with those in brines and especially Cd is high. A role for sea ice bacteria in the biomethylation of heavy metals like Hg, Pb and Cd has been reported before (Ponratz and Heumann, 1999), and sea ice can thus be a source to the atmosphere of volatile monomethylated Cd.

Figure 7. Frost flowers on young sea ice.

2. Brines

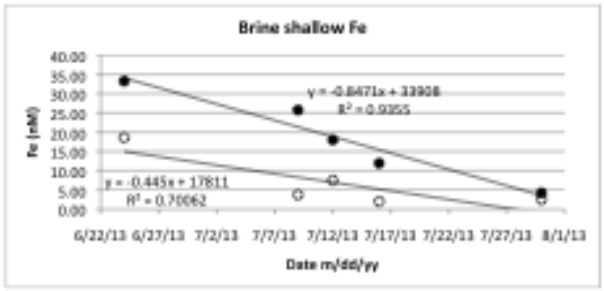
Brine concentrations collected from sack-holes generally exhibit enhanced concentrations (Table 4). Taken over time we observe a general decrease of the TM content of the brines. This coincides with the cruise track going from very cold regions of the Southeastern Weddell Sea to the warmer climatology of the Antarctic Peninsula. From colder to warmer conditions, the brine volumes will increase and brine drainage to the underlying seawater will occur, all leading to decreased concentrations. Interestingly, the exception to this trend is St 515 sampled on July 27, 2013 under very cold conditions (air temperature -20°C). The pack ice consisted of second year sea ice (perhaps landfast ice) (Lemke et al., 2014) with typical low bulk ice salinity and low brine volume, hence higher brine concentrations than would be expected for the location.

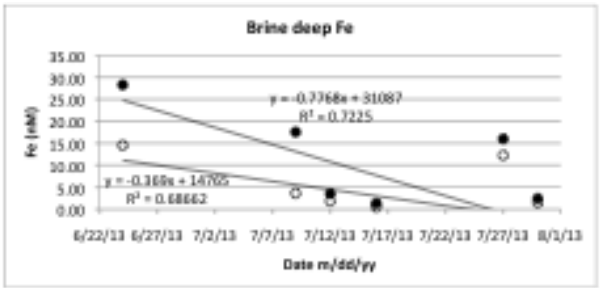
Table 4. Brine results AWECS

Unfiltered and dissolved trace metals		Fe	Fe	Ni	Ni	Cu	Cu	Zn	Zn	Mo	Mo	Cd	Cd	Pb	Pb	Al	Al	Mn	Mn	Co	Co
Sea ice brines	AWECS	nM	nM	nM	nM	nM	nM	nM	nM	nM	nM	pM	pM	pM	pM	nM	nM	nM	nM	pM	pM
	depht (cm)	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF
496-BR-SH	20	18.6	33.3	18.0	18.1	6.0	6.0	26.1	26.8	71	113	971	960	308	290	1.9	5.4	1.14	1.29	59	63
496-BR-D	45	14.5	28.3	15.3	15.2	5.4	5.2	16.4	16.8	115	179	711	703	196	444	3.0	6.3	0.94	1.03	54	55
503-BR-SH	30	3.8	25.8	18.3	19.2	5.3	5.9	29.2	32.7	133	127	822	880	280	292	1.2	2.3	0.83	1.16	34	39
503-BR-D	55	3.7	17.6	15.1	15.7	4.6	4.9	19.0	20.6	293	157	580	586	126	139	1.6	5.0	0.57	0.77	37	33
506-BR-SH	20	7.5	18.0	14.9	14.9	5.9	5.6	18.3	19.2	248	109	573	583	204	227	2.1	2.3	0.59	0.69	33	33
506-BR-D	40	1.9	3.5	11.3	11.4	3.1	3.1	7.9	8.1	220	166	561	571	40	42	5.3	3.2	0.30	0.32	30	28
506/2-BR-SH	20	2.0	11.9	14.3	14.5	4.3	5.0	26.0	26.7	145	194	679	689	441	165	1.0	2.8	0.41	0.50	33	38
506/2-BR-D	40	0.5	1.4	12.3	12.4	3.2	3.3	10.2	10.9	222	154	626	651	30	24	2.7	3.0	0.20	0.24	31	25
515-BR-D	90	12.3	16.0	8.7	8.8	3.3	4.0	6.0	6.3	102	292	282	294	97	108	2.6	5.0	0.71	0.74	59	58
517-BR-SH	15	2.5	4.3	14.4	14.4	4.4	4.7	25.7	28.0	106	166	2268	2337	73	71	0.9	1.8	2.70	2.78	72	74
517-BR-D	45	1.5	2.4	9.3	9.3	2.7	2.8	14.4	14.8	163	160	1453	1462	25	25	3.8	7.9	1.47	1.51	52	52

