Final Report

Vorhabensbeschreibung: Investigation of Submarine Groundwater Discharge for preventing pollution and eutrophication of the coastal Black Sea

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I. Kurze Darstellung

1 Aufgabenstellung

Nachhaltiges Management des küstennahen Meeres verlangt ein umfassendes Verständnis der Prozesse, die mit dem Transport gelöster und partikulärer Stoffe vom terrestrischen in das marine Environment im Zusammenhang stehen. Während Flüsse und Klärwassereinträge in das Meer an konkrete und problemlos lokalisierbare Orte gebunden sind, was eine unkomplizierte Bestimmung von Massenbilanzen erlaubt, stellt die Bilanzierung des Stoffeintrags durch untermeerisch austretende Grundwässer ("Submarine Groundwater Discharge" - SGD) eine wissenschaftliche Herausforderung dar. Zur generell schweren Lokalisierbarkeit von SGD Gebieten kommt dabei die sowohl zeitliche aus auch örtliche Variabilität von SGD.

SGD stellt einen wichtigen Pfad für den Stofftransport über das Interface Aquifer/Meer dar. Nährund Schadstoffe die mit dem Grundwasser in das Meer eingetragen werden, besitzen ein hohes Potential nachhaltig negative Veränderungen im Küstengewässer zu bewirken. Beispiele hierfür sind die Eutrophierung der küstennahen See, die Kontamination von Fisch, die Schädigung von Korallen und verstärkte Algenblüten.

Das wissenschaftliche Ziel des Projektes ist die Durchführung einer Multi-Tracer-Anwendung zur SGD Untersuchung an zwei exemplarischen Standorten an der Küste des Schwarzen Meeres. Es ist geplant verschiedene geeignete Tracermethoden zu kombinieren und die gewonnenen Ergebnisse durch einen landseitigen, auf einem digitalen Geländemodell aufbauenden Modellierungsansatz zu verifizieren.

Im Projekt sollen verschiedene Umwelttracer zum Einsatz kommen, d.h. natürliche oder anthropogene Substanzen, die sich aufgrund ihres allgegenwärtigen Auftretens ideal für großräumige SGD Untersuchungen eignen. Die Ergebnisse sind von Relevanz für das Wasserressourcenmanagement und das Management des küstennahen Meeres an den beiden Untersuchungsstandorten. Für die Wahl der beiden Standorte galten als Anforderungen (i) ein starker anthropogener Einfluss auf die küstennahe See und (ii) möglichst verschiedene geographische Gegebenheiten. Darüber hinaus werden die sich aus dem gebildeten wissenschaftlichen Netzwerk ergebenden Synergien die Entwicklung neuer bzw. modifizierter methodischer Ansätze zur SGD Untersuchung erbringen, welche insbesondere an die Gegebenheiten der Schwarzmeerregion angepasst sind. Die Synergien ergeben sich aus der Kombination von wissenschaftlichen Ansätzen und Methoden von vier Europäischen Forschungsinstitutionen.

2 Voraussetzungen, unter denen das Vorhaben durchgeführt wurde

Die Helmholtz-Zentrum für Umweltforschung GmbH - UFZ kann auf eine Reihe themenverwandter Arbeiten verweisen. Untersuchungsgebiete waren dabei Küstenabschnitte der Ostsee (Deutschland), des Indischen Ozeans (Südafrika), sowie des Atlantiks (Irland). Unter anderem wurde im Rahmen eines durch das Internationale Büro des BMBF unterstützten Kooperationsprojektes in Zusammenarbeit mit dem Council for Scientific and Industrial Research – CSIR (Südafrika) eine SGD-Fallstudie im Bereich der False Bay, Südafrika, durchgeführt. Das Projekt (SUA 08/046) war als Pilotprojekt geplant, um die Anwendbarkeit verschiedener grundsätzlich für SGD-Untersuchungen nutzbarer natürlich vorkommender Indikatoren ("Umwelttracer") unter den spezifischen klimatischen und geographischen Bedingungen der Western Cape Provinz an einem exemplarischen Küstenabschnitt zu untersuchen. Ein Folgeprojekt, das sich über die gesamte Südküste Südafrikas erstreckt, ist derzeit im Rahmen des Forschungsprogramms SPACES in Arbeit (SPACES 03V01279).

Am UFZ liegen Erfahrungen zur Bearbeitung entsprechend der Aufgabenstellungen vor. Die notwendige Expertise in den Arbeitsbereichen (1) Nutzung natürlicher Radioisotope als aquatische Tracer, (2) Nutzung Stabiler Isotope als aquatische Tracer, (3) Nutzung von Fernerkundungsdaten zur SGD Untersuchung sowie (4) Grundwassermodellierung wurden in das Projekt eingebracht.

Als geeignete und fachkompetente Partner wurden die Ilia State University Georgien (www.iliauni.edu.ge), das National Institute of Marine Geology and Geoecology – GeoEcoMar Rumänien (www.geoecomar.ro) sowie das Hellenic Center for Marine Research (HCMR) Griechenland – (www.hcmr.gr) gewonnen.

3 Planung und Ablauf des Vorhabens

Alle geplanten Aktivitäten konnten fristgemäß und vollständig durchgeführt werden.

Tab. 1 Planung und Ablauf des Vorhabens

Aktivität	geplant	Erfolgreich durchgeführt
Kick-Off in Rumänien	März 2012	März 28 und 29 2012
1. Field survey in Rumänien	Mai 2012	Mai 21 bis 23 2012
		zusätzliche GeoEcoMar Kampagne: Juni 13 und 14 2012
2. Field survey in Rumänien	September 2012	September 25 bis 27 2012
1. Field survey in Georgien	Oktober 2012	Oktober 14 bis 18 2012
1. Zwischenbericht	Februar 2013	Februar 2013
Abschlusstreffen in Athen	März 2013	März 2013
2. Field survey in Georgien	Mai 2013	Mai 2013
2. Zwischenbericht	August 2013	August 2013
Abschlussbericht	Dezember 2013	Dezember 2013

4 Wissenschaftlicher und technischer Stand

An nahezu allen Küsten weltweit kommt es zum langsamen aber kontinuierlichen untermeerischen Wasser- und Stoffaustausch zwischen dem küstennahem Aquifer (d.h. dem Grundwasser) und dem küstennahem Ozean. Die generell unter dem Begriff Submarine Groundwater Discharge ("SGD") zusammengefassten Prozesse wurden zum ersten Mal vor über 30 Jahren beschrieben [1] und treten in der Regel diffus auf bzw. zeigen eine starke räumliche und zeitliche Variabilität [2], was deren Untersuchung erschwert.

Nachdem zu Beginn der 1990er Jahre zunehmend deutlich wurde, dass SGD einen wesentlichen Bestandteil des globalen hydrologischen Zyklus' darstellt, wurde auch zunehmend zur Kenntnis genommen, dass die Wasserqualität des küstennahen Ozeans sehr stark vom Eintrag ggf. kontaminierter Grundwässer abhängt und dass daher Grundwasser und küstennaher Ozean nicht als separate Wasserkörper betrachtet werden können. Diesbezügliche Studien wurden bisher vornehmlich in den USA, Brasilien, Australien und Asien (Thailand, Korea) durchgeführt [z.B. 3,4,5,6,7].

Herkömmliche Methoden, die bei der Untersuchung von Wechselwirkungen zwischen Grund- und Oberflächenwässern zur Anwendung kommen, basieren in der Regel entweder auf großräumigen numerischen Modellen oder auf punktuell erhobenen Daten, die mit Hilfe sogenannter Seepage Meter gewonnen werden. Numerischen Modellen liegen dabei häufig Langzeitbeobachtungen von Massenbilanzen und Flussraten sowie hydrologisch/hydrogeologische Annahmen, wie die Leitfähigkeit des Aquifers oder der hydraulische Gradient zugrunde. Seepage Meter erlauben andererseits eine direkte Quantifizierung von SGD-Raten. Keine der beiden Methoden ist jedoch in der Lage Daten zu liefern, die für eine quantitative SGD-Studie hinreichend wären. Einerseits haben Erfahrungen gezeigt, dass hydrologische Modelle SGD-Raten häufig unterbewerten, was darin begründet liegt, dass die meisten Bilanzen nur den Zufluss meteorischen Wassers (Süßwasser) in den Ozean berücksichtigen und die periodische und kontinuierliche Zirkulation von Seewasser zwischen Ozean und Aquifer vernachlässigen. Seepage Meter haben andererseits den Nachteil, dass sie zwar die gesamte Flussrate des austretenden Wassers registrieren, also alle vorliegenden Wasserkomponenten einschließen, aber nur Punktmessungen zulassen. Entsprechend können sie in SGD-Untersuchungen, die größere zeitliche und räumliche Bereiche abdecken müssen, nur unterstützend eingesetzt werden und sind als alleiniges Werkzeug nur bedingt tauglich.

