# Cruise Report FK LITTORINA LIT/1914

(21<sup>th</sup>-25<sup>th</sup> October 2019)

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GEOMAR-Helmholtz Centre for Ocean Research, Kiel, Germany

in cooperation with

Department of Biology, University of Southern Denmark, Denmark (SDU)

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#### Introduction

The research cruise LIT/1914 was conducted in the frame of the two BONUS research projects SEAMOUNT (New Surveillance Tools for Remote Sea Monitoring and their Application on Submarine Groundwater Discharge and Seabed Surveys) and INTEGRAL (Integrated carbon and Trace Gas monitoring for the Baltic sea).

One objective of the SEAMOUNT project is to identify locations of submarine groundwater discharge (SGD) in the Western Baltic Sea, i.e. the subsurface flow of groundwater to the coastal ocean. Locations of SGD in relatively deep waters (> 10m) have been observed previously in the Eckernförde Bay, but occurrences outside this area are so far unknown. Identification of SGD mostly relies on tracers like the natural radionuclides radium and radon, which are enriched in groundwater but not in seawater (Burnett et al., 2006). Therefore, concentration anomalies of these radionuclides close to the shore or near the seafloor may be a first indication of SGD. In deep waters at Boknis Eck (Eckernförde Bay) we observed high radium. This deep water mainly consists of saline North Sea water advected via the Boknis Channel to Boknis Eck. Therefore, there is the possibility that high radium in deep waters of Boknis Eck is an indication of SGD occurring outside the Eckernförde Bay.

The objective of the INTEGRAL project is to use measurements of trace gases (e.g. methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O)) from all available platforms to estimate trace gas emissions from the Baltic Sea. Methane emissions from coastal areas contribute significantly to the oceanic emissions of CH<sub>4</sub>, however, oceanic CH<sub>4</sub> emissions, on the global scale, play only a minor role for the atmospheric CH<sub>4</sub> budget. In the Baltic Sea, CH<sub>4</sub> is mainly produced during the sedimentary decay of organic material (methylotrophic methanogenesis) and the fraction of CH<sub>4</sub> transferred from the sediment through the water column into the atmosphere is strongly governed by anaerobic CH<sub>4</sub> oxidation in the upper sediment as well as in the water column. Apart from sedimentary release of biogenic CH<sub>4</sub>, groundwater seepage can be a significant source of dissolved CH<sub>4</sub> in the water column of the Baltic Sea. Oceanic areas are a major source of atmospheric nitrous oxide (N<sub>2</sub>O) and its emissions from coastal areas contribute significantly to the overall oceanic emissions. The major production process of dissolved N<sub>2</sub>O in open and coastal regions of the Baltic Sea is nitrification in the water column, whereas its production during denitrification in sediments seems to be of minor importance.

 $N_2O$  can occur in very high concentrations in groundwater, however, the effect of SGD on the  $N_2O$  water column distribution in the Baltic Sea has not been determined yet. Literature data also indicate that there may be an association of methane and SGD (e.g., Bussmann and Suess, 1998; Santos et al., 2009). Thus, the joint research activity of the two BONUS projects INTEGRAL and SEAMOUNT may lead to a better understanding of the relations between SGD and trace gases occurrence in the Western Baltic Sea.

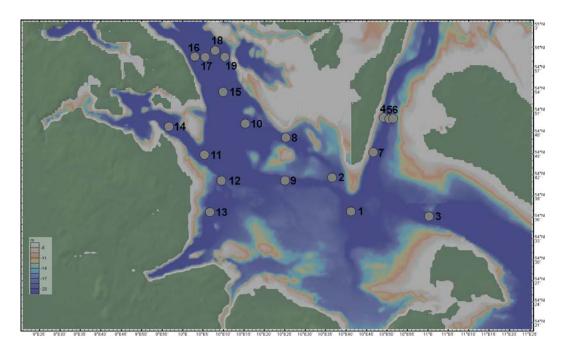
Oxygen availability has a huge influence on the structure of the ecosystem as well as a significant impact on fauna. The availability of oxygen could affect some species directly or indirectly through removing some of the higher trophic levels that impact phytoplankton structure during periods of hypoxia/anoxia. The impact of variable oxygen concentration on algae and cyanobacteria has been little studied. The variable oxygen content of water masses in the western Baltic Sea allows us to study how the phytoplankton composition changes and/or is affected by variable seawater oxygen contents.