In the case of Fe (Figure 8) the concentrations decrease in both shallow and deep brines with a rate of about 0.4 nM/d DFe and 0.8 nM/d TD-Fe. With an average ice thickness of 0.55 m this would correspond to fluxes of 0.22 µmol/m^2/d DFe and 0.44 µmol/m^2/d TD-Fe. Whether this is an efflux to the underlying seawater or a transfer from the brine solution to the solid ice, is not clear as yet. However we favor the idea of an efflux to the underlying seawater as may be indicated by the enhanced under-ice seawater concentrations at Sts 488 and 493 (see Table 5 below), which are higher than what would be typical for this region (Klunder et al., 2011). These results seem to suggest that also in winter sea ice is a source for trace metals to the water column, not only during the spring melt.

Figure 8. General decrease of Fe concentrations in brine as observed in Weddell Sea basin. Open symbols DFe, closed symbols unfiltered Fe. In the deep brine panel the data points on July 27, 2013 at St 515 were not taken into account for the linear regression.





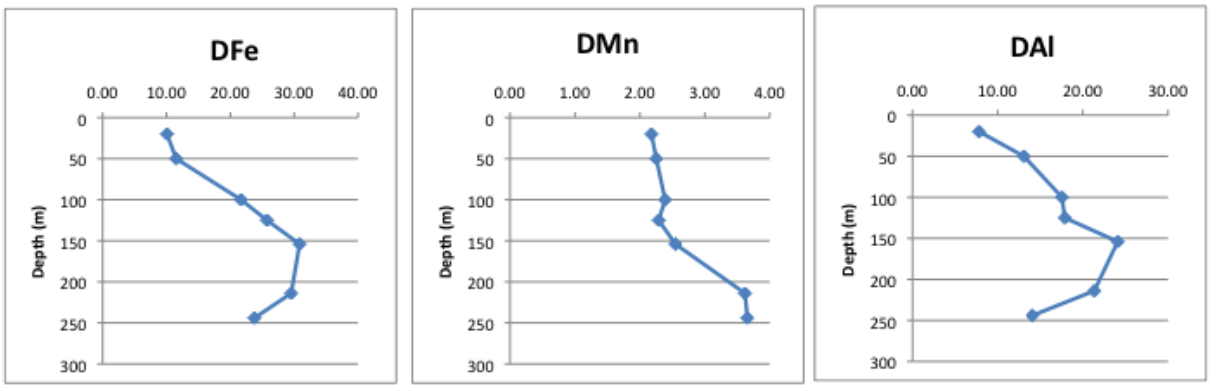
3. Seawater

One depth profile of an off shore transect near the Antarctic Peninsula has been analyzed sofar, notably the one nearest to shore (Table 5). The goal of this transect is to establish a TM gradient with increasing distance from the continent in order to estimate horizontal and vertical advective and diffusive fluxes into the open ocean. These fluxes will allow to determine and to quantify the provenance of high TM concentrations in the sea ice. At St 509, in shallow waters of 244 m depth, high Fe, Mn and Al concentrations point indeed at a continental shelf source for these metals (Figure 9). Enhanced concentrations near the seafloor point at a sedimentary source of these metals, caused by sediment resuspension and diffusion.

