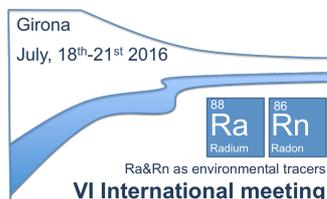




6th International Ra-Rn workshop

BOOK OF ABSTRACTS



6th International Ra-Rn workshop

SGD/COASTAL PROCESSES

T1.1 Solute transport into the Jiulong River estuary (China) via pore water exchange and submarine groundwater discharge: New insights from $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium

Qingquan Hong^{a, b}, Pinghe Cai^{a, b*}, Xiangming Shi^{a, b}, Qing Li^{a, b}, Guizhi Wang^{a, b}

^a State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, P. R. China

^b College of Ocean and Earth Sciences, Xiamen University, Xiamen 361005, P. R. China

Pore water exchange (PEX) and submarine groundwater discharge (SGD) input represent two mechanisms for solute transport from the seabed into the coastal ocean. However, the relative importance of the two mechanisms remains to be assessed. In this study, we utilize the newly developed $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach to quantify PEX fluxes of ^{224}Ra , dissolved inorganic carbon (DIC) and nutrients into the Jiulong River estuary, China. We demonstrated that PEX fluxes of ^{224}Ra were highly variable, both temporally and spatially, and can change by 1–2 orders of magnitude.

Moreover, we demonstrated that among the small-scale pore water exchange processes, irrigation was predominantly responsible for transport of ^{224}Ra across the sediment-water interface. Based on the derived benthic flux estimates of ^{224}Ra and the ^{224}Ra mass balance in the water column, we estimated the total flux of ^{224}Ra induced by PEX processes and the concomitant SGD fluxes of ^{224}Ra . By multiplying the DIC (nutrients)/ ^{224}Ra ratios, the fluxes of DIC and nutrients by SGD and PEX were determined. The results suggest that PEX represents an important mechanism of solute transport into an estuary. In addition, its role may be comparable to the river flux and SGD input. As such, this mechanism must be taken into account when constructing the budget of a dissolved component (like DIC, nutrients, Fe, and Mn) in the coastal ocean.

T1.2 A new heat tracer method to complement Ra-Rn methods for porewater transport

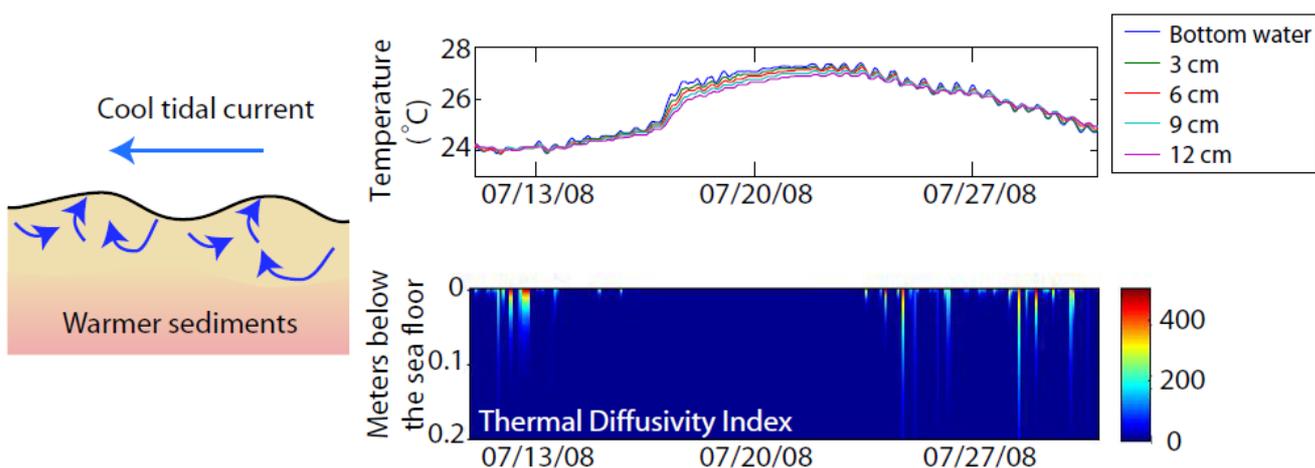
Alicia M. Wilson¹ and William Savidge²

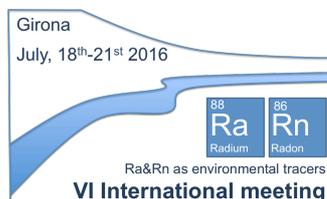
¹School of the Earth, Ocean and Environment, University of South Carolina, Columbia South Carolina 29208, U.S.A.