Eine geeignete methodische Alternative ist die Nutzung sogenannter Umwelttracer, d.h. von als Tracer nutzbaren, in natürlichen Wässern gelöst vorliegenden Stoffen. Die beiden hauptsächlichen Vorteile der Nutzung von Umwelttracern sind, dass sie zum einen, im Gegensatz zu hydraulischen Modellen, eine direkte Bestimmung von Stoffflüssen erlauben und zum anderen, im Unterschied zu Seepage Metern, Daten liefern, die vertikal über die Wassersäule und horizontal über ein gesamtes Untersuchungsgebiet integriert werden können. Eine ganze Reihe natürlich auftretender gelöster Komponenten sind für SGD-Studien als Umwelttracer geeignet. Ursprünglich kamen bevorzugt leicht detektierbare Stoffe, wie ausgewählte Elemente (z.B. Ca, Sr, Ba), Nährstoffe (z.B. Phosphat, Ammonium, Nitrat) oder auch Standard-Wasserparameter (Temperatur, Leitfähigkeit) zum Einsatz. Obgleich all diese Parameter grundsätzlich geeignet sind, haben die jeweils gewonnenen Daten den Nachteil, dass sie kaum Informationen über Aufenthaltszeiten ("residence times") von Wasservolumina im Untersuchungsraum geben. Hierfür sind eher kurzlebige natürliche Radioisotope geeignet (mit Halbwertszeiten von Tagen bis Wochen), die aufgrund ihres definierten Zerfalls nicht nur das Nachvollziehen von Migrationspfaden sondern auch die Erfassung der zugehörigen zeitlichen Komponente erlauben. Des Weiteren ermöglicht die Nutzung stabiler Isotope präzisere Aussagen zu Mischungsverhältnissen und Quellzuordnungen, als dies mit herkömmlichen Elementtracern möglich ist. Im Folgenden sind geeignete Radioisotope und stabile Isotope, die sich als Tracer in SGD-Studien eignen, zusammengefasst.

Das radioaktive, chemisch inerte Edelgas **Radon** (²²²**Rn**) ist ein natürliches Radioisotop, das seine Eignung als aquatischer Tracer in zahlreichen SGD-Studien unter Beweis gestellt hat [3,4,5,6,7,12].

Radon entsteht durch radioaktiven Zerfall des allgegenwärtig in der mineralischen Aquifermatrix vorhandenen Radiums (²²⁶Ra) und wird permanent durch Emanation aus der Matrix in das Grundwasser eingetragen. Radonkonzentrationen im Grundwasser liegen natürlicherweise zwischen etwa 5 und 50 Bq/l. Im küstennahen Ozean ist die Radonkonzentration demgegenüber in der Regel sehr gering; off-shore Hintergrundkonzentrationen sind vernachlässigbar. Ursache hierfür ist die nahezu fehlende Radonproduktion im Ozean und die kurze Halbwertszeit des Radons von nur 3,8 Tagen. Entsprechend ist am Interface zwischen Grund- und Meerwasser in der Regel ein starker Radon-Konzentrationsgradient ausgebildet, mit Hilfe dessen SGD Zonen über Maxima des Radonverteilungsmuster küstennahen im Ozeans nachgewiesen werden können. Die kurze Halbwertszeit des Radons erlaubt darüber hinaus eine Quantifizierung der Grundwasseraustrittsrate. Wegen seiner leichten und sehr genauen Detektierbarkeit mit Hilfe mobiler Messtechnik und wegen seiner Edelgaskonfiguration eignet sich Radon generell hervorragend als aquatischer Tracer. Nachteilig ist demgegenüber das Bestreben des Radons aus dem Wasser zu entgasen, was insbesondere bei starkem Wind und Wellengang einen nur schwer quantifizierbaren Verlust an Radon aus dem untersuchten Wasserkörper mit sich bringt.

Eine weitere Gruppe natürlich auftretender Radiotracer ist das sogenannte **"Radium-Quartett**", welches die beiden kurzlebigen Isotope ²²³Ra (t_{1/2} 11.4 Tage) und ²²⁴Ra (t_{1/2} 3.66 Tage) sowie die beiden langlebigen Isotope ²²⁶Ra (t_{1/2} 1600 Jahre) und ²²⁸Ra (t_{1/2} 5.7 Jahre) einschließt [2,10]. Bei Studien im küstennahen Ozean findet das "Radium-Quartett" verbreitet bei der Quantifizierung von Grundwasser/Seewasser Zirkulationsprozessen Verwendung. Während Meerwasser (Salzwasser), welches durch den küstennahen Aquifer migriert, in der Lage ist vergleichsweise hohe Radiumgehalte in Lösung zu halten und sich ein damit verbundener Discharge durch erhöhte Radiumsignale im Ozean lokalisieren lässt, wird das im Grundwasser (Süßwasser) vorliegende Radium nahezu vollständig vom Aquifer adsorbiert und liegt kaum gelöst vor.

Neben natürlichen Radionukliden eignen sind auch stabile Isotope für SGD-Studien [11]. Aufgrund natürlicher Fraktionierungsprozesse im hydrologischen Kreislauf weisen Oberflächenwässer und Grundwasser grundsätzlich verschiedene Isotopensignaturen bezüglich ¹⁸O/¹⁶O und ²H/¹H auf. Oberflächenwässer zeigen in der Regel signifikant höhere δ^{18} O und δ^{2} H Signaturen als Grundwässer, die in der Regel die mittlere isotopische Zusammensetzung des Niederschlages wiederspiegeln, der lokal für die Grundwasserneubildung verantwortlich ist. Aus diesem Grunde eignen sich δ^{18} O und δ^{2} H als hydrologische Tracer, die generell eine Detektion und Quantifizierung von Mischungsprozessen zwischen meteorischem Grundwasser und verdunstungsbeeinflussten Oberflächenwässern erlauben. Neben den stabilen Isotopen des Wassers eignen sich weitere stabile Isotope für die Untersuchung von Stoffflüssen die im Zusammenhang mit SGD stehen können. Beispielhafte isotopische Spezies schließen ¹³C/¹²C, ¹⁵N/¹⁴N sowie ³⁴S/³²S ein. Die biogeochemische Umsetzung gelöster Nährstoffe und Kontaminanten, wie sie beispielsweise bei der Nitrifikation/Denitrifikation oder der bakteriellen Sulfatreduktion/Sulfidoxidation stattfinden, kann in insbesondere an scharfen geochemischen Gradienten, wie sie am Interface zwischen Grund- und Oberflächenwasser auftreten, zu signifikanten Fraktionierungseffekten führen. Aus diesem Grunde können die entsprechenden Isotopensignaturen zur Quantifizierung von Mischungen gelöster Inhaltsstoffe, zur Bestimmung von Stoffflüssen am Grundwasser/Oberflächenwasser Interface und zur Identifikation von Schadstoffquellen herangezogen werden.

Obgleich zahlreiche Umwelttracer prinzipiell für SGD Untersuchungen geeignet sind und potentiell an SGD gekoppelte Prozesse Relevanz für das Wasser-Ressourcen-Management haben, ist (auch in Anbetracht der immensen Ausdehnung der globalen Küstenlinien) die Anzahl an weltweit durchgeführten Studien nach wie vor relativ gering [z.B. 3,4,5,6,7]. Diese ungenügende Datenlage ist darauf zurückzuführen, dass (i) die Bedeutsamkeit von SGD für den küstennahen Ozean erst während der vergangenen beiden Dekaden in das Zentrum der Aufmerksamkeit gerückt ist und dass (ii) die ideale Herangehensweise an eine SGD-Studie (mobile) Probenahme- und Messausrüstung sowie spezielle Fachkenntnis erfordert, die nicht zur Standardausrüstung eines jeden Institutes gehören oder nach wie vor im Entwicklungsstadium sind.

Zitierte Literatur

- [1] Johannes R.E. (1980). Marine Ecology Progress Series 3, 365–373.
- [2] Moore W.S. (2010). Annual Reviews of Marine Science 2, 59-88.
- [3] Burnett W.C., Dulaiova H. (2003). Journal of Environmental Radioactivity 691 (1-2), 21-35.
- [4] Burnett W.C. et al. (2006). Science of the Total Environment 367(2-3), 498-543.
- [5] Burnett W.C., Peterson R.N., Moore W.S., Oliveira J. (2008). Estuarine, Coastal and Shelf Science 76, 501-511.
- [6] Santos I.R. et al. (2008). Limnology and Oceanography 53. 705-718.
- [7] Stieglitz T. (2005). Marine Pollution Bulletin 51, 51–59
- [8] Schmidt A., Schubert M. (2007). Isotopes in Environmental & Health Studies 43/4, 387-400.
- [9] Schmidt A., Schlüter M., Schubert M. (2008). Applied Radiation and Isotopes, 1939-1944.
- [10] Moore W.S., Arnold R. (1996). Journal of Geophysical Research-Oceans 101, 1321-1329.
- [11] Böttcher M.E., Voss M., Schulz-Bull D., Schneider R., Leipe T., Knöller K. (2010). Journal of Marine Systems 82, S43-S53.
- [12] Schubert M., Knoeller K., Einsiedl F., Santos, I (2013). Journal of Hydrology, submitted.

5. Zusammenarbeit mit anderen Stellen

Intensiv zusammengearbeitet wurde in dem im Rahmen des Projektes etablierten wissenschaftlichen Netzwerk, bestehen aus:

- der Ilia State University, Georgien,
- dem National Institute of Marine Geology, GeoEcoMar, Rumänien
- und dem Hellenic Center for Marine Research (HCMR), Griechenland.

