Proposal for a SCOR Working Group on Subterranean Estuaries

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Abstract

Situated at the boundary between the land and sea, coastal aquifers are one of the most under-studied interfaces in earth science. Recent studies have revealed that mixing between meteoric and marine groundwater in a coastal aquifer sets up an important reaction zone, characterized by strong physical and chemical gradients. This zone, termed the "subterranean estuary" (STE), may strongly influence the oceanic cycling of trace elements and attenuate land-derived anthropogenic contaminants (e.g., nutrients, trace metals). While much research has been conducted on quantifying rates of groundwater discharge to coastal waters (submarine groundwater discharge, SGD), there is significantly less understanding of the functioning of STEs and the extent to which they alter the chemical composition of SGD. However, this knowledge is critical in order to predict contaminant and natural solute loading to coastal waters via SGD and the impact of SGD on local, regional, and global metal, nutrient, and carbon budgets. It has become evident that STEs are complex and dynamic systems with their functioning controlled by interacting biogeochemical, microbial and groundwater flow processes. This working group will bring together an interdisciplinary team of international experts to integrate knowledge of these interacting processes, which have to date mostly been considered in isolation. The main outcomes of this group will be (i) a consolidation of existing knowledge on STEs and identification of priority research needs via a review paper, (ii) development of a classification system for STEs, and (iii) interdisciplinary process studies at 1-2 field sites and a companion journal special issue.

Rationale

Groundwater is often a dominant pathway for the transport of nutrients into the coastal zone in areas where increases in human population within coastal watersheds has led to significant groundwater contamination. With 75% of the world's population expected to live within 35 miles of a coastline by 2020, it is vitally important that we understand how anthropogenic contamination is transformed and attenuated in the environment as it is transported from land to the ocean. Recent studies have shown that mixing of meteoric and marine groundwater in subterranean estuaries (STEs) has the potential to reduce nutrient loading via groundwater through nutrient removal processes such as denitrification and phosphate sorption onto mineral surfaces. While mixing and contaminant transformation processes in surface estuaries are well studied and quantified, they remain poorly quantified for STEs, their underground equivalent.

Of the studies that consider groundwater as a source or sink in ocean trace element and isotope budgets, few consider that the meteoric groundwater endmember may be reworked during passage through the STE. Such changes may alter our understanding of the residence time of key elements in the ocean and by extension their use as tracers of paleo-ocean chemistry. This particular STE research focus is of special interest to the International GEOTRACES effort, a global program interested in a better understanding of sources and sinks of trace elements and isotopes in the ocean.

While the biogeochemistry, ecology, and functioning of surface estuaries has been extensively studied, STEs are only beginning to be explored. When the study of STEs formally began approximately 10 years ago (Moore, 1999), the main motivation was to understand chemical cycling in these environments; most previous work focused on one aspect of STEs depending on the specific expertise of the research team. However, the community has come to realize that STEs are dynamic systems where the fate and transport of chemicals are controlled by complex interactions between geochemical, microbial and (groundwater and seawater) hydrological processes and the physical characteristics of the subsurface. Hence, the timing is ideal to organize a team of interdisciplinary scientists within the framework of a SCOR working group. Given the broad interest in STEs, we have commitments from 19 international experts in this field to serve as Full and Associate members on the working group.

Scientific Background

Fresh water flowing from aquifers into the sea may discharge from a seepage face, a narrow zone of sediment near the intertidal zone, or flow directly into estuaries or the continental shelf as submarine groundwater discharge (SGD). Fluctuations in coastal water levels (e.g., waves, tides) and the density difference between fresh groundwater and seawater leads to significant recirculation of saline water through the aquifer (Figure 1). The hydraulic gradient that drives freshwater toward the sea also drives the recirculating saline water back to sea. The fresh groundwater and the saline water mix prior to discharge producing a gradient in groundwater salinity from land to sea. Hence, SGD often consists of a substantial amount of brackish and saline water. The mixing of the fresh and

saline water in the aquifer creates an important reaction zone that alters the chemical composition of the discharging fluid. This zone is referred to as a subterranean estuary (STE, Moore 1999). In contrast to surface estuaries, STE are usually characterized by longer residence times, stronger particle-water interactions, and lower dissolved oxygen.