²Skidaway Institute of Oceanography, University of Georgia, Savannah, Georgia 31411, U.S.A.

Heat tracers complement Ra and Rn tracers in studies of submarine groundwater discharge (SGD) by providing an inexpensive way to map and monitor groundwater flow below the sediment-water interface. Here we focus on rapid exchange of seawater and porewater in shallow seafloor sediments. This flow, which will be referred to here as hydrodynamic exchange, is driven by such processes as flow of currents over ripples, the passage of waves, and thermal instability. Hydrodynamic exchange has important biogeochemical implications but has been very difficult to monitor in field settings. Here heat is used to map the timing, depth, and intensity of hydrodynamic exchange below the sediment-water interface.

We developed a new model, the Model for Advanced Thermal Time Series Inversion (MATTSI), to map hydrodynamic exchange below the sediment-water interface by inverting thermal time-series observations. The model uses an effective thermal dispersion term to emulate 3-D hydrodynamic exchange in a 1-D model. The effective dispersion declines exponentially below the sediment water interface. Application of the model to a synthetic dataset and two field datasets from 50 km offshore of Georgia (USA) shows that exchange events can be clearly identified from thermal data, with tidal periodicity that suggests that exchange is triggered by a combination of relatively high current velocity and thermal instability. Additional data from 5-20 km offshore of Charleston, SC, USA, suggests sustained periods of hydrodynamic exchange during spring of 2015. Model results also detect long-term flow in some locations. These heat tracer techniques indicate high priority sampling zones and provide a way to connect Ra and Rn signals detected in surface waters to groundwater flow processes in the subsurface.





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T1.3 Why are concentrations of NH₄, PO₄, DIC, and DOC often correlated with ²²⁶Ra and Ba in subterranean estuaries?

Willard S. Moore,^{1*} and Samantha Joye,²

¹Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208.

²Department of Marine Sciences, University of Georgia, Athens, GA 30602.

*Corresponding author. E-mail: moore@geol.sc.edu

In coastal aquifers dominated by freshwater, dissolved oxygen is the primary oxidizing agent for organic matter. Thus, concentrations of NH₄, PO₄, DIC, and DOC released from oxidation are limited by the solubility of dissolved oxygen. When O₂ is exhausted NH₄, PO₄, DIC, and DOC can only increase by less efficient processes such as coupled metal reduction and fermentation. However, the subterranean estuary with its abundance of sulfate ion has the power to oxidize far more organic matter and increase concentrations of NH₄, PO₄, DIC, and DOC up to 200 times that of freshwater systems. This is because seawater contains about 100 times higher concentrations of SO₄ than O₂ and because SO₄ can oxidize twice as much C compared to O₂. In systems dominated by seawater, the utilization of SO₄ can be calculated by subtracting the predicted SO₄ concentration based on salinity from the measured SO₄. Here we assume seawater entered the system with the oceanic SO₄/Salinity ratio and is the only source of SO₄. We call the depletion of SO₄ “del SO₄”. In many different subterranean estuaries del SO₄ is inversely correlated to increases in NH₄, PO₄, DIC, and DOC concentrations. In some systems del SO₄ is also inversely correlated to ²²⁶Ra and Ba concentrations. Generally ²²⁸Ra does not follow the same pattern; regeneration and desorption control its distribution. Here we will discuss several systems including the Okatee estuary in South Carolina, the Wadden Sea tidal flats in Germany, and a section of the Potomac subterranean estuary, a 45,000 km² system beneath the US east coast. We see similar patterns of enrichment of NH₄, PO₄, DIC, DOC, ²²⁶Ra, and Ba with del sulfate in some, but not all, system. Systems enriched in these components from anthropogenic sources will not necessarily follow these patterns.