Darüber hinaus war eine Zusammenarbeit insbesondere mit Zollbehörden und Transportunternehmen erforderlich (Gerätetransport).

II. Eingehende Darstellung

1 Verwendung der Zuwendung und der erzielten Ergebnisse im Einzelnen

Die Zuwendung wurde zweckdienlich für die in "3. Planung und Ablauf des Vorhabens" aufgezählten Aktivitäten verwendet. An jedem der zwei Standorte am Schwarzen Meer (Bereich Constanta, Rumänien und Bereich Batumi, Georgien) wurden zwei Probennahmekampagnen durchgeführt. Eine zusätzliche Kampagne in Constanta, Rumänien, wurde durch das National Institut of Marine Geology – GeoEcoMar – finanziert und durchgeführt. Grundsätzlich ist dabei zu sagen, dass die jeweils ersten Feldkampagnen in erster Linie der Bearbeitung logistischer und technischer Herausforderungen galten, die im Vorfeld der Feldaufenthalte nicht geklärt werden konnten.

Das Kick-Off Treffen wurde in Bukarest/Constanta und das Abschlusstreffen beim griechischen Partner Hellenic Center for Marine Research (HCMR) in Athen durchgeführt.

Alle wissenschaftlichen Ergebnisse sind in dem, dem Projektträger bereits vorliegenden, englischsprachigen Ergebnisbericht detailliert dargelegt. Das Verfassen dieses Ergebnisberichts in Englisch war unabdingbar, da dieser mit den internationalen Kooperationspartnern im Detail abzustimmen war. Eine komprimierte Diskussion der Ergebnisse ist für 2014 in einer (ebenfalls englischsprachigen) Veröffentlichung vorgesehen. Zentrale wissenschaftliche Ergebnisse sollen im Folgenden noch einmal zusammenfassend in deutscher Sprache wiedergegeben werden.

Untersuchungsgebiet Constanta, Rumänien

Im Untersuchungsgebiet Constanta, Rumänien, konnten im Zuge der **ersten Messkampagne** an zwei Stellen untermeerische Grundwasseraustritte festgestellt werden: Costinesti Hafen und "Hot Spring Bay" (im Rahmen des Projektes so genannt, da dort heiße Quellen austreten). Zur SGD Lokalisierung kam in erster Linie der natürliche Tracer ²²²Rn zum Einsatz. Die entsprechenden Ergebnisse werden durch die ebenfalls aufgezeichneten Salinitätsdaten bestätigt (Abb 1). Die Temperatur erwies sich an dem Standort als Tracersignal als weniger hilfreich.



Abb 1: Tracersignale ²²²Rn und Salinität entlang des Küstenprofils bei Constanta, Rumänien. Radonpeaks, d.h. SGD Austrittsgebiete wurden in zwei Bereichen festgestellt.

Zur Bestimmung der Endglieder der Mischungsgleichung bzgl. der stabilen Isotope (¹⁸O und ²H Signaturen), die ebenfalls als Umwelttracer genutzt werden sollten, wurden sowohl Grundwasser- als auch Meerwasserproben genommen und untersucht. Sämtliche Grundwasserproben plotten auf der Globalen Meteorischen Wasserlinie, was dafür spricht, dass es im Untersuchungsgebiet nicht zur Meerwasserintrusion in der Aquifer kommt (Abb 2).



Abb 2: Isotopensignaturen ¹⁸O und ²H am Rumänischen Untersuchungsstandort

Die **zweite Messkampagne** im Untersuchungsgebiet Constanta konzentrierte sich auf das lokalisierte SGD-Gebiet "Hot Spring Bay" und bestätigte die Ergebnisse der ersten Untersuchung (Abb 3&4).



Abb 3: Tracersignale ²²²Rn und Salinität im Gebiet "Hot Spring Bay"



Abb 4: Isotopensignaturen ¹⁸O und ²H zweite Messkampagne

In Abb 5 sind die im Zuge der zweiten Messkampagne aufgenommenen ²²²Rn-Aktivitäten semiquantitativ dargestellt. Die SGD anzeigenden erhöhten Radon-Aktivitäten im Bereich der Bucht sind sowohl auf dem Küstenprofil als auch auf dem 90° Profil gut zu erkennen.



Abb 5: Semiquantitative Darstellung der aufgenommenen ²²²Rn-Aktivitäten

Über die aufgenommenen Isotopensignaturen ¹⁸O und ²H entlang des 90° Profils (Abb 6) und die im Zuge der ersten Masskampagne bestimmten Endglieder der Mischungsreihe konnten Frischwassereinträge in den küstennahen Ozean von bis zu 7% quantifiziert werden.



Abb 6: Isotopensignaturen ¹⁸O und ²H entlang des 90° Profils.

Geringe Variabilitäten in den Oberflächenwassertemperaturen (SST), welche potentiell einen temperaturkonstanten Grundwasserzustrom (d.h. SGD) signalisieren, wurden in "Hot Spring Bay" und im Mangalia Harbour gefunden. Die Ergebnisse unterstützen somit die aus den Traceruntersuchungen gezogenen Schlussfolgerungen (Gebiete D und E in Abb 7).



Abb 7: SST Muster im Rumänischen Untersuchungsgebiet

Untersuchungsgebiet Batumi, Georgien

Im Untersuchungsgebiet Batumi, Georgien, konnte im Zuge der **ersten Messkampagne** an zwei Stellen der Austritt meteorischen Wassers in den küstennahen Ozean festgestellt werden: im Bereich der Stadt Kobuleti (nördlicher Radonpeak) und an der Flussmündung des Chaqvis-Tskali (südlicher Radonpeak). Die Wasseraustritte zeigten sich in erster Linie über den Tracer ²²²Rn. Die entsprechenden Ergebnisse werden aber auch durch die ebenfalls aufgezeichneten Salinitätsdaten bestätigt (Abb 8).



Abb 8: Tracersignale ²²²Rn (links) und Salinität (rechts) entlang des Küstenprofils und des 90° Profils am georgischen Standort nördlich von Batumi, 1. Kampagne

Die aufgenommenen Isotopensignaturen ¹⁸O und ²H entlang des 90° Profils bei Kobuleti und die aufgenommenen Endglieder der Mischungsreihe (Abb 9) konnten Frischwassereinträge in den küstennahen Ozean von bis zu 5% quantifiziert werden.



Abb 9: Isotopensignaturen ¹⁸O und ²H in den Endgliedern der Mischungsreihe (links) entlang des 90° Profils (rechts)

Die **zweite Feldkampagne** im Untersuchungsgebiet Batumi, Georgien, konzentrierte sich auf das lokalisierte Eintragsgebiet bei Kobuleti und bestätigte grundsätzlich die Ergebnisse der ersten Untersuchung. Nichtsdestotrotz zeigten sich die Anomalien (Radon und Salinität) leicht ortsverschoben (Abb 10). Gleichzeitig wurden teilweise deutlich erhöhte Aktivitäten an ²²²Rn in lokalen Flusswässern nachgewiesen. Entsprechend musste geschlussfolgert werden, dass im Untersuchungsgebiet Batumi ²²²Rn nicht als exklusiver Grundwassertracer (d.h. SGD Indikator) Verwendung finden kann, sondern auch über oberflächliche Fließgewässer eingetragen wird.



Abb 10: Tracersignal ²²²Rn (links) entlang des Küstenprofils am georgischen Standort nördlich von Batumi, 2. Kampagne

	²²² Rn [kBq/m³]	Temp	[°C]	Cond [µS/cm]
Thermal Well 1	3.1	34		-
Well 2	28.4	13		-
River-Achkva3	0.0	19		-
River-Achkva4	0.5	22		310
Well3	7.0	15		324
Well4	10.7	19		131

Tab. 2: Radonkonzentrationen in ausgewählten Flüssen und Messstellen

Die Auswertung der Ergebnisse der Traceruntersuchungen der zweiten Messkampagne ließen einen Eintrag von meteorischem Wasser in den küstennahen Ozean in erster Linie über zutretende Flüsse und weniger über SGD vermuten. Diese Vermutung wurde durch eine Untersuchung des küstennahen Ozeans im Bereich Kobuleti auf stabile Isotope überprüft und konnte bestätigt werden (Abb 11). Es wurde eine küstennahe, nordwärts gerichtete Meeresströmung festgestellt, die dem Fluss entstammendes meteorisches Wasser auch in den Bereich verfrachtet, in dem im Zuge der ersten Messkampagne ein ²²²Rn/Salinitätssignal gemessen wurde. Die stabilen Isotopen erlaubten eine Quantifizierung des Flusswasseranteils im küstennahen Ozean, der an der Flussmündung bei bis zu 19% liegt.