## 2. Objectives of the cruise

The objective of the cruise was to sample the water column at selected stations along the flow paths of saline North Sea deep waters through the Fehmarn Strait, Little Belt, Great Belt, Flensburg Firth and Kiel Bay.

More specifically the objectives were:

- To measure the distribution of radium, nutrients, CH<sub>4</sub> and N<sub>2</sub>O in the water column.
- To investigate the role of submarine groundwater discharge (SGD) as a potential source for dissolved CH4 and N2O in the water column.
- To examine changes of bacteria, DNA and particulate matter composition in relation to the oxygen content.
- To determine water current velocities at sampling location using Acoustic Doppler CurrentProfiler (ADCP).



**Figure 1.** Map of the Western Baltic Sea with sampling stations. Map created with *GeoMapApp* (http://geomapapp.org), based on Global Multi-Resolution Topography (GMRT) synthesis (Ryan et al., 2009).

#### 3. Cruise narrative

21.10.2019	08:00 Rigg-up of ADCP	
	11:45 Departure of <i>FK Littorina</i> from Kiel harbor	
	14:34 Start ADCP survey	
	15:26 Arrival at station 1	
	14:10 End ADCP survey	
	16:50 Arrival at station 2	
	17:45 Arrival at Bagenkop harbor	
22.10.2019	06:30 Departure Bagenkop harbor	
	08:16 Start ADCP survey	
	09:03 Arrival at station 3	
	10:33 End ADCP survey	

	12:01	Start ADCP survey
	12:40	Arrival at station 4
	13:25	Arrival at station 5
	14:30	Arrival at station 6
	16:20	End ADCP survey
	17:00	Arrival at station 7
	18:40	Arrival at Bagenkop harbor
23.10.2019	06:39	Departure Bagenkop harbor
	07:20	
	07:55	Arrival at station 8
	10:09	Arrival at station 9
	11:15	End ADCP survey
	12:05	Arrival at station 10
	13:32	Arrival at station 11
	14:47	Arrival at station 12
	16:10	Arrival at station 13
	18:30	Arrival at Olpenitz harbor
24.10.2019	06:30	Departure Olpenitz harbor
	07:38	Start ADCP survey
	08:10	Arrival at Station 14
	10:25	End ADCP survey
	12:00	Arrival at Station 15
	13:12	Start ADCP survey
	14:53	Arrival at station 16
	15:45	Arrival at station 17
	16:34	Arrival at station 18
	18:12	End ADCP survey
	18:19	Arrival at station 19
	23:30	Arrival at Kiel harbor
25.10.2019	08:00	Unloading equipment

# 4. Methods and Sampling

## Conductivity-Temperature-Depth probe (CTD) and water sampling rosette (GEOMAR)

At all stations a *HydroBios* MWS410 CTD probe with attached water sampling rosette was deployed to investigate the physical properties (salinity, temperature, oxygen) of the water column. Temperature, conductivity and oxygen saturation data was used to identify suitable water depths for water sampling. In general, water samples were obtained between 25m water depth and the surface in ~ 5m depth spacings.

#### Nutrients and dissolved trace gases (GEOMAR)

Sampling for methane and  $N_2O$  (each in triplicate) was immediately conducted after the CTD bottles were on deck to minimize any equilibration with air. Glass bottles (20ml) were filled

from the bottom to top using Nalgene PVC tubing which was flushed to remove possible air bubbles. Glass bottles were flushed three times their volume to remove any bubbles and to ensure that the water was not exposed to air. The tubing was carefully pulled out of the bottles, and a rubber stopper was inserted and secured using an aluminum crimp.



