#### Zwischenbericht

ZE: Helmholtz Centre for Environmental Research - UFZ PD Dr. habil. M. Schubert		Förderkennzeichen:	BSERANET-078
Vorhabenbezeichnung:	Investigation of Submarine Groundwater Discharge for preventing pollution and eutrophication of the coastal Black Sea		
Laufzeit des Vorhabens:	01.01.2012 - 30.06.2013		
Berichtszeitraum:	2012		· · · · · · · · · · · · · · · · · · ·

**Preface:** The progress report summarizes results of activities that were carried out within the project *"Investigation of Submarine Groundwater Discharge for preventing pollution and eutrophication of the coastal Black Sea"* (BSERANET-078) in 2012. The reported activities include the kick-off meeting in Romania, the 1<sup>st</sup> field campaign in Romania and the 1<sup>st</sup> field campaign in Georgia. The reported results do primarily include recorded data and preliminary evaluations thereof. A combined and concluding evaluation and interpretation of all achieved data will be presented in the final report.

## 1 Major project related events and scientific results

# Kick-Off Meeting:

A kick-off meeting was held in Bucharest / Constanta, Romania, on March  $28^{th}$  and  $29^{th}$ . Scientists from all project partners, i.e. Helmholtz Centre for Environmental Research – UFZ Germany (coordinator), Ivane Javakhishvili Tbilisi State University Georgia, National Institute of Marine Geology and Geoecology – GeoEcoMar Romania, and Hellenic Centre for Marine Research (HCMR) Greece, attended the meeting. Aims of the meeting were discussing the planned project approach, distributing the project related responsibilities, checking the available equipment and resources, and having a first visit to the part of the Romanian coastline that was previously chosen as study site. All tasks were fulfilled as planned. Due to the delayed start of the project (*cf.* sect. 2 of this progress report) it was decided to postpone the first field campaign in Georgia to the second half of 2012.

## First Field Campaign Romania:

**The first field campaign** in Romania was done between May 21<sup>st</sup> and 23<sup>rd</sup> 2012. The three day survey covered the coastline between Constanta and Mangalia as agreed upon by the project partners during the kick-off meeting. On the marine side water salinity, water temperature and the related coordinates were recorded continuously along a coastal profile. Simultaneously the seawater radon concentration was detected with a 10 minutes counting cycle. On the terrestrial side groundwater wells that proved representative for the terrestrial groundwater end-member were chosen and sampled.

**An additional two day sampling campaign** on the coastal sea was carried out by GeoEcoMar staff in June 2012 (June 13<sup>th</sup> and 14<sup>th</sup>). The motivation to carry out that campaign was to repeat the coastal survey with a smaller boat allowing a slower cruising speed and hence a higher resolution of radon data (again using a 10 min counting cycle).

Figures 1A and 1B summarize and compare the results of the boat cruise along the Romanian coastline between Constanta and Mangalia. The two areas that showed strongest indications for SGD were (1) Costinesti Harbour and (2) a bay located north of Mangalia that is known for its hot springs (in the following referred to as "Hot Spring Bay"). Both areas showed values for radon, salinity and temperature that are unusual for the local costal sea. The data is discussed in more detail in the following.

The results of the additional two day sampling campaign are displayed in Fig. 2A and 2B. The data, which is also discussed in more detail in the following, verify and improve the results of the May campaign.



*Fig. 1A: Radon concentration and salinity data recorded during the 1<sup>st</sup> sampling campaign along a North – South coastal profile in May 2012 (the salinity meter didn't work properly during the first two days). Displayed are the raw radon and salinity readings vs. time of the cruise. Major landmarks are indicated.* 



*Fig. 1B: Radon and temperature data recorded during the 1<sup>st</sup> sampling campaign along a North – South coastal profile in May 2012. Displayed are the raw radon and temperature readings vs. time of the cruise.* 



Fig. 2A: Radon concentration and salinity data recorded during the additional sampling campaign along a North – South coastal profile in June 2012. Displayed are the raw radon and salinity readings vs. time of the cruise. Major landmarks are indicated.