Abb 11: Isotopensignaturen ¹⁸O und ²H entlang des Küsten-Profils bei Kobuleti

Abb 12 vergleicht die im Zuge der beiden an der georgischen Küste gefahrenen Kampagnen aufgenommenen Radonmuster mit dem aus Satellitendaten gewonnenen Oberflächenwassertemperaturen (SST). Die Ergebnisse zeigen, das der temperaturkonstante Zustrom meteorischen Wasser im Bereich der Stadt Kobuleti (nördlicher Radonpeak) und an der Flussmündung des Chaqvis-Tskali (südlicher Radonpeak) sowohl über den ²²²Rn-Tracer als auch über die SST Muster angezeigt wird.



Abb 12: SST Muster im Rumänischen Untersuchungsgebiet

2. Notwendigkeit und Angemessenheit der geleisteten Arbeit

Der betriebene Aufwand war der Aufgabenstellung angemessen. Sowohl die logistische Vorbereitung als auch die Abhängigkeit von unbeeinflussbaren Umständen wie der Witterung (Seegängigkeit des Bootes) oder auch der reibungslosen Verschiffung und zeiteffizienten Zollabfertigung von Ausrüstungsgegenständen machen zwei Kampagnen pro Standort notwendig.

3. Voraussichtlicher Nutzens, insbesondere der Verwertbarkeit des Ergebnisses

Aufgrund der Ausdehnung des Schwarzen Meeres und der grundsätzlichen Relevanz der Fragestellung in Küstenregionen war das Projekt vornehmlich als Maßnahme zum Wissenstransfer konzipiert. Die gewonnenen Erkenntnisse sollen den Projektpartnern ermöglichen nachfolgend zur Projektlaufzeit die jeweilige gesamte nationale Küste bezüglich ihres SGD-Potentials zu bewerten. Mit Hilfe der durchgeführten Arbeiten vor Ort konnten Innovationskeime gesetzt bzw. Innovationspotenziale und FuE-Kapazitäten bei den Partnerinstitutionen erkannt und erschlossen werden. Des Weiteren konnten Partnerschaften vorbereitet bzw. ausgebaut werden, die es ermöglichen das Potenzial für eine künftige projektbezogene Zusammenarbeit voll auszuschöpfen.

Entsprechend lagt der Nutzen der Kooperation innerhalb der Projektes sowohl auf Seiten des Antragstellers (UFZ) als auch der rumänischen bzw. georgischen und griechischen Partner. Es war bzw. ist das Ziel, die diesbezüglichen Synergien durch Erschließung neuer und durch Sicherung bestehender FuE-Kooperation auch längerfristig und in größeren bzw. flexibleren Forschungsverbünden im Schwarzmeerraum zu nutzen. Die Vorbereitung der Antragstellung weiterer Folgeprojekte ist vorgesehen und wird insbesondere von georgischer Seite forciert. Neben dem wissenschaftlichen Nutzen und der Verwertbarkeit der zu Ergebnisse im Rahmen des jeweiligen lokalen Wasser-Ressourcen-Managements ergibt sich durch die Verbesserung der wissenschaftlichen Wettbewerbsfähigkeit der Projektpartner zusätzlicher Mehrwert für jede der beteiligten Partnereinrichtungen.

4. Fortschritt auf dem Gebiet des Vorhabens

Der Fortschritt auf dem Gebiet des Vorhabens ist insbesondere in der Verbesserung der wissenschaftlichen Wettbewerbsfähigkeit der Projektpartner zu sehen. Durch die praktischen Untersuchungen und die im Rahmen des Projektes abgehaltenen theoretischen Seminare war ein für die Partnerinstitutionen signifikanter Wissenszuwachs im Fachgebiet des Vorhabens zu verzeichnen. Darüber hinaus konnten im Ergebnis des Projektes für jeden der beiden Standorte konkrete Daten und Informationen bereitgestellt werden, die im Rahmen des jeweiligen lokalen Wasser Ressourcen Managements von Nutzen sind.

6. Geplanten Veröffentlichungen des Ergebnisses

Für das Jahr 2014 ist eine gemeinsame Veröffentlichung der Ergebnisse geplant.

III. Erfolgskontrollbericht

1 Beitrag des Ergebnisses zu den förderpolitischen Zielen

Die durchgeführten Arbeiten liefen im Rahmen der BMBF-Ausschreibung "BS-ERA.Net". Für die Ausschreibung war folgender genereller Inhalt definiert: "BS-ERA.NET is a networking project aimed at integrating the participating countries from the Black Sea extended region in the European Research Area by linking research activities within existing national, bilateral and regional RTD programmes.". Laut Ausschreibung waren zentrale Ziele der geplanten Aktivitäten:

- to reduce the fragmentation of the European Research Area (ERA) by improving the coherence and coordination of national and regional research programmes;
- to develop and strengthen the coordination of public research programmes conducted at national and regional level, which target a group of countries from the extended Black Sea region;
- to sustain the communication in order to develop better reciprocal knowledge and promote trustbuilding among programme owners and/or managers through a mutual learning process, and a systemic exchange of information and good practice;
- to promote a network and mutually open at national regional research programmes level which will lead to: concrete cooperation in the frame of the Black Sea Research Programme (BSRP) and to the development and implementation of joint programmes and activities in the region.

Die im Projekt durchgeführten Aktivitäten bedienten die o.g. zentralen Ziele, wie im Anschlußbericht beschrieben. Das Projekt lief unter dem Förderschwerpunkt *"1. Climate & Environment; 1.2. Water pollution prevention options for coastal zones and tourist areas*". Beide ausgewählten Untersuchungsgebiete waren in diesem Sinne ausgewählt worden.

2 Wissenschaftlich-technische Ergebnis des Vorhabens

Im Rahmen des Projektes konnten Erfahrungen zur Machbarkeit von SGD Studien im Schwarzmeerraum an zwei exemplarischen Standorten gemacht werden. Die Standorte wurden so gewählt, dass sie zum ersten einen westlichen Küstenabschnitt des Schwarzen Meeres mit eher flachem Hinterland und zum zweiten einen östlichen Küstenabschnitt des Schwarzen Meeres mit eher bergigem Hinterland repräsentieren. Neben den generellen Erfahrungen die im Sinne der Aufgabenstellung bzw. der förderpolitischen Zielen gemacht wurden, konnten standortspezifische Daten erhoben werden, die dem Wasser Ressourcen Management in den jeweiligen Regionen zur Verfügung stehen.

3 Fortschreibung des Verwertungsplans

Erfindungen oder Schutzrechtsanmeldungen bzw. erteilte Schutzrechte liegen nicht vor.

Konkrete wirtschaftliche Erfolgsaussichten nach Projektende können nicht genannte werde, da es primär um wissenschaftliche Arbeiten ging, die im Rahmen des Wasser Ressourcen Managements indirekt auch von wirtschaftlicher Relevanz sein können.

Wissenschaftliche und/oder technische Erfolgsaussichten nach Projektende basieren insbesondere auf der im Zuge des Projektes entstandenen Verbesserung der wissenschaftlichen Wettbewerbsfähigkeit der Projektpartner. Durch die praktischen Untersuchungen und theoretischen Seminare ist für die Partnerinstitutionen signifikanter Wissenszuwachs im Fachgebiet des Vorhabens (SGD Untersuchung und Evaluierung) zu verzeichnen. Die im Ergebnis des Projektes für jeden der beiden Standorte erhobenen konkreten Daten und Informationen, die ins besondere im Rahmen des Wasser Ressourcen Managements von Nutzen sind, stellen eine Basis für zukünftige themenverwandte Arbeiten dar. Dabei ist auch eine Zusammenarbeit mit anderen Einrichtungen (Behörden, Firmen, Forschungsstellen) anzustreben. Die Aufrechterhaltung des entstandenen internationalen wissenschaftlichen Netzwerks wird unbedingt angestrebt, um die wissenschaftliche (und ggf. wirtschaftliche) Anschlussfähigkeit für eine mögliche nächste Phase zur erfolgreichen Weiterverwertung der FE-Ergebnisse zu gewährleisten.

4 Arbeiten, die zu keiner Lösung geführt haben

Als solche sind die Untersuchungen auf Radiumverteilungsmuster im küstennahen Ozean zu nennen. Aufgrund der fehlenden Gezeiten im Schwarzen Meer war die Verwendung von Radiumnukliden als SGD-Indikator praktisch nicht umsetzbar.

5 Präsentationsmöglichkeiten

Für das Jahr 2014 ist eine gemeinsame Veröffentlichung der Ergebnisse geplant.

6 Einhaltung der Kosten- und Zeitplanung

vgl. Tab 1

Preface: The final 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). The reported activities include (1) the kick-off meeting held in Constanta/Romania, (2) two field campaigns at each of the two study sites, one close to Constanta/Romania and the other one close to Batumi/Georgia and (3) the final meeting held in Anavyssos/Greece. The reported results include recorded data and an evaluation thereof.

1 Summary

1.1 General Scope of Work

The sustainable management of the coastal sea requires comprehensive understanding of the processes related to solute and particulate material transport from the terrestrial to the marine environment. Submarine Groundwater Discharge (SGD) provides a major pathway for material transport across the aquifer/ocean interface. Nutrients and contaminants carried by the groundwater have a significant potential to cause a deterioration of the overall quality of the coastal marine environment. Related detrimental environmental impacts include contamination and eutrophication of the coastal sea, contamination of seafood, coral reef damage, and harmful algal blooms.