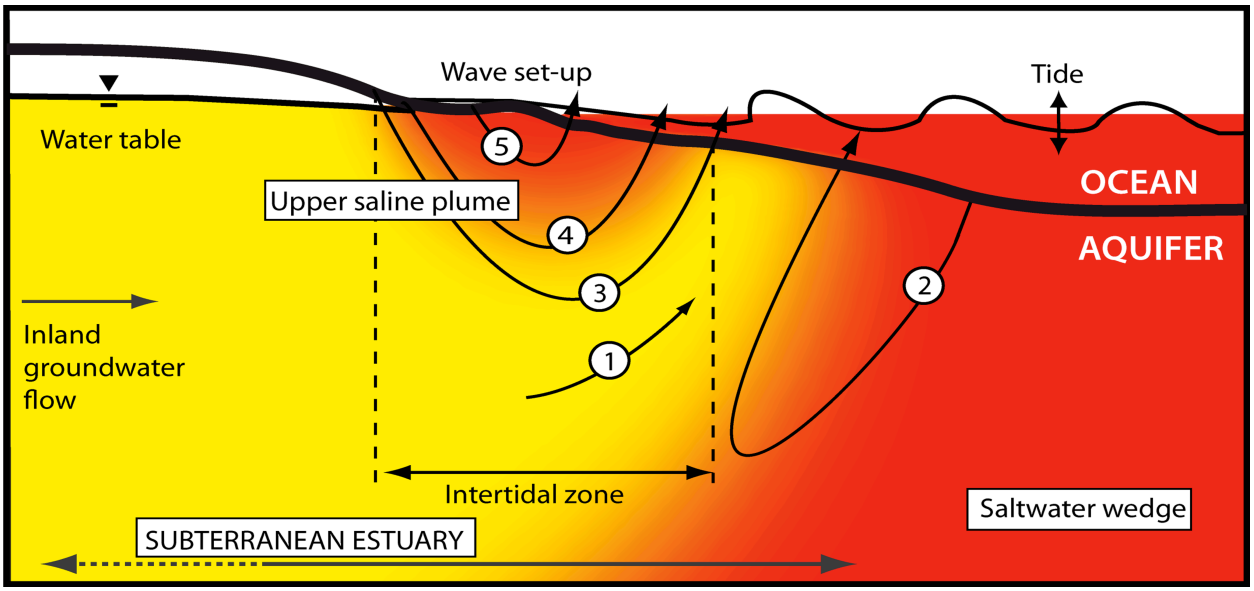

Figure 1. Conceptual view of STEs including major nearshore flow processes: freshwater discharge, (2) density-driven recirculation, (3) wave-set up driven recirculation, (4) tide-induced recirculation, and (5) recirculation driven by wave-bedform interactions. The degree of shading indicates a typical salinity distribution in a subterranean estuary subject to oceanic forcing. The flow processes set up strong physical and chemical gradients that significantly alter the chemical composition of groundwater and recirculating water prior to discharge into the sea.

In coastal watersheds with soils of high hydraulic conductivity and permeable coastal sediments, groundwater-derived anthropogenic nitrogen can be a major source of pollution to coastal waters. It is not unusual to observe dissolved inorganic nitrogen (DIN) concentrations in groundwater 100-1,000 times greater than in the receiving waters (Slomp and van Cappellen, 2004). Advection through STEs, driven by fluctuations in coastal water levels and the regional groundwater hydraulic gradient, accelerates biogeochemical activity within the sediments. The recirculating saline water also introduces particulate matter into the system, which serves as a "bio reactor" for many metabolic processes. Understanding metabolic processes in the STE and associated SGD fluxes into the coastal ocean may help to reconcile large imbalances in the current global budgets of metals, carbon, and nitrogen.