*Fig. 2A: Radon and temperature data recorded during the additional sampling campaign along a North – South coastal profile in June 2012. Displayed are the raw radon and salinity readings vs. time of the cruise. Major landmarks are indicated.* 

As shown in Figs. 1 and 2 the two surveys revealed significantly elevated **radon concentrations** at Costinesti Harbour and in Hot Spring Bay. During the <u>May campaign</u> background values along the coastline of about 10 Bq/m<sup>3</sup> and an offshore value of about 5 Bq/m<sup>3</sup> were detected. The peak values at both, Costinesti Harbour and Hot Spring Bay, were at about 110 Bq/m<sup>3</sup>. The background values detected in the coastal sea during the <u>June campaign</u> were again around 10 Bq/m<sup>3</sup>. The peak values at Costinesti Harbour and Hot Spring Bay were about 110 Bq/m<sup>3</sup> and 40 Bq/m<sup>3</sup>, respectively (i.e. in Hot Spring Bay less than in May).

In accordance with the radon distribution patterns Figs. 1 and 2 show also low **salinities** at Costinesti Harbour and Hot Spring Bay. Furthermore, low salinities were detected at the gate of Mangalia Harbour. During the <u>May campaign</u> background values valid for the coastal sea were found to be between about 10.2 - 10.6 (the probe only worked properly during the 3<sup>rd</sup> day of campaign, i.e. no readings for Costinesti Harbour). At Hot Spring Bay the salinity decreased locally to about 9.4; at the gate of Mangalia Harbour the salinity dropped slightly from 10.6 to 10.2 and stayed low south of it (probably due to river water influence). During the <u>June campaign</u> background values of about 16.5 - 17.0 were detected, i.e. values that were significantly higher than the values found in May. A potential explanation for that observation is a poor calibration of the salinity probe, i.e. an artefact. However, since salinity gradients were in the focus of interest rather than absolute values the data can still be used for interpretation. In accordance with the May campaign the June data showed a significantly decreased salinity in Hot Spring Bay. At Costinesti Harbour the salinity dropped as well. However, in contrast to the May campaign the salinity rose significantly at the gate of Mangalia Harbour in June (possibly due to sewage influence).

The water temperatures measured in about 50 cm water depth during both campaigns does not show a distinct pattern that correlates with radon and does neither give clear indication for SGD. The gradual rise of the water temperatures during the courses of each individual day is most likely due to the changing air temperature. Besides that generally irregular behaviour temperatures were significantly elevated in Hot Spring Bay during the <u>May campaign</u>. The same is the case for Costinesti Harbour on the evening of the first day of the cruise (the 2<sup>nd</sup> day started much cooler). In contrast to Costinesti Harbour the temperatures dropped sharply at the gate of Mangalia Harbour. During the <u>June campaign</u> no elevated temperatures were detected in Hot Springs Bay. However, high temperatures were found again at Costinesti and also a sharp temperature drop at the gate of Mangalia Harbour.

**Stable isotope** signatures of water (Fig. 3) were determined in groundwater samples representing the expected groundwater discharge for two potential SGD locations indicated by the coastal radon survey (Costinesti Harbour and Mangalia Harbour). Also, sea water samples were taken close to the two expected SGD spots as well as from locations where no groundwater discharge was expected. Generally, groundwater samples from the Costinesti region showed higher isotope values compared to groundwater samples from the Mangalia region. Nevertheless, samples from both regions plot on the meteoric water line, which indicates no backward fluxes from the sea into the respective aquifers (i.e. no sea water intrusion). No significant differences in isotope signatures were observed between background (off shore) sea water samples and sea water samples from potential SGD locations. This may be due to a quick mixing of discharging groundwater into the sea water body and/or due to an amount of submarine groundwater discharge that is below the detection limit of the stable isotope method generally characterized by a relatively low sensitivity.



Fig. 3: Isotopic composition of groundwater and sea water samples from the Constanta region

The thermal satellite data that was evaluated for the localization of potentially SGD prone areas provide consistent results in certain areas only. On the one hand small variabilities in the sea surface (SST) variability, temperature which conceptually indicate continuous spatio-temporal groundwater influx, occur in the Hot Spring Bay and the Mangalia Harbour and do support the radon and salinity findings. On the other hand at least two further areas with low temperature variabilities were found (see areas B and C in Fig. 8). Both locations could not or only to a certain extend be verified as SGD areas by the radon/salinity data. We assume the reason to be related to either (1) SGD that was insignificantly low as result of the long term weather pattern prior to the sampling campaign

Fig. 8: SST image of the coastal sea and potential water accumulation based on digital elevation model evaluation.



(note that all thermal satellite data were exclusively recorded prior to the campaign), to (2) temporal discharge originating in agricultural drainage channels occurring only after intense rainfall events or to (3) a spatio-temporal upwelling, induced through landwards oriented sea currents. All three processes can cause low SST variability and have to be considered during future SGD related investigations.