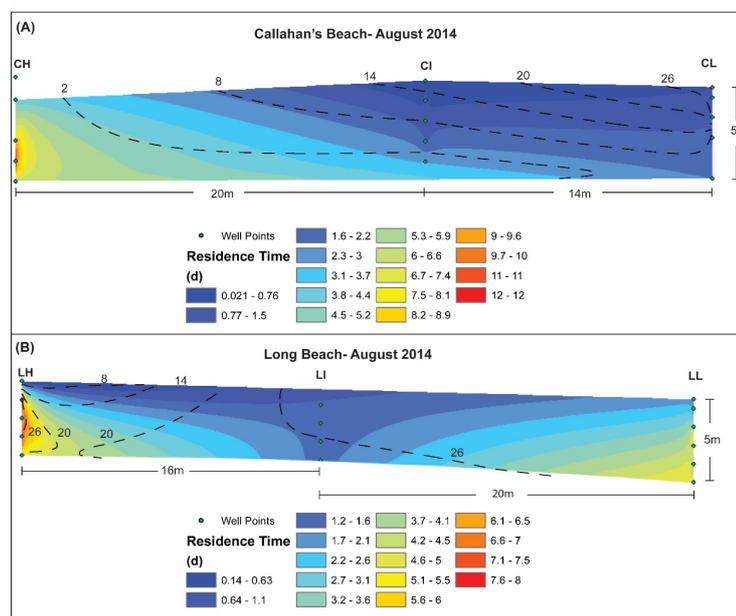
T1.4 Residence time of pore water in the subterranean estuary in Smithtown Bay

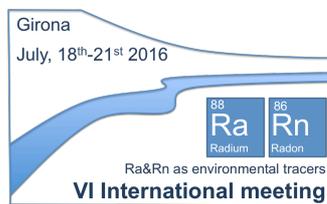
Joseph Tamborski, J. Kirk Cochran, Henry Bokuniewicz

Stony Brook University, Stony Brook NY 11720

The subterranean estuary (STE) of Smithtown Bay (Long Island Sound) was investigated at a coastal bluff and a barrier beach site, over 12 months between 2014 and 2015. Intertidal pore water profiles revealed distinct geochemical differences between the two sites that were driven by the primary hydrogeologic forcing mechanisms. The coastal bluff site was dominated by a large hydraulic gradient that drove fresh groundwater discharge, while the barrier beach site was physically controlled by tidal forcing mechanisms, where pore waters were saline. These forcing mechanisms resulted in notably different pore water radionuclide (^{222}Rn , $^{223,224,226,228}\text{Ra}$) and trace metal (Fe, Mn, Ba) distributions in the STE. Temporally variable radionuclide and trace metal concentrations suggest that the barrier beach STE was naturally transient and was not in steady-state, while the coastal bluff STE was in steady-state. Twelve sediment core incubation experiments were used to estimate the equilibrium activity of ^{224}Ra and ^{222}Rn within the coastal aquifer. A one-dimensional advective transport model was developed to estimate the residence time of circulated seawater within the STE using measured radionuclide activities. There are inherent uncertainties within the model, set by the radioactivity of deep groundwater that has mixed with the circulated seawater, the initial radioactivity of seawater that has infiltrated the coastal aquifer and the radionuclide production rate. The method provided a quantitative understanding, subject to simplifying assumptions, of pore water residence times within the STE. Residence times generally increased with depth from 0.1 – 15 d and were greater in the low tide well of the barrier beach (4.9 ± 3.8 d) compared to the coastal bluff (1.1 ± 0.7 d). Variable pore water residence times within the subterranean estuary may have a profound effect on the cycling of carbon, nutrient and trace metal fluxes to the coastal ocean.

Figure 1. Estimated pore water residence times for a coastal bluff (Callahan's Beach; A) and a barrier beach site (Long Beach; B) during August 2014. Multi-level well points are represented by green circles. Interpolated salinity contours are represented by black dashed lines, with values labeled.