Figure 2. Water sampling for methane and N<sub>2</sub>O analyses

N<sub>2</sub>O and CH<sub>4</sub> samples taken in the period from 21 to 23 October were poisoned with HgCl<sub>2</sub>(aq) on 23 October. The N<sub>2</sub>O/CH<sub>4</sub> samples from 24 October were poisoned immediately after sampling. Samples for nutrient analyses were filled in pre-rinsed 50 ml PE bottles and stored in a freezer.\_Samples will be analyzed at GEOMAR by applying state-of-the-art methods (autoanalyzer for nutrients, GC-FID/ECD for trace gases).

#### Sampling for bacterial analyses, DNA, organic matter and pigments (SDU)

For the analyses of bacteria by means of flow cytometry, about 1.9 ml of water was filled in 2 ml vials (in triplicate) and 20  $\mu$ l of paraformaldehyde was added, shaken, and incubated for 4-12 h in the fridge. Thereafter the samples were frozen at -20 °C. For DNA analyses 0.3 – 0.5 l of water was filtered over membrane filters; the filters were folded, placed in a vial and stored in a freezer. For the determination of particulate organic matter and pigments 0.3 – 0.5 l of water was poured over pre-combusted glass microfiber filters; and the filters were stored in the

freezer. During the cruise in total 39 samples for DNA analyses, 153 samples for flow cytometry and 126 samples for the analyses of particulate organic matter were obtained.

#### Sampling for radium analyses (IFG)

Water sampling for Ra isotope analyses was performed using two *WASP-P5* submersible pumps, which allow water sampling from up to 30 m water depth. The pumps were attached to the CTD and the water hose was fixed to the cable of the CTD. At all stations (Tab. 2) two samples, one from the upper mixed layer (~ 5m water depth) and one close to the sea floor (~ 2 m above bottom) were obtained. At selected stations (stations 3, 5, 14, 18) the water column was sampled in higher resolution.

For each sample approx. 120 l of seawater was filled in barrels and subsequently filtered over manganese impregnated acrylic fibers with a flow rate <1 l/min (Figure 3). On-board the ship the Mn-fibers were analyzed for <sup>223</sup>Ra and <sup>224</sup>Ra using *Scientific Computer Instruments RaDeCC* radium delayed coincidence counters. Seawater salinity and temperature of each water sample were determined using a hand-held *MTW Cond3310* salinity and temperature probe.



**Figure 3.** Radium sampling: Seawater in the blue barrels is filtered over Mn-impregnated fibers which adsorb radium; the volume of filtered water is measured using water meters.

# ADCP (IFG)

About 2.5 nm before arriving at selected stations (stations 1, 3, 4, 8, 9, 14, 16-18) the ADCP (TRDI ADCP, 1200 kHz) was deployed. Additional ADPC profiles were run across the Little Belt, Great Belt and Flensburg Firth.