Generally the results emphasize the fact that the SST variability analysis (also called "thermal analysis") does provide indications but needs to be backed by supplementary methods to confirm the conclusions. The additionally conducted **morpho-structural analysis** can be applied as such a method, as it allows localization of subterraneous depression lines where groundwater accumulation and drainage is most likely. At intersections of such depression structures with the coastline potential SGD sites can be assumed. Along the investigated stretch of coastline the results from the morphological analysis match the SST results except for Mangalia Harbour. Hence it can be stated that both, thermal and morpho-structural analysis, do allow identification of potential SGD sites but that the conclusions need to be validated with in-situ (radon/salinity) measurements. In-situ campaigns on the other hand do only represent a temporal snapshot and may not reveal SGD and related processes. Thus, the synergy of thermal-, morphological and in-situ analysis appear to represent the most suitable approach for SGD assessment.

#### First Field Campaign Georgia:

The first field campaign in Georgia was carried out in October 2012. The visit, which included long drives from Tbilissi to Batumi and back as well as several time-consuming logistical tasks, lasted from October 14<sup>th</sup> to October 18<sup>th</sup> 2012. The coastal survey was carried out on two days and covered the coastline between the mouth of river Natanebi/Choloki in the North and the northern suburbs of Batumi in the South. The northern part of the profile, completed on October 16<sup>th</sup>, covered about two thirds of the whole profile distance. On October 17<sup>th</sup> the remaining southern part and a perpendicular profile were measured. The parameters that were continuously recorded in the coastal sea included water salinity, water temperature, and the related coordinates. Simultaneously the seawater radon concentration was detected with a 5 minutes counting cycle. On the terrestrial side groundwater samples were taken from wells and springs that proved representative for the terrestrial groundwater end-member.

Fig. 4 illustrates the radon concentrations and the related salinities that were detected along the coastline and on the perpendicular profile. Fig. 5 displays the same data as diagrams. Fig. 4 illustrates the occurrence of considerably elevated **radon concentrations** off the town of Kobuleti. Another area with less but still significantly elevated radon concentrations was localized further south at the mouth of river Chaqvis-Tskali. The radon patterns indicate two potential SGD regions. The **salinity** data are in accordance with the radon readings and back this assumption. The salinity of the coastal sea decreases considerably in the Kobuleti area at a landmark that was named "concrete structure on beach" (*cf.* Fig. 5A). Less distinct but still significant is the low salinity pattern at the mouth of river Chaqvis-Tskali (landmark "Hotel Oasis"; *cf.* Fig. 5B). Due to a malfunctioning handheld GPS sensor the perpendicular profile that was measured for evaluation of the off-shore extent of the radon/salinity plume didn't end exactly in the shore facing end the plume but some hundred meters north of it. However, the pattern can still be made out clearly. Whereas the conductivity stays at background level until very close to the shore, the radon concentration starts rising in a distance of about 1500 m from the shoreline already (*cf.* Fig. 4A, Fig. 5C). That confirms radon as a much more sensitive SGD tracer than salinity.

Fig. 4A (left): Radon concentration data recorded during the 1<sup>st</sup> sampling campaign on a North – South coastal profile in September 2012. The size of the circles corresponds to the detected radon concentration.

Fig. 4B (right): Salinities recorded during the 1<sup>st</sup> sampling campaign on a North – South coastal profile in September 2012. The size of the circles corresponds to the detected salinity values.





Fig. 5A: Radon concentration and salinity recorded along the northern part of the coastal survey on a North - South coastal profile in September 2012. Major landmarks are indicated.

Fig. 5B: Radon and salinity (conductivity) recorded along the southern part of the coastal survey on a North - South coastal profile in September 2012. Major landmarks are indicated.

*Fig. 5C: Radon and salinity recorded along the perpendicular profile in September 2012.* 



The **temperature** readings made in 50 cm water depth were, as described for the 1<sup>st</sup> field campaign in Romania, of hardly any informative value. Hence, as additional parameter the **ph of the seawater** was recorded. As it becomes obvious in Fig. 6A the pH showed a distinct peak at the same location where elevated radon concentrations occur (Kobuleti), indicating strong SGD. The data displayed in Fig. 6B, illustrating the findings along the southern part of the survey, do also show a negative correlation between radon and pH, which is however not as distinct as the observation displayed in Fig. 6A.