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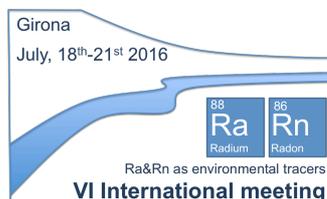
T1.5 Groundwater discharge at the outflow face of a microtidal sandy beach

Chaillou Gwénèlle¹, Lemay-Borduas Frédérique¹, Couturier Mathilde¹ and Biehler Antoine¹

¹Canada Research Chair in geochemistry of coastal hydrogeosystems and Département Biologie. Chimie. Géographie. Université du Québec à Rimouski. 300 Allée des Ursulines. Rimouski. QC. G5L 3A1. Canada

At the nexus of marine and freshwater environments, intertidal and nearshore zone of beach aquifers play a key role at the land-sea interface. The biogeochemical reactivity of this zone is closely linked to physical flow and solute transport. Radon (²²²Rn) is an effective qualitative and quantitative groundwater tracer because it is typically present in elevated concentrations in groundwater relative to the coastal seawater, regardless of fluid origin or composition. We will present ²²²Rn surveys performed in beach groundwater and in seawater in the front of the beach (surface ~ 0.139km²). The objective was to characterize the hydrodynamics dynamics beneath the discharge zone and to estimate the associated discharge to the bay. These radio-isotope approach was coupled to water stable isotope measurements ($\delta^{18}\text{O}$, $\delta^2\text{H}$) and water table monitoring along a cross-shore beach transect. The surveys were performed in May 2013, in spring-tide conditions when tidal pumping is supposed to dominate the flow beneath the outflow face.

The vertical and horizontal distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in beach groundwater showed that fresh groundwater dominated the system. The expansion of the intertidal recirculation cell was limited despite spring-tide conditions. The dominance of groundwater was also supported by the vertical ²²²Rn activity distribution that showed a very strong gradient in the first 0.5m below the surface with activities that reached ~16000 Bq/m³ in the deep. A detailed examination of the tide propagation based on time series of water table levels revealed that tide propagated as a dynamic wave within the beach instead of a mass displacement. The recirculation cell and its associated mixing zone resulted from the vertical infiltration of seawater during the ebb flood within the unsaturated zone. This up and down movement of the water table induced upward pulses of ²²²Rn enriched deep groundwater to the surface few hours before the maximum low tide. In the front of the beach, the distribution of ²²²Rn was highly variable (0 to 50 Bq/m³). The zone was thus fragmented into three boxes which communicate with each other in terms of ²²²Rn fluxes, by flood and ebb tide. A radon-based mass balance model was used in each box and a special interest was given to the determination of ²²²Rn activity in the groundwater end-member. This approach led to shore-normal discharges ranging from 3.1 at the shore to 1.6 and 1.1 m³/m/d in the bay. The nearshore discharge agreed quite well with Darcy fluxes calculated in the outflow face and were in the same range than direct measurements previously performed in the intertidal zone of the site. The offshore fluxes, however, reflected probably deep seawater discharge, with no input of fresh groundwater.



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P1.1 Tracing point-source submarine groundwater discharge in a karst aquifer system in Maro-Cerrogordo Coastal Area (Spain) using Rn-222

Daniel Montiel¹ (dmontielmartin@crimson.ua.edu)
Natasha Dimova¹, Bartolome Andreo² and Jorge Prieto²

¹Department of Geological Sciences, University of Alabama, Tuscaloosa, AL

²Center of Hydrogeology of the University of Malaga, Malaga, Spain

Water scarcity in coastal regions of Malaga and Granada provinces (Spain) has been a problem since the 16th century, and is related to the variability and uneven distribution of rain events throughout the year. During the past three decades two main economic activities have been exacerbating the local water demand: 1) agriculture and 2) tourism. Local water supply depends mainly on groundwater extractions from Sierra Almjara aquifer unit, located along the Maro-Cerrogordo Coastal Area.

The *Sierra Almjara* aquifer unit is mainly comprised of fissured and karstified marble and it is known to be hydraulically connected to the sea. It is expected therefore, that submarine groundwater discharge (SGD) is significant part of the *Sierra Almjara* water balance. Previous studies in the area estimate that the total discharge is 6×10^6 m³/year. However, SGD has never been reliably localized nor quantified in Maro-Cerrogordo Coastal Area. This is mostly due to the local geological complexity resulting in highly heterogeneous SGD spatial distribution.