Whereas river and sewage discharge into the ocean are bound to distinct locations, thus allowing uncomplicated quantification of discharge rates and material budgets, the investigation of material transport via SGD is more challenging. Adding to the general difficulties in locating SGD spots is the spatial and temporal variability that is typical for SGD. Aqueous tracers can be used as appropriate tool for related investigations. "Environmental Tracers" are particularly suitable in this regard. They are defined as natural or anthropogenic substances that are present in the environment originating from defined sources and have the general advantage of not necessitating any introduction of chemicals into the environment that may prove persistent. Due to their ubiquitous occurrence, environmental tracers are most suitable for large-scale studies, as they are essential for comprehensive SGD investigations.

The scientific aim of the research project reported here was the application of a multi-tracer approach for SGD investigation. Studies were carried out at two exemplary sites on the Black Sea coast. Several appropriate tracer methods and a DEM based modelling approach were applied and the results compared. The two study sites had been chosen in order (i) to show strong exposure to anthropogenic pressure and (ii) to represent two different geographical settings, one located on the mountainous eastern coast and the other on the flat western coast of the Black Sea. Besides site specific data a general outcome of the project was a mutual knowledge transfer within the established scientific network. Inter-institutional synergies that resulted from combining experiences, approaches and methodologies from the four participating European research institutions made the project activities beneficial for all project partners.

1.2 Research Program

The central goals of the research project were (1) to localize and if possible to quantify SGD along the coastline of two exemplary and representative study sites, (2) to roughly estimate the importance of SGD to the respective coastal nutrient/contaminant budget, and (3) to assess the relative importance of the potential SGD drivers. In order to achieve the required data, two sampling campaigns were carried out at each of the two chosen study sites. The execution of two visits to each site was also necessary since several logistical prearrangements had to be made on site. The campaigns, each lasting for about

one week, were scheduled in a way that they yielded datasets were representative for both spring and autumn. Additional activities were carried out by the local partner institutes in between the campaigns.

During the field surveys the following indicators and tracers were employed. They all show a significant gradient between groundwater and ocean resulting, in the case of SGD occurrence, in distinct tracer distribution patterns in the coastal sea. The coastal water column integrates the respective tracer signals, thereby smoothing out small-scale variations that are irrelevant in the given context.

- ²²²Rn in seawater and groundwater using mobile radon monitors
- Radium isotopes in seawater and groundwater using the RaDeCC detection system
- Stable isotopes (²H, ¹⁸O) using isotope ratio mass spectrometry
- Progenies of ^{222, 220}Rn and ⁴⁰K in seawater using in situ gamma spectrometry (KATERINA system)
- Temperature, pH, and salinity of water using mobile detection equipment
- Wind speed, wind direction using locally available data

The naturally occurring radioactive noble gas radon (²²²Rn) was applied as main tracer throughout the project. Mobile radon monitors were applied for end-member definition of groundwater and off-shore water and for mapping of radon distribution patterns coastal sea. Spatial changes in the radon inventory of the coastal sea were used to localize SGD areas and to estimate the related groundwater fluxes. In addition, continuous stationary in situ measurements at exemplary sampling points using the underwater gamma spectrometer KATERINA were carried out for ²²²Rn and ²²⁰Rn progenies.

Besides radon short-lived radium isotopes and stable isotopes were applied as SGD indicators. ²²³Ra and ²²⁴Ra are useful tools for evaluating residence times of groundwater that is discharged into the coastal sea. Stable isotopes are suitable for SGD assessment because the discharging groundwater (²H, ¹⁸O) is characterized by isotopic signatures that differ significantly from the isotopic signatures found in seawater. Thus, radium species and stable isotopes allow an independent determination of the mixing ratios between groundwater, near shore and offshore waters. For setting up the related mixing equations offshore samples and samples taken from monitoring wells that tap the aquifer which is hydraulically interacting with the coastal sea were taken and analysed for end-member definition. In addition salinity (conductivity), temperature, and pH were monitored in parallel.

Besides interpretation of tracer data collected in ocean and groundwater a conceptually completely independent land-based modelling approach was used for validation of the conclusions drawn from the tracer studies. For this purpose regional digital elevation models (DEM) were used to provide data for a GIS-based raster calculation, allowing the identification of preferential surface water accumulation zones along the investigated coastlines for roughly indicating potential SGD-prone areas. As a result, conclusions drawn from tracer data and from the DEM analysis were cross-checked and mutually validated. In addition thermal satellite images (Landsat ETM) of the coastal ocean were applied. Small variabilities in the sea surface temperature (SST) conceptually indicate continuous spatio-temporal groundwater influx and can hence be used for SGD localization.

1.3 State of the Art related to the Research Program

Conventional methods for SGD studies do either employ numerical models or seepage meter spot measurements. Numerical models are based on long-term mass and water balances and hydrological/hydrogeological assumptions. Seepage meters allow direct quantification of water fluxes.

However, neither of the two approaches completely meets the demands of modern SGD studies because of two general reasons: (1) Hydrological models often underestimate actual groundwater discharge rates in coastal areas, a problem which arises because most balance calculations and models only evaluate the meteoric groundwater flow to the coastal sea and disregard seawater that is continuously re-cycling through the coastal aquifer by periodical forces such as the changing tides; (2) Seepage meters allow only spot measurements and can thus in large-scale investigations only be used as a complementary tool. Hence, it investigation of SGD and related processes using solely the two mentioned conventional approaches is not achievable. An appropriate alternative is the application of environmental tracers, i.e. naturally occurring dissolved components. The two major advantages of environmental tracers are (1) that they allow, in contrast to hydrological models, a direct quantification of water fluxes, and (2) that they produce, unlike seepage meters, data that can be integrated vertically through the water column and laterally over the studied area leading to integrated flux estimates.

A range of environmental tracers are currently utilized for SGD studies. Originally, easily accessible dissolved chemical components such as selected elements or the standard physico-chemical water parameters temperature and salinity had been employed. Although these parameters are relatively easy to measure, they do not yield any information about residence times of water volumes. Hence, innovative approaches that use the following isotopic tracers were developed during the last decade.

The radionuclide ²²²Rn (half-life $t_{1/2}$ 3.82 days, hereafter referred to as "radon") has the advantage of being a radioactive noble gas, i.e. a (short-lived) radionuclide that is chemically inert and can easily be detected on site. Since radon is produced in every mineral matrix and is fairly soluble in water, it occurs ubiquitously in all natural waters. Radon concentrations that are usually found in groundwater are about three to four orders of magnitude higher than radon concentrations typical for the coastal sea. The resulting very distinct concentration gradient at the groundwater/seawater interface allows the localization of SGD spots by using elevated radon-in-seawater concentrations as indicator. Besides the localisation of diffuse or focussed SGD occurrence, radon can also be used as quantitative tool for estimating groundwater discharge rates.

Another set of naturally occurring radiotracers is the "radium quartet", including the two short-lived isotopes ²²³Ra ($t_{1/2}$ 11.4 days) and ²²⁴Ra ($t_{1/2}$ 3.66 days), and the two long-lived ²²⁶Ra ($t_{1/2}$ 1600 yrs) and ²²⁸Ra ($t_{1/2}$ 5.7 yrs). Extensive use is made of the radium quartet by the marine community as tracers of seawater re-circulation processes. Whereas saline water re-circulating though coastal aquifers yields relatively high radium concentrations and even small inputs of that water into a coastal zone can be recognized as a strong positive radium signal, radium is mainly adsorbed to the aquifer matrix in the case of freshwater aquifers, i.e. is not mobile in fresh groundwater.

Besides naturally occurring radionuclides, stable isotopes are being increasingly used as environmental tracers for SGD investigation. Due to naturally occurring stable isotope fractionation processes in the hydrological cycle surface waters and groundwater generally display significantly different isotope ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$). Seawater shows significantly higher $\delta^{18}O$ and $\delta^{2}H$ values than the groundwater, which mainly reflects the weighted mean isotopic composition of the local precipitation. Thus, stable isotopes represent an excellent hydrological tracer enabling the recognition and quantification of mixing processes between meteoric groundwater and the coastal ocean (and any other evaporation affected surface water bodies).

2 Detailed Report of Activities and Results

2.1 Kick-Off Meeting

A kick-off meeting was held in Bucharest and Constanta, Romania, on March 28th and 29th. 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.

2.2 Field Campaigns in Romania

The first field campaign in Romania was carried out between May 21st and 23rd 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 while cruising with a speed of about 5 km/h along a coastal profile. Simultaneously the seawater radon concentration was detected with a 10 minutes counting cycle. On the terrestrial side groundwater wells that were found 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 on June 13th and 14th. 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). The data recorded during the two sampling campaigns is illustrated in the following figures Fig. 1A/B (campaign May 2012) and Fig. 2A/B (campaign June 2012). The results of the additional two day sampling campaign campaign carried out by GeoEcoMar staff are displayed in Fig. 2A and 2B. The data recorded during the June campaign allowed verifying and refining the results of the May campaign.



Fig. 1A: Radon concentration and salinity data recorded during the 1^{st} sampling campaign along a North – South coastal profile in May 2012 (the salinity meter failed to work 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^{st} *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. 2B: 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.