Table 5. Seawater results AWECS

Unfiltered and dissolved trace metals		Fe	Fe	Ni	Ni	Cu	Cu	Zn	Zn	Mo	Mo	Cd	Cd	Pb	Pb	Al	Al	Mn	Mn	Co	Co
Seawater	AWECS	nM	nM	nM	nM	nM	nM	nM	nM	nM	nM	pM	pM	pM	pM	nM	nM	nM	nM	pM	pM
	depht (m)	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF
488-SW-5m	5	1.6	14.0	6.1	6.2	2.1	2.4	9.5	8.7	120	119	533	536	163	176	2.5	6.9	0.31	0.46	29	30
493-SW-0m	0	3.3	17.6	7.2	7.5	2.3	2.6	16.4	15.1	119	116	695	699	144	182	5.5	28.0	0.54	0.71	51	51
493-SW-1m	1	3.7	12.2	7.0	7.1	2.3	2.5	12.7	12.7	120	118	697	698	127	135	7.8	13.5	0.47	0.53	42	44
509-SW-N22	20	10.1		6.7		2.1		6.3		119		721		52		7.8		2.18		76	
509-SW-N19	50	11.5		6.6		2.0		5.1		118		718		18		13.1		2.25		78	
509-SW-N10	100	21.7		6.7						119		720				17.5		2.39		81	
509-SW-N8	125	25.7		6.7		2.0		5.3		118		717		17		7.9		2.29		79	
509-SW-N6	154	30.9		6.7		2.0		5.4		121		721		24		24.1		2.55		84	
509-SW-N3	214	29.5		6.7		2.1		5.4		121		724		17		21.3		3.62		108	
509-SW-N1 (bottom)	244	23.8		6.7		2.1		6.0		121		732		21		14.1		3.66		110	

Figure 9. Fe, Mn and Al concentrations at St 509, on the inner continental shelf close to the tip of the Antarctic Peninsula.



4. Ice growth experiment

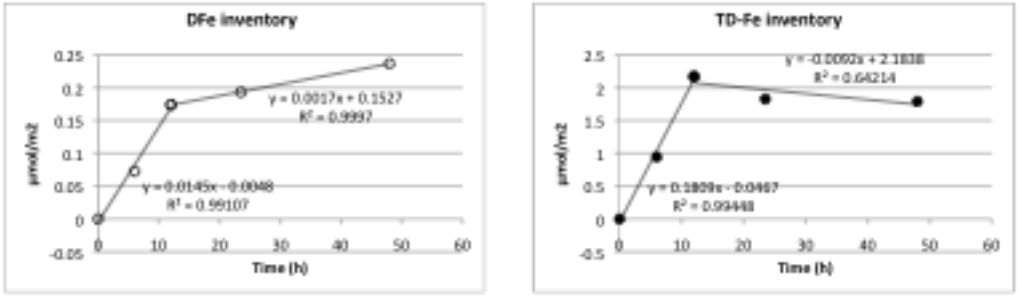
An ice growth experiment was conducted by drilling a series of holes into the sea ice at station 517, and to sample each refreezing hole at fixed intervals in time. The results suggest a rapid initial growth phase together with an increase of the TM inventory (Table 6, Fe given as example below, Figure 10). A slow down occurred after 12 h, probably due to a transition from frazil ice accumulation to columnar ice formation. DFe build up continued at a slower pace than initially, but the TD-Fe inventory slightly decreased, probably as a result of a remineralization of PFe to DFe. Probably the build up of Fe in sea ice will continue with the proliferation of sea ice algae.