Temperature, electrical conductivity and ²²²Rn surveys have been performed in May, July and December of 2015 along the Maro-Cerrogordo Coastal Area coastline to identify areas of enhanced SGD. Two main areas of high SGD were clearly identified by all surveys: A1) Maro, and A2) Cantarriján; with significantly lower salinity (33 ppt compared to regional 35 ppt) values and elevated radon concentrations (40 and 25 dpm/L respectively). Five ²²²Rn time-series were deployed in both locations during July and December to quantify SGD fluxes. Total SGD was 1.9×10^6 m³/year at A1 in July; whereas in December SGD was 2.6×10^6 m³/year at A1 and 2.2×10^6 m³/year at A2. Based on this study, the total SGD along the Maro-Cerrogordo Coastal Area is 4.7×10^6 m³/year. It is important to be noted that all sampling campaigns were conducted during a statistically dry period and higher SGD should be expected on average in this area. Along with the two areas previously cited, SGD was also detected to be occurring as three deep submarine springs along the Cerrogordo area that will be also studied in the near future.



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P1.2 Artificial water sediment regulation scheme influences morphology, hydrodynamics and nutrient behavior in the Yellow River estuary

Bochao XU^{1,2,3}, Disong YANG^{1,2}, William C. Burnett⁴, Xiangbin Ran⁵, Zhigang YU^{1,2,3}, Maosheng GAO⁶, Shaobo DIAO⁶, Xueyan JIANG^{1,2}

¹Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

²Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China

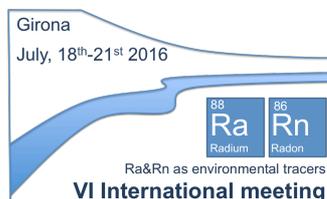
³College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

⁴Department of Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, FL 32306, USA

⁵Research Center for Marine Ecology, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China

⁶Qingdao Institute of Marine Geology, Qingdao 266071, China

Anthropogenic controls on water and sediment may play important roles in river system transformations and morphological evolution, which could further affect coastal hydrodynamics and nutrient behavior. We used geochemical tracers to evaluate the influence of the Water-Sediment Regulation Scheme (WSRS) on estuarine morphology, hydrodynamics and nutrients in the Yellow River estuary, China. We discovered that there was a newly formed small delta in the river mouth after the 2013 WSRS. This new morphologic feature altered terrestrial material distribution patterns from a single plume to a two-plume pattern within the estuary. Our results show that the WSRS significantly influenced the study area in the following ways: (1) Radium and nutrient concentrations were significantly elevated (two to four times), especially along the two river outlets. (2) Estuarine mixing was about two times stronger during WSRS than before. Average aerial mixing rates before and during WSRS were $50 \pm 26 \text{ km}^2 \cdot \text{d}^{-1}$ and $89 \pm 51 \text{ km}^2 \cdot \text{d}^{-1}$, respectively. (3) Our data is consistent with P limitation and suggest that stoichiometrically based P limitation was even more severe during WSRS. (4) All river-derived nutrients were thoroughly consumed within one to two weeks after entry to near-shore waters. (5) The extent of the area influenced by terrestrial nutrients was two to three times greater during WSRS. Human influence, such as triggered by WSRS regulations, should thus be considered when studying biogeochemical processes and nutrient budgets in situations like the Yellow River estuary.



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P1.3 Sequential variations of ^{224}Ra in coastal waters: evidence for input of SGD to the coastal zone off Da-Chia River, Taiwan

Feng-Hsin Hsu¹ and Chih-Chieh Su¹

¹Institute of Oceanography, National Taiwan University, Taipei, Taiwan

Submarine groundwater discharge (SGD) has been recognized as an important pathway for materials exchanging between land and sea. Input of SGD carries the associated nutrients, trace metals, and inorganic carbon that may make great impacts on ecosystem in the coastal zone. In Taiwan, the SGD study is rare and the intrusion of seawater in the coastal aquifer is reported in previous studies. According to the information from Hydrogeological Data Bank (Central Geological Survey, MOEA), some areas still show potentiality of SGD.