Figures 1 and 2 summarize and compare the results of the boat cruises carried out in May and June 2012 along the coastline between Constanta and Mangalia. The two areas that showed strongest SGD indications 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.

Radon: During the <u>May campaign</u> background values along the coastline of about 10 Bq/m³ and an offshore background value of about 5 Bq/m³ were detected. The peak values at both, Costinesti Harbour and Hot Spring Bay, were at about 110 Bq/m³. The background values detected in the coastal sea during the <u>June campaign</u> were again around 10 Bq/m³. The peak values at Costinesti Harbour and Hot Spring Bay were about 110 Bq/m³ and 40 Bq/m³, respectively (i.e. in Hot Spring Bay less than in May).

Salinity: 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 3rd day of campaign, i.e. no readings are available 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 provided by GeoEcoMar Romania, 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).

Temperature: 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 of the survey is most likely due to the changing atmospheric 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 second day started much cooler, though. 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 isotopes: ¹⁸O and ²H signatures of water (Fig. 3) were determined in groundwater samples that represent the SGD occurring at the two locations indicated by the coastal radon/salinity survey (Costinesti Harbour and Mangalia Harbour). Also, sea water samples were taken close to the two indicated SGD spots as well as from locations where no groundwater discharge was expected (background). 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 re-circulation of seawater into the respective aquifers (i.e. no seawater intrusion). This result is reasonable since a major driver for re-circulation of seawater are the changing tides which are of no significant relevance in the Black Sea. No significant differences in isotope signatures were observed between background sea water samples (off shore) and sea water samples from detected SGD locations. This may be due to a quick mixing of



discharging groundwater into the seawater body and/or due to an amount of submarine groundwater discharge that is below the detection limit of the stable isotope method.

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

The second field campaign in Romania was carried out on Sept. 26st and Sept. 27th 2012. The two day survey covered an about 5 km stretch of coastline along a bay north of Mangalia where SGD had been located during the first campaign ("Hot Spring Bay").

During the coastal survey water salinity, water temperature, water depth and the related coordinates were recorded continuously while cruising with a speed of about 5 km/h. Simultaneously the seawater radon concentration was detected applying a 5 minutes counting cycle. Subsequently the same parameters were recorded along a ca. 3 km profile perpendicular to the coastline. The profile started offshore and ended at the SGD location Hot Spring Bay. Both cruise tracks are displayed in Fig. 5. Eight additional samples were taken at discreet locations for the detection of short-lived radium isotopes along the perpendicular profile. The water was sampled by using buoys anchored in 500m distances. Five additional water samples were taken close to the beach using seepage meters. The sampling locations are shown in Fig. 6 (yellow and blue triangles, respectively). Furthermore nutrients and stable isotopes were analysed at six sampling locations within Hot Spring Bay and at six groundwater wells that were found to be representative for the terrestrial groundwater end-member; the respective locations are shown in Fig. 7.

Figures 4A and 4B display the data recorded during the boat cruise parallel to the Hot Spring Bay coastline north of Mangalia (4A) and perpendicular to it (4B). The area showed the most distinct indications for SGD during the first sampling campaign. During the second campaign Hot Spring Bay showed again significant anomalies for radon and salinity indicating SGD. Both profiles revealed significantly elevated radon concentrations close to the central part of the bay close to the coastline. The peak value on the coastal profile reached 140 Bq/m³, which is comparable to the peak value detected in May (110 Bq/m³). The perpendicular profile, which started off-shore with values of about 5 Bq/m³ (as during the May cruise) ended close to the shoreline with about 100 Bq/m³, thereby confirming the coastal profile peak value.

In accordance with the radon distribution patterns Figs. 4A and 4B show also low salinities in the central part of Hot Spring Bay close to the coastline. The background values valid for the coastal sea were found to be about 16, i.e. comparable to the background values detected during the first

campaign (16.5). Congruent with the radon peak in Hot Spring Bay the salinity decreased locally to about 15, which is also in accordance with the data detected during the first campaign.

The water temperatures measured during the two earlier surveys did not show any distinct pattern that correlates with radon or salinity. The same was found to be the case for the second campaign. Hence, the temperature data is not displayed here. The gradual rise of the water temperatures during the courses of each individual day is believed to be due to the diurnally changing atmospheric temperature.



Fig. 4A: Radon concentration and salinity recorded during the September campaign along a coastal profile (Hot Spring Bay). Displayed are the radon and salinity readings vs. time of the cruise (distance $N \rightarrow S$ *).*



Fig. 4B: Radon concentration and salinity recorded during the September campaign along a profile perpendicular to the coast at Hot Springs Bay. Displayed are the radon and salinity readings vs. time of the cruise (distance east \rightarrow west).

Short lived radium isotopes were sampled within Hot Spring Bay at eight locations. Radium was samples by adsorption onto MnO₂-fibre. For the purpose of ²²³Ra/²²⁴Ra ratio determination eight buoys with MnO₂-fibre bags were placed along a profile at fixed locations within the bay (Fig. 6). The buoys were placed on Sept. 26st at 03:00 p.m. and retrieved after 19 hours on Sept. 27th at 10:00 a.m.. For the purpose of absolute ²²³Ra and ²²⁴Ra determination two additional samples were taken on the profile at the locations 500 and 1000 m from the beach, respectively. The two samples were taken by pumping seawater through MnO₂-fibre filled cartridges (200 litres each with a pump rate of 1 l/min). All ten MnO₂-fibre samples were shipped to Germany and measured at the radionuclide laboratory at the UFZ

in Leipzig by means of a RaDeCC detector. Unfortunately the laptop with the data was stolen from the laboratory after the measurements were finished. Hence no radium data can be presented.

Furthermore five seepage metres SM1 - SM5 were installed by a professional diver close to the beach within Hot Spring Bay in depths between 2.2 and 3.2 metres. The seepage meters were placed on September 26^{st} between 04:00 and 05:00 p.m. and retrieved after 21 hours on September 27^{th} between 01:00 and 02:00 p.m. Compared to the offshore salinities detected at the eight MnO₂-fibre buoys (16.6) the salinity in the seepage metres (15.3) was about 8% lower, which indicates freshwater discharge into the seepage meters. However, the significantly different fill levels of the seepage meters and the still high water salinities indicate a substantial share of seawater entering the seepage metres, which does not allow SGD quantification at the distinct spots.

	depth (m)	salinity	fill volume (cm ³)
SM1	2.34	15.3	1900
SM2	2.39	15.3	200
SM3	3.15	15.2	2500
SM4	2.23	15.4	overflow
SM5	2.48	15.4	750

Tab.1: Seepage metres S1 – S5 installed close to the shore within Hot Spring Bay

Nutrients were sampled and measured at six groundwater wells and at six sampling locations within Hot Spring Bay (S1 - S9; samples labelled with A and B indicate different depth at the same sampling point). The results are summarized in Table 2.

Tab.2: Samples for nutrients within Hot Spring Bay (indicated by depth values) and in wells in the surrounding area (without depth values); the seawater samples labelled with A and B indicate different depth at the same sampling point

	depth	N-NO ₂	N-NO ₃	PO ₄	SO_4	Susp. Sol.	Conduct.	Salinity
	m	mg/l	mg/l	mg/l	mg/l	mg/l	μS/cm	
Monastery	_	0.004	46.00	0.09	157.5	0	2510	1.1
F08	_	0.024	0.10	0.32	14.0	42	353	_
F13 - Aviasan	_	0.004	15.00	0.10	150.0	2	1980	_
MN 01 – I.Nec.	_	0.002	0.02	0.02	60.0	1	1484	_
MN 02 - GESS	_	0.017	0.10	0.00	0.0	0	1771	_
MN 03 - Saturn	_	0.004	0.02	0.02	11.0	5	1638	_
S1A	0.5	0.008	0.12	0.02	1100.0	0	22500	13.6
S2B	3.0	0.007	0.12	0.00	1100.0	0	22500	13.6
S3A	0.5	0.009	0.11	0.00	1125.0	1	22200	13.3
S4B	13.0	0.007	0.12	0.01	1175.0	0	24000	14.5
S5	0.5	0.007	0.13	0.00	1150.0	0	22500	13.5
S6	0.5	0.008	0.11	0.01	1125.0	0	22500	13.5
S7	0.5	0.008	0.10	0.00	1200.0	0	22600	13.6
S8A	0.5	0.006	0.11	0.04	1150.0	1	21700	13.0
S9B	3.0	0.007	0.11	0.01	1100.0	1	21800	13.1



Fig. 5: Semi-quantitative illustration of radon concentration recorded during the 2^{nd} sampling campaign in Hot Springs Bay (cf. Fig. 4)



Fig. 6: Locations of Ra-buoys (yellow) and seepage meters (blue) during the 2nd sampling campaign in Hot Springs Bay



Fig. 7: Sampling points for nutrients and stable isotope samples during the 2nd sampling campaign in Hot Springs Bay and surroundings

The stable isotope survey during the 2^{nd} sampling campaign focused on the Costinesti region and on the Mangalia region. One objective of the sampling campaign was to reliably define the isotopic endmember of the groundwater that discharges into the Black Sea in the region. Groundwater samples were taken from monitoring wells in the Costinesti and Mangalia regions. Additional groundwater samples were collected at cliff springs that were assumed to represent the aquifer that is most likely to contribute to SGD in the region.