The initial DFe accumulation amounted to 0.35 µmol/m^2/d and slowed down to 0.041 µmol/m^2/d. For TD-Fe this was 4.3 µmol/m^2/d but turned into a slight loss of 0.22 µmol/m^2/d. This means that about 0.18 µmol/m^2/d DFe is lost from the sea ice again while it is forming, probably via brine drainage. This estimate corresponds remarkably well with the one in the brine section above.

Table 6. Ice growth experiment results.

Unfiltered and dissolved trace metals				Fe	Fe	Ni	Ni	Cu	Cu	Zn	Zn	Mo	Mo	Cd	Cd	Pb	Pb	Al	Al	Mn	Mn	Co	Co
Ice growth experimen		thickness	growth	nM	nM	nM	nM	nM	nM	nM	nM	nM	nM	pM	pM	pM	pM	nM	nM	nM	nM	pM	pM
St 517	ΔT	cm	cm/h	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF	F	UF
t0	0	0																					
ICE EXP t1	6.0	4.5	0.75	1.6	21.0	3.6	3.7	1.7	1.7	22.0	22.9	60	59	486	605	39	43	17.5	49.0	0.49	0.80	29	63
ICE EXP t2	12.0	6	0.25	2.9	36.2	4.6	4.9	1.8	2.4	26.6	30.8	54	51	501	653	158	215	10.7	32.1	1.34	1.85	44	52
ICE EXP t3-top	23.5	10.5	0.39	1.8	16.8	2.0	2.1	1.0	1.2	26.8	27.6	35	35	242	242	126	144	6.5	26.3	0.32	0.44	27	55
ICE EXP t3-bot	23.5			1.8	18.0	1.7	1.7	0.9	1.1	23.8	24.6	27	26	739	743	113	138	12.6	25.2	1.35	1.37	29	40
ICE EXP t4-top	48.0	21.5	0.45	1.7	8.3	2.1	2.2	1.1	1.3	13.3	12.8	36	36	251	244	84	91	9.8	18.3	0.29	0.34	19	25
ICE EXP t4-mid	48.0			0.9	5.7	1.4	1.4	0.5	0.7	6.7	7.0	24	24	244	242	32	37	3.3	7.1	0.30	0.32	14	21
ICE EXP t4-bot	48.0			0.7	11.0	1.6	1.6	1.0	1.3	24.4	25.0	26	25	864	862	37	52	6.7	22.0	1.65	1.66	26	28

Figure 10. Evolution of the sea ice Fe inventory during an ice growth experiment.



References

Becquevort S, I Dumont, J-L Tison, D Lannuzel, M-L Sauvée, L Chou, V Schoemann. (2009) Biogeochemistry and microbial community composition in sea ice and underlying seawater off East Antarctica during early spring. Polar Biology. 32 (6): 879-895, DOI :10.1007/s00300-009-0589-2.

Biller, D. and K.W. Bruland. 2012. Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS), Mar. Chem. 130-131, 12–20.

De Jong, J., V. Schoemann, J.-L. Tison, D. Lannuzel and N. Mattielli. 2007. High-accuracy determination of iron in seawater by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for pre-concentration and matrix separation. Analytica Chimica Acta. 623, 126-139. doi:10.1016/j.aca.2008.06.013.

De Jong JTM, V. Schoemann, N. Maricq, N. Mattielli, P. Langhorne, T. Haskell, J.L. Tison. 2013. Iron in land-fast sea ice of McMurdo Sound derived from sediment resuspension and wind-blown dust attributes to primary productivity in the Ross Sea, Antarctica. Marine Chemistry, 24-40, doi:10.1016/j.marchem.2013.07.001.

Gerringa, L.J.A., Rijkenberg, M.J.A., Schoemann, V., Laan, P. and H.J.W. de Baar. 2015. Organic complexation of iron in the West Atlantic Ocean. Marine Chemistry, In Press, Corrected Proof, Available online 25 April 2015.