Here, we report the preliminary investigation result of SGD at the Gaomei Wildlife Conservation Area which located at the south of the Da-Chia River mouth. The study area is characterized by a great tidal range and a shallow aquifer with high groundwater recharging rate. Time-series measurement of the short-lived ^{224}Ra in surface water was done in both dry (May, 2014; December, 2014) and wet (August, 2014) seasons at a tidal flat site. It shows different trends of excess ^{224}Ra between dry and wet seasons. High excess ^{224}Ra activities (>20 dpm 100L^{-1}) occurred at high tide in dry season but at low tide in wet season. The sources of the extra excess ^{224}Ra include (1) desorption of Ra from river-bone particles due to the increasing ion strength and (2) SGD input. The plot of salinity vs. excess ^{224}Ra , showing a non-conservative curve, suggests that the high excess ^{224}Ra activities derive mainly from desorption in dry season but might from SGD input in wet season.



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P1.4 Temporal changes of ^{226}Ra , ^{228}Ra and ^{224}Ra in pore waters of an intertidal sandy beach (Truc Vert, SW France)

Sabine Schmidt¹, J. Kirk Cochran², Céline Charbonnier³, Stéphane Buan¹, Pierre Anschutz³, Pascal Lecroart³

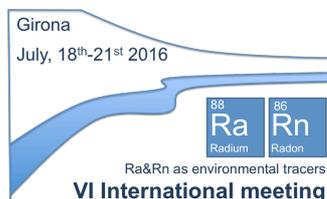
¹CNRS, EPOC, UMR 5805, F-33615 Pessac, France.

²School of Marine and Atmospheric Sciences, State University of New York, Stony Brook, USA.

³Univ. Bordeaux, EPOC, UMR 5805, F-33400 Talence, France.

The Aquitanian coast, bordering the Bay of Biscay in the North Atlantic, is a long and continuous straight sandy coastline of about 250 km, located between the Gironde and Adour estuaries. Here we present an investigation of the temporal changes in the radium triplet (^{226}Ra , ^{228}Ra , ^{224}Ra) activities in pore waters of the Truc Vert Beach (TVB), representative of this littoral but still well-preserved due to a difficult access. Samples were recovered at low tides along a cross-shore profile, between March-2011 and March-2013. In particular changes in radium were followed during a neap - spring tide cycle from November 12 to 29 2012. Pore waters were sampled at the top of the water-saturated zone in the intertidal zone of the beach. Shore seawater and sand were also sampled.

Activities in pore waters ranged from 4.5 and 21.4 dpm/100 L for ^{226}Ra , from 4.2 to 126.6 dpm/100 L for ^{228}Ra , and from 0 to 1682 dpm/100 L for ^{224}Ra . Pore waters in the intertidal zone of TVB are always enriched in Ra isotopes compared with shore waters. However, the enrichment factor (EF), compared to a coastal water reference, shows large variability, from ~ 1 to 18 for ^{228}Ra , depending on the sampling time and on the distance from the dune. Surficial beach sediments are composed of fine to medium quartz sand, with low activities of the radioactive parents of the Ra radionuclides. The large range of Ra activities and activities in pore waters thus may indicate multiple processes including mixing of fresh water and recirculated seawater, and variable residence times of pore water in the sandy Truc Vert Beach.



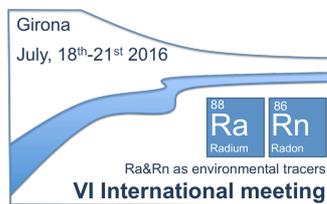
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P1.5 Effects of naturally occurring radium and radon activity heterogeneity on derived water mass ages and SGD: lessons learned from a semi-arid south Texas estuary.