The net effect of STE on land-derived nitrogen fluxes to coastal waters depends on a balance between the sources and sinks of reactive nitrogen within STEs. While organic matter mineralization associated with tidal pumping may dramatically increase the fluxes of land-derived nitrogen in some STEs (Santos et al., 2009), denitrification may attenuate terrestrial loads in other systems (Kroeger and Charette, 2008). In addition to

denitrification, anaerobic ammonium oxidation (anammox) is a microbial process that may be so significant as to require recalculation of existing global N budgets (Dalsgaard et al. 2003, Kuypers et al. 2003). Anammox has not been fully investigated in these environments, yet preliminary evidence suggests that it may be an important pathway for dinitrogen gas formation (Kroeger and Charette, 2008).

Several recent studies provide evidence that biogeochemical reactions can lead to the large-scale enrichment of trace elements and isotopes in STEs and subsequently in the coastal ocean via SGD. For example, Shaw et al. (1998) and Windom and Niencheski (2003) reported groundwater barium (Ba) enrichments at intermediate salinities that far exceeded the background concentration in coastal waters. These observations were consistent with similar studies suggesting that groundwater is a major source of Ba (and its sister element radium [Ra]) to coastal waters (Moore, 1997; Duncan and Shaw, 2003). In a study of strontium (Sr) in the Ganges-Brahmaputra (G-B) delta, Basu et al. (2001) concluded that SGD was a potential source of strontium to the oceans equal in magnitude to the dissolved Sr concentrations carried to the oceans by the G-B river water. Their estimate of SGD-derived Sr was enough to have a major effect on the Sr isotope composition of seawater, yet the role of Sr transformations in the STE was not considered.

Heavy metals of anthropogenic origin have been a recent focus of study in the STE. Beck et al. (2010) found substantial enrichments relative to surface water of cobalt and nickel in the mixing zone of a Long Island (USA) STE, which they attributed to the a redox-driven release with manganese (hydr)oxides. Bone et al. (2007) and Black et al., (2009) reported that mercury and monomethylmercury are actively cycled in the STE, which may exacerbate the impact of this land-derived contaminant in groundwater fed estuaries.

The mixing of fresh and saline water in aquifers has also been shown to remove dissolved materials from coastal waters. For example, Charette and Sholkovitz (2002) reported an accumulation of iron (hydr)oxides in the STE that were accumulating fresh and saline groundwater-derived phosphorous. Both Windom and Niencheski (2003) and Duncan and Shaw (2003) observed significant uranium (U) depletion in STEs, which they attributed to removal under anoxic conditions during seawater recirculation through the aquifer. Charette and Sholkovitz (2006) showed that this removal process was strong enough to create a U deficit in the surface waters of a coastal bay. These observations have led to additional uncertainty in the marine U budget that require a reevaluation of U and U isotopes as paleooceanographic tools. STEs are also important for both Fe and Mn cycling. Dellwig et al (2007) observed that as a result STEs may cause the periodic enrichment and depletion of Mo in coastal environments.

Numerical model simulations are necessary to provide insight into the controlling processes and functioning of STEs and to translate local field understanding to a wide range of coastal conditions. Numerical variable-density groundwater flow models have been developed, in combination with field experiments, to understand the flow paths and the intensity of fresh-saline water mixing in STEs. Studies have identified that key factors that control the way coastal water levels and the saline-groundwater density contrast

affect the extent of mixing and the configuration of the STE for sandy coastal aquifers (Michael et al. 2005; Xin et al., 2010; Robinson et al., 2007).

Reactive groundwater transport models have been used to further assess the impact of the flow and mixing processes in STEs on the transport of groundwater-derived anthropogenic contaminants. Studies focused on the transport of nutrients and aerobic biodegradable organic compounds (e.g., BTEX) have demonstrated considerable attenuation of contaminants in STEs (Robinson et al., 2009; Spiteri et al., 2008a,b). In order to improve predictions, however, numerical models must be validated with field studies with the reaction networks modified and extended as needed to incorporate real world geochemical, microbial and groundwater complexities. This requires strong interdisciplinary collaboration between field researchers (geochemists, geophysicists, microbiologists, hydrogeologists) and numerical modelers.