Hassler, C.S. and V. Schoemann (2009). Discriminating between intra- and extracellular metals using chemical extractions-the case of iron. Limnology and Oceanography: Methods. 7:479-489

Klunder, M. B., D. Bauch, P. Laan, H. J. W. de Baar, S. van Heuven, and S. Ober. 2012. 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., P. Laan, R. Middag, H.J.W. De Baar, J. van Ooijen (2011), Dissolved iron in the Southern Ocean(Atlantic sector), Deep-Sea Research 58, 2678–2694.

Lannuzel, D., A.R. Bowie, P.C. van der Merwe, A.T. Townsend and V. Schoemann. (2011). Distribution of dissolved and particulate metals in Antarctic sea ice. Marine Chemistry. 124, 134-146.

Lannuzel, D., V. Schoemann, J. de Jong, B. Pasquer, P. van der Merwe, F. Masson, J.-L. Tison, and A. Bowie (2010) Distribution of dissolved iron in Antarctic sea ice: Spatial, seasonal, and interannual variability, J. Geophys. Res., 115 (3), G03022, doi:10.1029/2009JG001031.

Lannuzel, D., V. Schoemann, J. de Jong, L. Chou, B. Delille, S. Becquevort and J.-L. Tison (2008). Iron study during a time series in the western Weddell pack ice. Marine Chemistry. 108, 85-95.

Lannuzel, D., V. Schoemann, J. de Jong, J.-L. Tison and L. Chou (2007) Distribution and biogeochemical behaviour of iron in the East Antarctic sea ice. Marine Chemistry. 106, 18-32.

Lemke P. and contributors (2014), The Expedition of the Research Vessel "Polarstern" to the Antarctic in 2013 (ANT-XXIX/6), Berichte zur Polar- und Meeresforschung 679, 159, http://doi.org/10.2312/BzPM_0679_2014.

Milne, A., W. Landing, M. Bizimis, P. Morton. 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). Anal. Chim. Acta. 665, 200–207.

Pongratz R. and K.G. Heumann (1999), Production of methylated mercury, lead, and cadmium by marine bacteria as a significant natural source for atmospheric heavy metals in polar regions, Chemosphere 39, 89–102.

Sohrin, Y, S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye and S. Umetani. 2008. Multielemental determination of GEOTRACES key trace metals in seawater by ICPMS after preconcentration using an ethylenediaminetriacetic acid chelating resin, Anal. Chem. 80, 6267–6273.

4. Perspectives for future collaboration between units

Two proposals have been submitted and await the decision for funding:

- Functional micro-BIOdiversity controls on biogeochemical cycles in the sea ice-covered SOUTHern Ocean (BIOSOUTH) has been submitted to the BELSPO Brain call in February 2015 in which I'm partner together with B. Delille (ULg), J.-L. Tison (ULB), F. Dehairs & F. Fripiat (VUB), H. Goosse & S. Moreau (UCL) and M. Vancoppenolle (UPMC);

- An advanced Grant ERC project "Isotopes in Sea Ice" has been submitted by Prof. J.-L. Tison in June 2015, in which I'm part of his team, being in charge of trace metals biogeochemistry and isotopes in sea water and sea ice.

The following papers are currently in preparation with Belgian (J.-L. Tison, J.T.M. de Jong, G. Carnat, T. Goossens & J. Zhou: ULB, B. Dellile & W. Champenois: ULg, F. Fripiat: VUB, S. Moreau: UCL) and international units (D. Lannuzel, P. van der Merwe & K. Meiners: IMAS, Hobart, Australia; T. Haskell: Industrial Research Ltd., Dunedin, New Zealand, H.J.W. de Baar, L.J.A. Gerringa, C.-E. Thuróczy, M. Le Guitton: NIOZ, The Netherlands):