Audrey R Douglas¹, Dorina Murgulet¹, and Nicholas Spalt¹

¹Texas A&M University— Corpus Christi

Many studies have used naturally occurring radium and radon isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra , and ^{222}Rn) to quantify water mass ages, coastal mixing rates, and submarine groundwater discharge (SGD); however, there is much variability in the Ra isotope activity and the derived activity ratios (AR) due to natural heterogeneities that result in a wide range of groundwater Ra and Rn concentrations. Therefore, determination of the Ra endmember activities and ARs is complicated by selection of sampling locations (both spatially and vertically) and groundwater flow paths. The common application of average groundwater activities and ARs, may obscure accurate estimates of SGD rates and sources. Additionally, surface water Ra sources to coastal embayments are also used to assess water mass ages relative to surface inflows. To assess radium constraints on water mass ages and SGD, sixteen wells were sampled around Nueces Bay, Texas, and 15 stations were sampled quarterly for two years in Nueces Bay and Nueces River. SGD calculations were based on ^{226}Ra activities as well as continuous ^{222}Rn in water measurements conducted using a RAD-7 continuous radon gas monitor. Additionally, electrical resistivity imaging was applied to delineate between shallow, deep, and recirculated groundwater sources. Nueces Bay exhibits some of the highest dissolved radium activities observed (295-1102 dpm/m³ seasonal mean ^{224}Ra and 348-983 dpm/m³ seasonal mean ^{226}Ra) in coastal waters despite being in a semi-arid region with inconsistent surface water inflows. The surrounding groundwater contains large variations in ^{222}Rn (10421 to 1,292,812 dpm/m³), ^{224}Ra (78.7 to 15,199.7 dpm/m³) and ^{226}Ra (5483.9 to 344,389 dpm/m³) activities and 224/226 ARs (0.00144 to 0.52432). Such large variations in activities and ARs significantly impact derived water mass ages and SGD estimates, demonstrating the necessity to further constrain radium source terms.



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P1.6 Coupling ²²²Rn Measurements and Geophysical Techniques to Constrain SGD: Occurrences in Relation to Estuarine Depositional Environments.

Nicholas Spalt¹, Dorina Murgulet¹, Audrey Douglas¹

¹Texas A&M University— Corpus Christi

The Uranium-Thorium decay series has proven to be an effective resource in the hydrogeologist's repertoire for identifying the abundance of submarine groundwater discharge (SGD) for a given area. Radiogenic isotope measurements are often up-scaled to estimate SGD to an entire basin. However, application of these sparse measurements as a realistic representation of the hydrologic characteristics across various depositional environments could introduce significant errors. This study used continuous resistivity profiling (CRP) and seismic measurements from published records to locate different depositional environments within a 1.5 square kilometer (km²) area for improved SGD estimates. A secondary bay shoreline, interfluvial, paleovalley, paleovalley margin, and oyster reef were investigated for variation in radiogenic isotopes (i.e. radon (Rn) and radium (Ra)) and subsequently SGD measurements. Geochemical and radiogenic isotope measurements from grab samples and continuous monitoring were conducted in each of these environments. ²²²Rn ranged from 20 to 324 Bq/m³ (n = 16) in surface waters and 150 to 10,277 Bq/m³ (n = 4) in porewater indicating not only that large SGD variations could be expected at small-scale but that relationships between hydrogeologic heterogeneities and location and extent of SGD are highly important. To further constrain these preliminary findings, stationary time-series resistivity and continuous Rn measurements will be used to provide insight on subsurface transport dynamics. This study is expected to improve understanding of the relationship between hydrogeologic heterogeneities as related to estuarine depositional environments and Rn distribution and transport across the sediment-water interface for improved basin-wide SGD calculations.

P1.7 Combining airborne thermal infrared images and radium isotopes to study SGD along the French Mediterranean coastline

Bejannin Simon¹, van Beek Pieter¹, Souhaut Marc¹, Stieglitz Thomas²

¹ LEGOS, Toulouse, France

² CEREGE, Aix-en-Provence, France

Submarine Groundwater Discharge (SGD) is now recognized as an important vector for many chemical elements that may impact the quality of the coastal environment and the marine ecosystem. Although these fluxes have been investigated in many places of the world, few studies have been conducted along the French Mediterranean coastline. In this study, we acquired airborne Thermal infrared (TIR) images to detect fresh groundwater inputs along this coastline. Due to the temperature difference between groundwater and seawater, we could locate several “hotspots” along this coastline. We also report radium data (^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra) that were obtained in several of these hotspots. The Ra isotopes allow us i) to confirm the presence of groundwater discharge, ii) to quantify SGD fluxes, iii) to estimate the age of coastal or lagoon waters and iv) to quantify the fluxes transported between the coastline and the open sea.