Table 2: List of stations and depths of water sampling

Station	Date	Time (CET)	La	titude N	Lo	ngitude E	Water Depth (m)	Sampling Depths Gases & Nutrients (m)	Sampling Depths Radium (m)
1	21.10.2019	15:26	54°	36.862	10°	41.185	24.7	0, 5, 10, 15, 20	5, 20
2	21.10.2019	16:50	54°	41.654	10°	36.575	21.5	0, 5, 10, 15, 20	5, 20
3	22.10.2019	09:03	54°	36.154	11°	00.287	41	0, 5, 10, 15, 20, 25	5, 15, 20, 25
4	22.10.2019	12:40	54°	50.114	10°	49.157	21	0, 5, 10, 15, 18	5, 18
5	22.10.2019	13:25	54°	49.920	10°	50.575	22.3	0, 5, 10, 15, 20	5, 15, 20
6	22.10.2019	14:30	54°	49.981	10°	51.501	20	0, 5, 10, 15, 19	5, 19
7	22.10.2019	17:00	54°	45.214	10°	46.641	32	5, 10, 15, 20, 25	5, 25
8	23.10.2019	07:55	54°	47.297	10°	25.264	28	0, 5, 10, 15, 20, 25	5, 25
9	23.10.2019	10:05	54°	41.234	10°	25.069	30.5	0, 5, 10, 15, 20, 25	5, 25
10	23.10.2019	12:05	54°	49.270	10°	15.350	29	0, 5, 10, 15, 20, 25	5, 25
11	23.10.2019	13.37	54°	44.880	10°	05.335	27	0, 5, 10, 15, 20, 25	5, 25
12	23.10.2019	14:49	54°	41.218	10°	09.495	31.5	0, 5, 10, 15, 20, 25	5, 25
13	23.10.2019	16:15	54°	36.767	10°	06.684	25	0, 5, 10, 15, 20, 23	5, 23
14	24.10.2019	08:10	54°	48.839	9°	56.637	26	0, 5, 10, 15, 20, 24	5, 15, 20, 24
15	24.10.2019	12:00	54°	53.729	10°	09.926	32	0, 5, 10, 15, 20, 25	5, 25
16	24.10.2019	14:53	54°	58.666	10°	02.995	35	0, 5, 10, 15, 20, 25	25
17	24.10.2019	15:50	54°	58.617	10°	05.527	36	0, 5, 10, 15, 20, 25	25
18	24.10.2019	16:39	54°	59.541	10°	07.954	38	0, 5, 10, 15, 20, 25	5, 15, 20, 25
19	24.10.2019	18:28	54°	58.633	10°	10.329	34	0, 5, 10, 15, 20, 25	25

# 5. Preliminary results

Initial results of the CTD profiles indicate a relatively well-mixed upper water column and more saline waters below  $\sim 15$  m water depth (Figures 4, 5). Temperature and salinity range between 12.6 °C and 14.3 °C and between 14.960 and 25.295, respectively. Oxygen saturation in saline deep waters is generally low ( $\sim <50$  %).

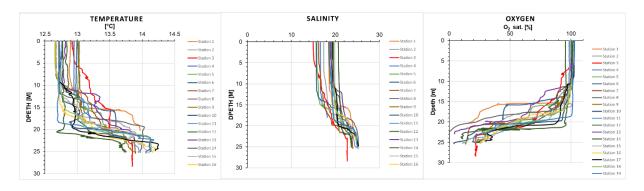
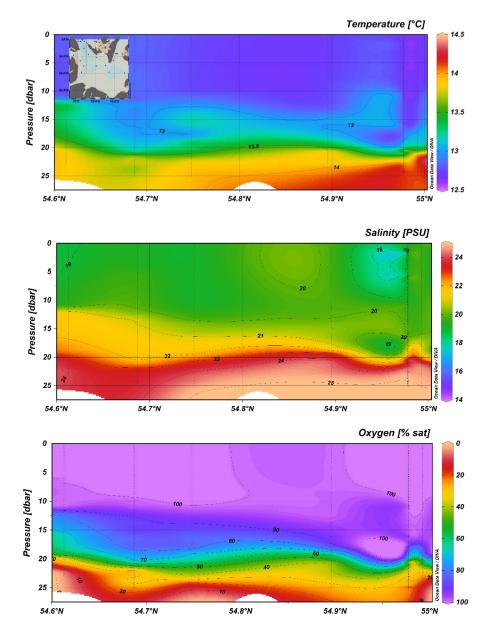


Figure 4.: Profiles of temperature, salinity and O<sub>2</sub> saturation at investigated locations during Litt/1914 cruise.



**Figure 5:** N-S transect of temperature, salinity and oxygen saturation compiled from CTD measurements in the western Baltic Sea. (*OceanDataView 4.8* (Schlitzer, 2018)).

#### 6. Scientific crew

Name	Function	Institution
Jan Scholten	Chief scientist	IFG
Annike-Sofie Schlaubke	Student	IFG
Friederike Zadow	Master student	GEOMAR
Hans Frederik Hansen	Ph.D student	SDU Odense

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