Statement of Work/Terms of Reference

Our proposed working group ideally fits the SCOR mission of bringing together scientists of diverse expertise to solve a problem in ocean science that is hindering research. Two previously funded working groups had complementary themes but studied different problems to those outlined here. SCOR WG112 on Submarine Groundwater Discharge addressed the need for better quantification techniques of land-ocean fluid exchange. SCOR WG114 on Permeable Sediments studied the dynamics of flow and biogeochemical reactions in marine dominated coarse-grained sediments. In our case, we contend that our field has an incomplete knowledge of the driving forces of water recirculation and the groundwater flow and mixing dynamics within contrasting STE environments. This in turn has hindered our knowledge of the subsurface fluid chemical reactions (salinity, pH, oxidation-reduction) and whether or not dissolved constituents may be mobilized to the water column or sequestered in the STE. The answers to these questions are required to address local scale issues such coastal water quality and global scale problems such as trace element mass balances. To this end the proposed working group would engage in the following activities:

Task: Summarize past results on STEs including experimental and modeling findings and based on this information develop a list of key questions that require focused study in the future.
Deliverable: The related field of SGD has been covered in a large number of overview papers (e.g., Burnett et al., 2003, 2006; Taniguchi et al., 2002). To date there has not been such a synthesis on STEs. As an outcome of our first year meeting as a SCOR working group, we propose to write a review paper for publication in "Progress in Oceanography" or a similar journal.

Task: Development of a STE classification system.
Deliverable: There exists a logical and well organized classification system for surface estuaries (e.g. Durr et al., 2011). In general, there are two categories of classification: by geology (e.g. fjord-type) and by stratification/extent of fresh-salt water mixing (e.g., stratified, partially stratified and well-mixed). We aim to develop a similar system for STEs

along the lines of that proposed by Slomp and van Cappellen (2004) and Robinson et al (2007). This will be disseminated on our working group website and as a peer-reviewed publication arising from our year 2 meeting.

Task: Conduct 1-2 process studies at locations mutually agreed upon by the committee.
***Deliverable*:** The first and second year meetings will provide the opportunity for members to identify and prioritize the major uncertainties and questions regarding the functioning of STEs. As a group we will seek external funding to conduct up to two process studies that will take place at contrasting STEs (according to our new classification system). These studies will require combined geochemical, hydrological and microbiological expertise and have both a field and numerical modeling component. The results will be published in a Special Issue of *Biogeosciences* (or similar open-access journal). This embedding of process studies within working group activities was used previously by SCOR WG112 on Submarine Groundwater Discharge. As most of our members are actively working in this research area, we do not feel that significant additional resources beyond the travel funds provided by SCOR will be required to carry out such a project.

Three working group meetings will be organized over a three-year period and will be held in association with international meetings. The first meeting will occur in spring 2012, likely in conjunction with the annual European Geophysical Union meeting (Vienna). At this meeting the working group will outline how the terms of reference will be met, including delegation of tasks, and will also identify funding sources and sites for collaborative process field studies. Each group member will also present their research work. This will lead to discussion on key research needs for advancing understanding of STEs and detailed planning for a review publication. The group will also review existing modeling approaches, their limitations and outline the needs for future code development, including data requirements. Finally, we will discuss the uncertainties and required information for developing a classification system for STEs.

A second meeting will be convened approximately one year following the initial meeting. It is proposed that this meeting will be held in 2013, possibly in association with the American Society of Limnology and Oceanography's bi-annual winter meeting. The location, however, will be finalized at the first working group meeting. In addition to the working group meeting, a Special Session on STEs will be organized by the working group members.

The final meeting will take place approximately three years following the initial meeting and will enable the working group to complete publications and obtain input for the Working Group's final report. The location and timing of this meeting will be finalized at the first meeting of the working group and may be conducted in concert with one of the proposed process field studies.

Working Group Membership: Our working group membership will consist of 10 Full Members and 9 Associate Members all with expertise or interest in this field (Tables 1 and 2). The Full Members include those with expertise in geochemistry, geophysics, microbiology, and groundwater flow dynamics and with field and/or numerical modeling

expertise. In addition to broad international representation, our membership includes a balance of junior and senior scientists. Co-chair M. Charette is a geochemist and has been involved in the study of subterranean estuaries since the landmark W.S. Moore paper in 1999. Co-chair C. Robinson has expertise in groundwater flow dynamics and numerical modeling and has published a series of well-cited papers on subterranean estuaries that arose from her Ph.D. in 2007.