- **Schoemann, V.,** de Jong, J.T.M., Tison, J.-L., Haskell, T., de Baar, H., Champenois, W., Zhou, J., Carnat, G., Fripiat, F., Goossens, T., Moreau, S. and B. Delille. Dust as a source of bio-essential trace elements for coastal sea ice in McMurdo Sound, Antarctica.
- D. Lannuzel, J. de Jong, M. Grotti, K.M. Meiners, J. Nishioka, **V. Schoemann**, B. Saenz, L. Tedesco, M. Vancoppenolle, P. van der Merwe. Iron in sea ice: a review.
- **Schoemann, V.,** de Jong, J.T.M., Thuróczy, C.-E., Gerringa, L.J.A., Le Guitton, M. and H.J.W. de Baar. Distribution and organic complexation of Fe in the Central Arctic Ocean.

Collaborative work is planned with J. Brown (NIOZ) on seawater samples collected at Rothera for measurements of Fe and Zn isotopes. Due to methodological problems, those analyses had to be postponed. Experiments on sea ice and dust iron availability will be done in collaboration with C. Hassler and S. Blanco-Ameijeiras.

5. Valorisation/Diffusion (including Publications, Conferences, Seminars, Missions abroad...

Publications list

Articles in international peer reviewed journals

1. De Jong, J.T.M., Stammerjohn, S.E., Ackley, S.F., Tison, J.-L., Mattielli, N. and **V. Schoemann**. 2015. Sources and fluxes of dissolved iron in the Bellingshausen Sea (West Antarctica): The importance of sea ice, icebergs and the continental margin. Marine Chemistry, In Press, Corrected Proof, Available online 14 August 2015.
2. Gerringa, L.J.A., Rijkenberg, M.J.A., **Schoemann, V.,** Laan, P. and H.J.W. de Baar. 2015. Organic complexation of iron in the West Atlantic Ocean. Marine Chemistry, In Press, Corrected Proof, Available online 25 April 2015.
3. Hassler, C.S., Norman, L., Mancuso Nichols, C.A., Clementson, L.A., Robinson, C., **Schoemann, V.,** Watson, R.J. and M.A. Doblin. 2015. Iron associated with exopolymeric substances is highly bioavailable to oceanic phytoplankton. Marine Chemistry, 173, 136-147.
4. Delille, B., M., Vancoppenolle, N.-X., Geilfus, B., Tilbrook, D., Lannuzel, **V., Schoemann**, S. Becquevort, G., Carnat, A., Vieira Borges, D., Delille, C., Lancelot, L., Chou, G.S., Dieckmann and J.-L. Tison. Southern Ocean CO2 sink: The contribution of the sea ice. Journal of Geophysical Research: Oceans, 119 (9), 6340-6355.
5. Carnat, G., J. Zhou, T. Papakyriakou, B. Delille, T. Goossens, T. Haskell, **V. Schoemann**, F. Fripiat, J.-M. Rintala, and J.-L. Tison (2014), Physical and biological controls on DMS,P dynamics in ice shelf-influenced fast ice during a winter-spring and a spring-summer transitions, J. Geophys. Res. Oceans, 119, doi:10.1002/2013JC009381.

6. Rijkenberg, M.J.A., R. Middag, P. Laan, L.J.A. Gerringa, H.M. van Aken, **V. Schoemann,** J.T.M. de Jong, H. van Haren, and H.J.W. de Baar. 2014. The Distribution of Dissolved Iron in the West Atlantic Ocean. PLosONE, 9(6): e101323.doi:10.1371/journal.pone.0101323
7. De Jong JTM, **V. Schoemann**, N. Maricq, N. Mattielli, P. Langhorne, T. Haskell, J.L. Tison. 2013. Iron in land-fast sea ice of McMurdo Sound derived from sediment resuspension and wind-blown dust attributes to primary productivity in the Ross Sea, Antarctica. Marine Chemistry, 24-40, doi:10.1016/j.marchem.2013.07.001.
8. Lannuzel, D., **V. Schoemann**, I. Dumont, M. Content, J. de Jong, J.-L. Tison, B. Delille, and S. Becquevort. 2013. Effect of melting Antarctic sea ice on the fate of microbial communities studied in microcosms. Polar Biology. DOI: 10.1007/s00300-013-13-1368-7.
9. Gledhill M, Hassler C.S. and **Schoemann V.** 2013. The environmental bioinorganic chemistry of aquatic microbial organisms. Frontiers in Microbiology, 4, 100. doi: 10.3389/fmicb.2013.00100.