All groundwater samples from the Costinesti region display a very similar isotopic composition with δ^{18} O values between -9.8 and -9.2 ‰ and δ^{2} H values between -67.2 and -58.2 ‰. In contrast, groundwater samples from the Mangalia region show significantly lower isotope signatures of around -12 ‰ for δ^{18} O and of around -85 ‰ for δ^{2} H. The results are comparable to the data achieved during

the first sampling campaign (May). The difference in isotope signatures is believed to be due to the specific local hydrogeological conditions in the "Hot Spring Bay" area that favour the uprising of deep, hydrothermally impacted groundwater (Fig. 8).



Fig. 8: Isotopic composition of groundwater and samples from the Mangalia and Costinesti regions compared to seawater samples

To investigate the influence of submarine groundwater discharge on the isotopic composition of coastal seawater in the region, two seawater profiles were sampled for stable isotopes both running perpendicular to the coastline, one starting at the Costinesti harbour, the other one starting close to Mangalia harbour. While the Costinesti profile did not indicate any SGD impact on the stable isotope signature of coastal seawater, a significant impact was evident for the Mangalia profile (Fig. 9). Up to 750 m from the shore line, the δ^{18} O and δ^{2} H values are lower by 0.4 and 2 ‰, respectively. Using a simple mixing equation and the isotope signatures of the two end members (Mangalia groundwater and average Black Sea off-shore water) a groundwater content of up to 7% was calculate for the water samples from the Mangalia perpendicular profile taken close to the coastline.



Fig. 9: Isotopic composition of seawater samples taken off Costinesti and Mangalia

The thermal satellite data that was evaluated for the localization of potential SGD areas provide consistent results in certain areas only. On the one hand small variabilities in the sea surface temperature (SST), which conceptually indicate continuous spatio-temporal groundwater influx (i.e. SGD), occur in the Hot Spring Bay and the Mangalia Harbour and do support the tracer findings discussed above (areas D and E in Fig. 10). On the other hand at least two other areas with significantly low SST temperature variabilities were found: areas B and C in Fig. 10. Both locations could not be verified as SGD areas by the tracer data. We assume the reason to be related (1) to SGD that was insignificantly low during the survey as result of the long term weather pattern prior to the sampling campaigns (note that all SST data were recorded prior to the campaign), (2) to temporal discharge agricultural originating in drainage systems occurring only after intense rainfall events or (3) to a spatio-temporal upwelling, induced through landwards oriented sea currents. All three processes can cause low SST variabilities and will have to be considered during future SGD related investigations.



Fig. 10: SST image of the coastal sea and potential water accumulation based on digital elevation model evaluation.

The results generally emphasize the fact that the SST variability analysis does provide indications for SGD occurrence but needs to be backed by supplementary methods that 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 spots where such depression structures intersect with the coastline 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. Tracer campaigns on the other hand do only represent a temporal snapshot and may not reveal temporarily variable SGD and related processes. Thus, the synergy of thermal-, morphological and tracer methods appear to represent the most suitable approach for SGD assessment.

2.3 Field Campaigns in 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 14th to October 18th 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 16th, covered about two thirds of the whole profile distance. On October 17th the remaining southern part and a profile running perpendicular to the coastline 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 while cruising at a speed of about 5 km/h. On the terrestrial side groundwater samples were taken from wells and springs that were found to be representative for the terrestrial groundwater end-member.

Radon: Fig. 11A illustrates the radon concentrations and the related salinities that were detected along the coastline and on the perpendicular profile semi-quantitatively. Fig. 12 displays the same data as quantitative diagrams. The data reveals 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. Hence, the radon patterns indicate two potential SGD regions.

Salinity: The salinity data are in accordance with the radon readings and back the assumption of SGD occurrence in two distinct areas (*cf.* Fig. 11B). The salinity of the coastal sea decreases considerably in the Kobuleti area at a landmark that was named "concrete structure on beach" (*cf.* Fig. 12A). Less distinct but still significant is the low salinity pattern at the mouth of river Chaqvis-Tskali (landmark "Hotel Oasis"; *cf.* Fig. 12B). Due to a malfunctioning handheld GPS sensor provided by the Ivane Javakhishvili Tbilisi State University the perpendicular profile that was measured for evaluation of the off-shore extent of the radon/salinity plume did not end exactly in the localized high-radon / low-salinity spot 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. 11A, Fig. 12C). That confirms radon as a much more sensitive trace parameter than salinity (at least in the given context).

Fig. 11A (left): Radon concentrations recorded during the 1st sampling campaign on a North \rightarrow South coastal profile in September 2012. The size of the circles corresponds to the detected radon concentration.

Fig. 11B (right): Salinities recorded during the 1st sampling campaign on a North \rightarrow South coastal profile in September 2012. The size of the circles corresponds to the detected salinity values.





Fig. 12A: Radon and conductivity recorded along the northern part of the coastal survey on a North \rightarrow South coastal profile in September 2012. Major landmarks are indicated.

Fig. 12B: Radon and conductivity recorded along the southern part of the coastal survey on a North \rightarrow South coastal profile in September 2012. Major landmarks are indicated.

Fig. 12C: Radon and conductivity recorded along the perpendicular profile in September 2012.

The temperature readings made in 50 cm water depth were, as described for the 1st sampling campaign in Romania, of hardly any informative value. Hence, the ph of the seawater was recorded as additional parameter.



Fig. 13A (left): Radon and pH recorded along the northern part of the coastal survey along a North \rightarrow South coastal profile in September 2012. Fig. 13B (right): Radon and pH recorded during along the southern part of the coastal survey along a North \rightarrow South coastal profile in September 2012.

As it becomes obvious in Fig. 13A the pH showed a distinct peak at the same location where elevated radon concentrations occur (Kobuleti), indicating strong water discharge into the sea. The data displayed in Fig. 13B illustrate the findings along the southern part of the survey and do also show a negative correlation between radon and pH, which is however not as distinct as the data displayed in Fig. 13A.

Stable isotope signatures were measured in groundwater and spring water samples that were considered as representative for the groundwater potentially discharging locally into the coastal sea. Additionally, sea water samples were taken from six locations along the perpendicular profile (*cf.* Fig. 11B). 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 ‰ (δ^{18} O) and -22.2 ‰ (δ^{2} H) (Fig. 14A). 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 taken at the location closest to the shore line has a depleted isotope signature of both oxygen and hydrogen indicating the impact of discharging meteoric water (Fig. 14B). Using a simple mixing equation and the observed isotope signatures of the sea water and the groundwater end-member, a meteoric water content in the seawater of approximately 5 % can be estimated for location of the perpendicular profile that is closest to the shore.



The second field campaign in Georgia was carried out in May 2013. The visit, which again included long drives from Tbilissi to Batumi/Kobuleti and back, lasted from May 27th to May 31st. The actual coastal survey had to be stopped several times due to strong winds and high waves, which didn't allow sampling. It was carried out on two days (May 29th and May 30th) and covered an about 20 km stretch of coastline north and south of Kobuleti (Fig. 15A). The parameters that were continuously recorded in the coastal sea included water salinity and the related coordinates. Simultaneously the seawater radon concentration was detected applying a 5 minutes counting cycle while cruising with a speed of about 5 km/h. On the terrestrial side groundwater samples were taken from twelve wells and springs that proved representative for the terrestrial groundwater end-member (Fig. 15A).

Fig. 15A illustrates the radon concentration pattern that was detected along the coastline (first sampling day in yellow, second sampling day in blue). Fig. 15B shows the consistency between radon and conductivity (i.e. salinity) exemplarily for an about 8 km stretch of coastline around the Achkva river mouth south of Kobuleti recorded during the first day of the campaign. Both figures show the occurrence of significantly elevated radon concentrations (and depleted salinities) at the mouth of river

Achkva. Another area with less pronounced but still significantly elevated radon concentrations was localized further south at the mouth of river Chakvi. As already concluded from the data of the first sampling campaign, which revealed elevated radon concentrations at more or less the same locations, the radon patterns indicate two regions with meteoric water discharge into the sea. The conductivity data is in accordance with the radon readings. The conductivity of the coastal sea decreases considerably at both the mouth of river Achkva and less distinct but still significantly at the mouth of river Chakvi.

However, in contrast to the results of the 1st sampling campaign the radon/salinity anomaly, which was detected north of the Achkva river mouth in September 2012, appeared in the 2nd campaign immediately at the Achkva river mouth, i.e. about 2 km south of its location detected ealier. That gave reason to an Achkva river water sampling close to the coastline (sample "River-Achkva4"), which revealed a radon value of 500 Bq/m³, i.e. a value that is unusually high for a running surface water stream (Tab. 3). Hence it was concluded that the radon plume that was found in the coastal sea during both the 1st and the 2nd sampling campaign doesn't have its origin in discharging groundwater (i.e. SGD) but in river water discharge (Achkva River). The plume is drifting from the river mouth to the north (where the signal was found during the 1st sampling campaign) with the coastal current. That assumption was backed by a drifter experiment that was carried out ad hoc and by the stable isotope results discussed below.