Fig. 6A (left): Radon and pH recorded along the northern part of the coastal survey along a North - South coastal profile in September 2012.

*Fig.* 6B (right): Radon and pH recorded during along the southern part of the coastal survey along a North - South coastal profile in September 2012.

In the Batumi region, **stable isotope signatures** were measured in groundwater and spring water samples that were considered as representative for the groundwater potentially discharging locally into the black sea. Additionally, sea water samples were taken from six locations along a perpendicular profile following the potential discharge line from the radon hot spot close to Kobuleti coast towards the open sea. While groundwater samples display oxygen and hydrogen isotope signatures between - 11.1 and -9.5 ‰ (VSMOW) and between -73.8 and -57.4 ‰ (VSMOW), respectively, sea water samples show much higher signatures of around -3 ‰ ( $\delta^{18}$ O) and -22.2 ‰ ( $\delta^{2}$ H) (Fig. 7A). No clear indication for a mixing line between those two end members is given. However, the perpendicular profile shows significant variations as the water sample from the location close to the shore line has a depleted isotope signature of both oxygen and hydrogen indicating the impact of discharging groundwater (Fig. 7B). Using a simple mixing equation and the observed isotope signatures of the sea water and groundwater end member, a groundwater content in the seawater of approximately 5 % can be estimated for location 1 of the perpendicular profile.





Fig. 7A: Isotopic composition of groundwater and background sea water samples from the Batumi region



Activity	Planned	Successfully Executed
Kick-Off Meeting in Romania	March 2012	March 28 <sup>th</sup> and 29 <sup>th</sup> 2012
1 <sup>st</sup> Field survey in Romania	May 2012	May 21 <sup>st</sup> to 23 <sup>rd</sup> 2012
		Additional GeoEcoMar sampling campaign: June 13 <sup>th</sup> and 14 <sup>th</sup> 2012
2 <sup>nd</sup> Field survey in Romania	September 2012	September 25 <sup>th</sup> to 27 <sup>th</sup> 2012
1 <sup>st</sup> Field survey in Georgia	October 2012	October 14 <sup>th</sup> to 18 <sup>th</sup> 2012
Progress Report	February 2013	February 2013
Final Meeting in Greece	March 2013	March 2013
2 <sup>nd</sup> Field survey in Georgia	May 2013	on time
Final Report	June 2013	on time

### 2 Comparison between planned project schedule and actual progress

Due to administrative obstacles in the beginning the project started somewhat delayed. However, the overall progress was made as planned. Unfortunately the Romanian colleagues did not have the opportunity to postpone the end of their sub-project (even though no additional costs were involved); the sub-project ended as originally planned in December 2012, which did not allow them to consider the results of the second campaign in Georgia in their final report and to participate in the final meeting. The results of the Romanian colleagues, which are so far only available in their final report (in Rumanian) will be included in the final project report.

Another noteworthy change of the project is the point that the final meeting will be held at the HCMR institute in Anavyssos, Greece, instead of the UFZ in Leipzig, Germany. All partners agreed upon this idea since it allows all partners (except the Romanians) to visit the HCMR radio lab in Anavyssos, where the KATARINA detection device is being build and calibrated. All related costs were rededicated respectively without creating any additional costs.

Other changes of plan are mainly due to logistical "teething troubles" at either site, Constanta/Romania and Batumi/Georgia. Malfunctioning equipment, unexpected delays in international equipment shipping, unpredictable military exercises that temporarily prohibited site access, unfavourable weather conditions, etc. limited the opportunities to carry out two full field campaigns at either site as intended (one in spring and one in autumn). On both sites the second campaign was rather used for completing the tasks that could not be completed during the first campaign.

Furthermore the intended 12 to 24 hours time series at fixed locations in the coastal see were not recorded due to two reasons: 1.) the chance that the equipment might get stolen was to high; 2.) since tidal effects are negligible, the measurements were not compulsory.

# **3** Further remarks

The general goals of the project did not change during the course of the project. The overall objective did not change.

No data or information were received from third parties during the course of the project that interfered with the project or are of greater relevance for its execution.

As it can be assessed so far, the participation of the four European research institutions in a multidisciplinary and intersectoral research activity in the still emerging field of SGD investigation including senior scientists as well as young researchers and doctoral students for capacity building purposes helps to improve the SGD related methodological repertoire and to gain international experience for each of the partner institutes. Thus, the respective participation has major positive impact on the individual research groups significantly improving their prospects in the fields of academia and industry.