Published proceedings and abstracts

10. Vanderstraeten, A., Bonneville, S., **Schoemann,V.,** Mattielli, N., Flament, P., Deboudt,K., Grobéty, B., De Vleeschouwer, F., Le Roux, G., Tison, J.-L., Debaille, V. Dust Deposition in Snow from Northeast Antarctica: Mineralogical, Morphological and Chemical Characterisation, Goldschmidt Conference, 16-21 August 2015, Prague, Czech Republic. Poster presentation
11. Vanderstraeten, A., Bonneville, S., Mattielli, N., **Schoemann,V.,** Flament, P., Deboudt,K., Grobéty, B., De Vleeschouwer, F., Le Roux, G., Gieré, R., Tison, J.-L., Debaille, V. Dust Deposition in Snow from Northeast Antarctica: Mineralogical, Morphological and Chemical Characterisation, SEGH Conference, July 2014, Newcastle, UK. Poster presentation
12. **Schoemann, V.,** de Jong, J.T.M., Tison, J.-L., Haskell, T., de Baar, H., Champenois, W., Zhou, J., Carnat, G., Fripiat, F., Goossens, T., Moreau, S. and B. Delille. Dust as a source of bio-essential trace elements for coastal sea ice in McMurdo Sound, Antarctica. DUST 2014 International Conference on Atmospheric Dust, Castellaneta Marina (TA), Italy, June 1-6 2014
13. Hassler, C., Norman, L., **Schoemann, V.** Influence of Australian desert dust on marine iron chemistry and bioavailability to phytoplankton. DUST 2014 International Conference on Atmospheric Dust, Castellaneta Marina (TA), Italy, June 1-6 2014
14. J.-L. Tison, B. Delille, G. Dieckmann, J. de Jong, J. Janssens, J. Rintala, A. M. Luthanen, N. Gussone, C , Uhlig, D. Nomura, **V. Schoemann**, J. Zhou, G. Carnat, F. Fripiat. Snow cover and short-term synoptic events drive biogeochemical dynamics in winter Weddell Sea pack ice (AWECS cruise - June to August 2013), Geophysical Research Abstracts, Vol 16, EGU2014-1605.
15. **Schoemann, V.,** de Jong, J.T.M., Tison, J.-L., Haskell, T., de Baar, H., Champenois, W., Zhou, J., Carnat, G., Fripiat, F., Goossens, T., Moreau, S. and B. Delille. Land-fast sea ice of McMurdo Sound as a source of bio-essential trace metals for primary productivity in the Ross Sea, Antarctica, IGS International Symposium on Sea Ice in a Changing Environment, 10-14 March 2014
http://www.igsoc.org/symposia/2014/hobart/proceedings/procsfiles/procabstracts_64.htm#A667
16. J.-L. Tison, B. Delille, G. Dieckmann, J. de Jong, J. Janssens, J. Rintala, A. M. Luthanen, N. Gussone, C ; Uhlig, D. Nomura, **V. Schoemann**, J. Zhou, G. Carnat, F. Fripiat. Snow cover and short-term synoptic events drive biogeochemical dynamics in winter Weddell Sea pack ice (AWECS cruise - June to August 2013), IGS International Symposium on Sea Ice in a Changing Environment, 10-14 March 2014
17. G. Carnat, J., Zhou, J.-L., Tison, B. Delille, T. Goossens, **V. Schoemann**, and T.Papakyriakou. Biological and physical controls on DMS,P dynamics in ice-shelf-influenced fast ice, IGS International Symposium on Sea Ice in a Changing Environment, 10-14 March 2014
18. B. Delille, Haskell, T., Champenois, W., Heinesch B., Zhou, J., **Schoemann, V.**, Carnat, G., Fripiat, F., Goossens, T., Moreau S., Vancoppenolle M., Vivier F., Lourenço, A. and Tison, J.-L. Year Round survey of Ocean-Sea Ice-Air Exchanges – the YROSIAE survey, IGS International Symposium on Sea Ice in a Changing Environment, 10-14 March 2014