Besides the two radon peaks discussed above, a minor radon peak was detected in the middle between the Achkva and Chakvi river mouths (Fig. 15A). The anomaly is in accordance with the very high radon concentration (30 kBq/m³) that was found in a well located close to the coast in this area ("Well 2"; *cf.* Fig. 15A and Tab. 3). The well collects groundwater from a fractured hard rock aquifer in order to drain a hotel building site. It is likely that minor amounts of the water that discharge into the sea cause the detected radon peak.









	²²² Rn [kBq/m ³]	Temp [°C]	Cond [µS/cm]
Thermal Well 1	3.1	34	-
Well 2	28.4	13	-
River-Achkva3	0.0	19	-
River-Achkva4	0.5	22	310
Well3	7.0	15	324
Well4	10.7	19	131

Tab.3: Radon concentration detected in selected wells

The stable isotope survey carried out during the second sampling campaign focused on three different water compartments: groundwater, Black Sea water, and river water. The latter compartment moved into focus since the radon survey yielded significant local radon anomalies at the river mouths of Achkva and Chakvi River (as discussed above). Therefore, water from the discharging rivers has to be considered as a potential source for radon in the coastal sea.

The isotopic composition of groundwater shows a quite significant variability throughout the study region. While δ^{18} O values vary between -11.1 and -9.2 ‰, δ^{2} H values range from -73.5 to -58.3 ‰. A very similar variation range is observed for the river water samples (Fig. 16). This observed variability is most likely due to a local impact of deep thermal waters on both groundwater and river water systems (*cf.* "Thermal Well 1" with a temperature of 34°C).



Fig. 16: Isotopic composition of groundwater and river water samples from the Kobuleti region as well as seawater samples

As mentioned above it was hypothesized as a result of the radon survey that water from the Achkva River discharging into the coastal sea and drifting north along the coast (due to the regional current dynamics) might be responsible for the radon signal detected at the Achkva river mouth (2nd sampling campaign) and north to it close to Kobuleti (1st sampling campaign). To test this hypothesis, stable

isotope measurements were conducted in a seawater profile along the coastline north of the Achkva river mouth. The profile started close to the river mouth and ended ca. 4 km north of it. All sea water samples taken from the profile showed a lower isotope signature for both oxygen and hydrogen compared to the isotopic composition of the off-shore sample. Using a two component mixing equation, the relative proportions of meteoric water in the seawater were calculated. The freshwater content close to the river mouth was up to 19 %. Farther north, even 4 km away from the river mouth, meteoric water contents between 6 and 11 % were still found (Fig. 17).



Fig. 17: Isotopic composition of coastal seawater sampled at a 4000m profile along the coastline running from the Achkva river mouth to the north

Thermal satellite data (SST - variability) and the results of the morpho-structural analysis were evaluated for the localization of potentially SGD prone areas within the Kobuleti / Batumi region. The related activities were started prior to the first sampling campaign in November 2012. As for the campaign at the Romanian coastline, the procedure was based on (1) a multi-temporal sea surface temperature (hereafter "MT-SST") and (2) a morpho-structural analysis (hereafter "MSA").

As a first step the sea surface temperature (SST) from Landsat ETM+ data (path/ row 172/031) for 15 different dates between 2001 and 2011 were calculated. The recording dates vary between March and December, thus allowing a subdivision in a hydrological winter (November until March – 7 SST images) and a summer (April until October – 8 SST images) investigation period. Fig.18 displays the winter image. For each of the periods the standard deviation per pixel of the period-corresponding SST images were calculated in order to investigate SST variability over time. Small standard deviations represent a steady spatial-temporal influx that stabilizes the SST within the proximal area off the discharge location and allow a qualitative localization of potential freshwater discharge locations. The origin of the discharge (groundwater or surface water) can however not be differentiated solely from MT-SST data.

For morpho-strucutral analysis (MSA) along the Georgian Black Sea shoreline 12 tiles of the ASTER Global Digital Elevation Model (ASTER GDEM) were processed. Each tile has a spatial dimension of 1-by-1-degree (3601 by 3601 pixel). Individual datasets were previously merged in a GIS environment. The data processing necessitates several steps before hirarichal flow accumulation stream segments can be achieved. Here the spatial analysis of topographic stream flow directions constitutes the most sensitive part, which is based on the established D8 algorithm for resolving

topographic gradients and directions. With respect to previously assigned stream strahler orders, respective stream segments and related sub-basins are extracted. Numerous stream lines of strahler order 4 and less were identified along the entire Georgian Black Sea coastline. Their intersection with the shoreline gives an indication of potentially occurring discharge of meteoric water (including SGD) that is driven by natural water drainage from the terrestrial hinterland towards the shoreline. Here, hirarichal flow accumulation stream segments are related to preferential flow paths along morphological depressions, lithostratigraphic contacts of different hydrogeological units, geological structural elements or fracture zones.

Since both remote sensing based approaches (MT-SST & MSA) can be applied completely independent from each other, they allow mutual verification. Certain aspects, such as known river mouths, can be taken as supplementary information for an approximate origin indication from the terrestrial perspective. A final differentiation between surface water and groundwater is only possible through on-site hydrochemical measurements using e.g. natural radioactive isotopes and stable isotopes as discussed above.

The results obtained from MT-SST and MSA provide six potential study areas (A-F in Fig.8) along the Georgian / Turkey Black Sea coastline, where small SST standard deviation and the existence of hirarichal flow accumulation segments indicate potential freshwater discharge sites. Upon the agreement with the Georgian project partner we focused on study area C as it represents the most populated and touristic relevant part of the Georgian coast.



Fig. 18: Large scale screening prior to the first sampling campaign at the example of the winter investigation – insets A-F show potential freshwater discharge sites based on the result of MT-SST and MSA; area C was chosen as study area for on-site measurements

Fig. 19 shows the result for the MT-SST and MSA in comparison to the radon results discussed above. For clarification we indicate potential discharge sites with the letters A, B and C. During the 1st sampling campaign (Nov. 2012) significantly elevated radon concentrations were observed at two sites, A and B. Both MT-SST and MSA do also indicate freshwater discharge at location A but with a less pronounced extent than the radon data. For site B it is similar. MSA and radon result match spatially, while the MT-SST indication is shifted towards the south. It is interesting and noteworthy to mention that during the 2nd sampling campaign (May 2013) the elevated radon concentrations appear also shifted towards the south. The MT-SST indication apparently outlines the centre point of this fluctuation.

The results of the winter MT- SST investigation and the 2^{nd} radon campaign (May 2013) at site A reveal that both results match in terms of location and extent along the coastline. Elevated radon values start exactly at the northern end where low standard deviation values of the MT-SST of <2.8°C indicate freshwater discharge. Radon values maintain elevated over a distance of about 1 km. Over the same distance low SST standard deviations are present backing the interpretation of the radon results.



Fig. 19: Comparison of the multi-temporal / geomorphological analysis results and radon concentrations [in Bq/m^3] along a North \rightarrow South section of the Georgian Black Sea shoreline of study area C: campaign 11/2012 (left) and 05/2013 (right) - note that solid white lines represent the hirarichal flow accumulation stream segments and solid blue lines indicate the location and courses of surface waters

The only location where radon values show elevated concentrations and hence indicate freshwater discharge (SGD) while standard deviation values from the MT-SST show no clear signal (about 3.1°C) is at site C. As mentioned above, the elevated radon concentrations detected over that minor stretch of coastline are in accordance with the very high radon concentrations found in "Well 2"

located close to the coast in this area (30 kBq/m³). The radon pattern indicates a small discharge site that is detected by the radon measurements but is too insignificant to be detected by satellite-based MT SST analysis. The presence of an identified small stream line segment at site C confirms that hypothesis.

Concluding it can be stated that MSA and MT-SST spatially outline identical potential freshwater discharge locations (as it could also be shown for the Romanian coast). This holds true for the on-site radon measurements for all sites except for site C. Thus, the synergy of MT-SST, MSA and on-site tracer analyses appear to allow the most complete picture related to freshwater discharge into the coastal sea. The approach does allow not only temporal snapshots from on-site measurements but also the monitoring of long-term situations.

2.4 Final Meeting

The final meeting was held March 4th to 7th at the HCMR institute in Anavyssos, Greece (instead of the UFZ in Leipzig, German, as originally planned). All project partners agreed upon this location since it allowed 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.

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

3 Control of Success

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); their sub-project ended as originally planned in December 2012, which did not allow them to participate in the final meeting and to consider the results of the second campaign in Georgia in their

final report. The results of the Romanian, Georgian and Greece colleagues are also available in their respective final reports.

Other changes of plan were mainly due to logistical "teething troubles" during the beginning of the project 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 survey.

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.

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 unexpectedly from third parties during the course of the project that interfered with the project or were of greater relevance for its execution.

As it can be assessed, 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 helped to improve the SGD related methodological repertoire and to gain international experience for each of the partner institutes. Thus, the respective participation had major positive impact on the individual research groups significantly improving their prospects in the fields of academia and industry.