Table 1. Full Members of the SCOR Working Group on Subterranean Estuaries.

Member	Affiliation	Expertise
Matt Charette (co-chair)	Woods Hole Oceanographic Institution, USA	Biogeochemistry of trace metals and nutrients
Clare Robinson (co-chair)	University of Western Ontario, Canada	Numerical modeling and groundwater flow dynamics
Hans Brumsack	Oldenburg University, Germany	Biogeochemistry of trace metals and nutrients
Jorge Herrera-Silveira	University of Merida, Mexico	Nutrient cycling and biological impacts
Guebum Kim	Seoul National University, Korea	Radionuclides and nutrient cycling
Jose Marcus Godoy	Pontíficia Universidade Católica do Rio de Janeiro, Brazil	Radionuclides
Vincent Post	Flinders University, Australia	Reactive transport modeling
Alyson Santoro	University of Maryland, USA	Microbiology and nitrogen cycling
Thomas Stieglitz	James Cook University, Australia	Geophysics
Yishai Weinstein	Hebrew University of Jerusalem, Israel	Radionuclides and nutrient cycling

Table 2. Associate Members of the SCOR Working Group on Subterranean Estuaries.

Member	Affiliation	Expertise
Pierre Anschutz	Université Bordeaux, France	Biogeochemistry and nutrient cycling
Aaron Beck	Virginia Institute of Marine Science, USA	Trace metal biogechemistry
Jaye Cable	University of North Carolina – Chapel Hill, USA	Biogeochemistry and nutrient cycling
Jordi Garcia-Orellana	Universitat Autònoma de Barcelona, Spain	Radionuclides
Kevin Kroeger	U.S. Geological Survey, USA	Biogeochemistry and nutrient cycling
Adina Paytan	UC Santa Cruz, USA	Biogeochemistry and nutrient cycling
Richard Peterson	Coastal Carolina University, USA	Radionuclides and geophysics
Isaac Santos	Southern Cross University, Australia	Carbon cycling
Caroline Slomp	Utrecht University, The Netherlands	Biogeochemistry, nutrient cycling, and modeling

References

Basu, A.R., Jacobsen, S.B., Poreda, R.J., Dowling, C.B. and Aggarwal, P.K. 2001. Large groundwater strontium flux to the oceans from the Bengal Basin and the marine strontium isotope record. *Science*, 293:1470-1473.

Beck, A.J., J.K. Cochran, S.A. Sañudo-Wilhelmy. 2010. The distribution and speciation of dissolved trace metals in a shallow subterranean estuary. *Marine Chemistry*, 121: 145–156.

Black, F. J., A. Paytan, K. L. Knee, N. De Sieyes, P. Ganguli, E. Gray, A. R. Felgal. 2009. Submarine Groundwater Discharge of Total Mercury and Monomethylmercury to Central California Coastal Waters. *Environmental Science & Technology*, 43: 5652-5659.

Bone, S.E., M.A. Charette, C.H. Lamborg, and M.E. Gonneea. 2007. Has submarine groundwater discharge been overlooked as a source of mercury to coastal waters? *Environmental Science and Technology*, 41: 3090-3095.

Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdofer, J.A., Oliveira, J., Ozyurt, N., Povinec, P., Prititera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M. and Turner, J.V., 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Science of the Total Environment,* 367: 498-543.

Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W.S. and Taniguchi, M., 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry,* 66: 3-33.

Charette, M.A. and Sholkovitz, E.R., 2002. Oxidative precipitation of groundwater-derived ferrous iron in the subterranean estuary of a coastal bay. *Geophysical Research Letters*, 29: 2001GL014512.

Charette, M.A. and Sholkovitz, E.R., 2006. Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. *Geochimica et Cosmochimica Acta*, 70: 811-826.