List of missions and participation to scientific conferences

5 June 2013, Brussels**:** FNRS contact group "Geochemistry" workshop day. Invited speaker: Sea ice as a source of bioavavailable Fe to the Southern Ocean. V. Schoemann.

16 Sept- 28 Sept 2013, Texel, The Netherlands: Visit to the Netherlands Institute for Sea Research (Dr. L. Gerringa and Prof. H. de Baar) for the measurements of Fe organic complexation by voltametry (CLE-ACSV) in samples of sea ice and underice seawater from Central Arctic (IceArc cruise). Samples from the Ice Arc cruise were brought to Brussels for further analysis of trace metals and isotopes.

16 January 2014, Brussels. Oral presentation: Schoemann, V., J. de Jong, J.-L. Tison, B. Delille, W. Champenois, J. Zhou, G. Carnat, T. Goosens, S. Moreau, T. Haskell, H. de Baar, C.-E. Thuróczy, K. Baker, M. Le Guitton, L. Gerringa. Biogeochemistry of trace metals in the sea ice. BIGSOUTH Science day.

10-14 March 2014, Hobart, Australia: IGS International Symposium on sea ice in a changing Environment. Speaker for the oral presentation on Land-fast sea ice of McMurdo Sound as a source of bio-essential trace metals for primary productivity in the Ross Sea, Antarctica (see proceeding #15) and co-author of 3 oral presentations (see proceedings #16, 17, 18)

16 May 2014, Brussels: "ULB / VUB International Lecture Series in Geosciences. Invited speaker: "Sea ice as a source of bioavailable iron to the Southern Ocean, V. Schoemann.

1-6 June 2014, Castellaneta Marina (TA), Italy: DUST 2014 International Conference on Atmospheric Dust. Co-chair with Christel Hassler for 3 Sessions on " Dust in the Sea- impact on biogeochemistry and climate". Speaker for the oral presentation on Dust as a source of bio-essential trace elements for coastal sea ice in McMurdo Sound, Antarctica (see abstract #12) and co-author of the oral presentation on the "Influence of Australian desert dust on marine iron chemistry and bioavailability to phytoplankton" (see abstract #13).

10-12 May 2015, University of Geneva, Jury member for the pre-doctoral exam (mid-term exam) of Sonia Blanco-Ameijeiras (Promoter: Prof. C. Hassler)

6. Skills/Added value transferred to home institution abroad

I have brought my skills in trace metals biogeochemistry and on microbial eco-physiology to the home institution (ULB) to better assess the role of sea ice in affecting the biogeochemistry of our oceans, the associated biological response and the global carbon cycle. This is reflected by my co-authored publications with members of the Laboratory of Glaciology: J.-L. Tison, G. Carnat, T. Goossens & J. Zhou (see #1, 4, 5, 7, 8, 10, 11, 12, 14, 15, 16, 17, 18) as well as with members of the Geochemistry, Isotopic tracing - mineral and elements analysis unit: N. Mattielli, J.T.M. de Jong, A. Vanderstraeten (see #1, 6, 7, 8, 10, 11, 12, 14, 15, 16) and members of the Biogeochemistry and Modeling of the Earth System: L. Chou and S. Bonneville (#4, 10, 11).