Dalsgaard, T., Canfield, D.E., Petersen, J., Thamdrup, B. and Acuna-Gonzalez, J. 2003. N_2 production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. *Nature*, 422:606-608.

Dellwig, O., Beck, M., Lemke A., Lunau, M., Kolditz, K., Schnetger B., Brumsack., H., 2007. Non-conservative behavior of molybdenum in coastal waters: Coupling geochemical, biological, and sedimentological processes, *Geochimica et Cosmochimica Acta,* 71: 2745-2761.

Duncan, T. and Shaw, T.J., 2003. The mobility of rare earth elements and redox sensitive elements in the groundwater/seawater mixing zone of a shallow coastal aquifer. *Aquatic Geochemistry*, 9: 233-255.

Dürr, H., G. Laruelle, C. van Kempen, C. Slomp, M. Meybeck, and H. Middelkoop. 2011. Worldwide typology of nearshore coastal systems: defining the estuarine filter of river inputs to the oceans. *Estuaries and Coasts*, doi:10.1007/s12237-011-9381.

Kroeger, K.D., and M.A. Charette. 2008. Nitrogen biogeochemistry of submarine groundwater discharge. *Limnology and Oceanography*, 53: 1025-1039.

Kuypers, M.M.M., Sliekers, A.O., Lavik, G., Schmid, M., Jorgensen, B.B., Kuenen, J.G., Damste, J.S.S., Strous, M. and Jetten, M.S.M. 2003. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature*, 422: 608-611.

Michael, H.A., Mulligan, A.E. and Harvey, C.F., 2005. Seasonal oscillations in water exchange between aquifers and the coastal ocean. *Nature,* 436: 1145-1148.

Moore, W.S., 1997. High fluxes of radium and barium from the mouth of the Ganges-Brahmaputra River during low river discharge suggest a large groundwater source. *Earth and Planetary Science Letters*, 150: 141-150.

Moore, W.S., 1999. The subterranean estuary: a reaction zone of ground water and sea water. *Marine Chemistry*, 65: 111-125.

Robinson, C., Brovelli, A., Barry, D.A. and Li, L., 2009. Tidal influence on BTEX biodegradation in sandy coastal aquifers. *Advances in Water Resources,* 32: 16–28.

Robinson, C., Li, L. and Barry, D.A., 2007. Effect of tidal forcing on a subterranean estuary. *Advances in Water Resources,* 30, 851-865.

Santos, I. R.; Burnett, W. C.; Dittmar, T.; Suryaputra, I. G. N. A.; Chanton, J. 2009. Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary. *Geochimica et Cosmochimica Acta*, 73: 1325-1339.

Shaw T. M., Moore W. S., Kloepfer J., and Sochaski M. 1998. The flux of barium to the coastal waters of the southeastern USA: the importance of submarine groundwater discharge. *Geochimica et Cosmochimica Acta*, 62: 3047-3054.

Slomp, C. P.; Van Cappellen, P., 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology*, 295: 64-86.

Spiteri, C., Slomp, C., Tuncay, K. and Meile, C., 2008a. Modeling biogeochemical processes in subterranean estuaries: Effect of flow dynamics and redox conditions on submarine groundwater discharge of nutrients. *Water Resources Research,* 44: W04701.

Spiteri, C., Slomp, C.P., Charette, M.A., Tuncay, K. and Meile, C., 2008b. Flow and nutrient dynamics in a subterranean estuary (Waquoit Bay, MA, USA): Field data and reactive transport modeling, *Geochimica et Cosmochimica Acta,* 72: 3398-3412.

Taniguchi, M., Burnett, W.C., Cable, J.E. and Turner, J.V., 2002. Investigation of submarine groundwater discharge, *Hydrological Processes,* 16: 2115-2129.

Windom, H. and Niencheski, F., 2003. Biogeochemical processes in a freshwater-seawater mixing zone in permeable sediments along the coast of Southern Brazil. *Marine Chemistry*, 83: 121-130.

Xin, P., Robinson, C., Li, L., Barry, D.A. and Bakhtyar, R., 2010. Effects of wave forcing on a subterranean estuary, *Advances in Water Resources,* 46: W12505.