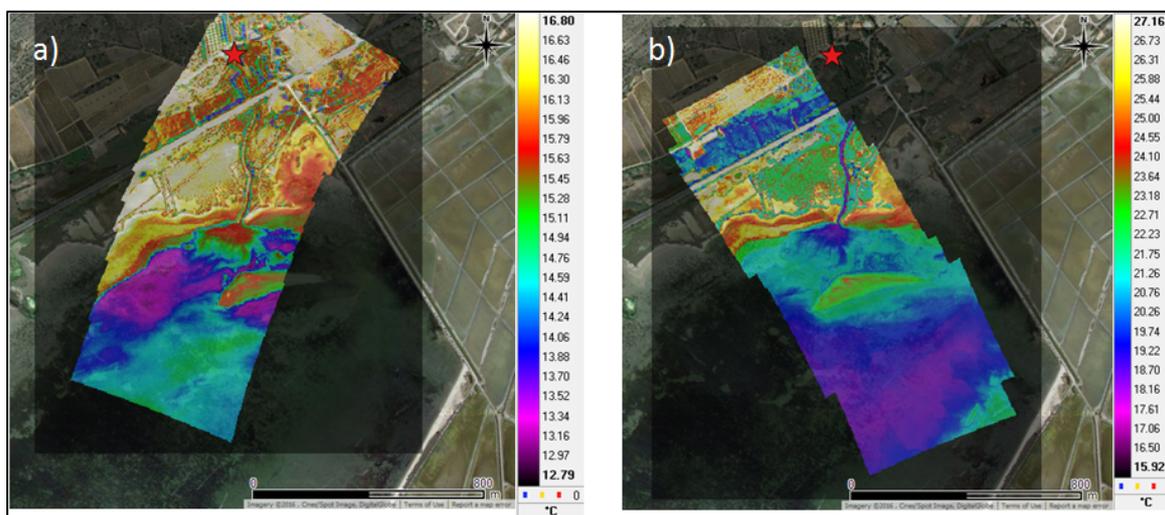
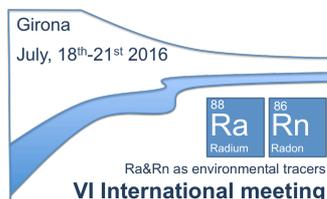


Figure 1 : Airborne thermal Infrared Images collected in La Palme lagoon, France. The two images were obtained at different periods of the day on 20/09/2012, at a) 9h26 and b) 16h55. The red star indicates the location of the spring.



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P1.8 Radium Isotopes Assess Water Mixing Processes and Their Ecological Influence in the Pearl River Estuary

GUO Xiaoyi^{1,2,3}, XU Bochao*^{1,2,3}, YU Zhigang^{1,2,3}, NAN Haiming³, JIAN Huimin, JIANG Xueyan^{1,2,3}, DIAO Shaobo⁴, GAO Maosheng⁴

¹Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

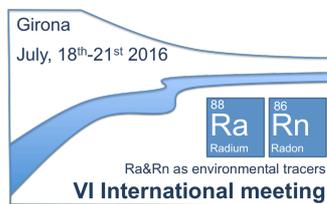
² Laboratory of Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266100, China

³ College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

⁴Qingdao Institute of Marine Geology, Qingdao 266071, China

Radium (Ra) isotopes are useful for tracing water mass transport and examining estuarine hydrological dynamics. In this study, several hydrological parameters, nutrients, chlorophyll-*a* (chl-*a*), suspended particulate matter (SPM) and Ra isotopes (²²³Ra, ²²⁴Ra and ²²⁶Ra) of surface waters of the Pearl River Estuary (PRE) were measured. This was done for both winter (December) and summer (July) seasons, to quantitatively understand the seasonal characteristics of river plume flow rate and trajectories, as well as the ecological response. The results showed that Ra concentrations in summer were higher than in winter, especially ²²⁴Ra (about 2-5 times higher). High concentration of SPM in summer significantly contributed to the elevated Ra. The spatial distribution of three Ra isotopes and relative Ra water ages indicated that river water mainly flushed out of PRE through the western side in winter, where the water transport was 5-6 times higher than in the eastern zone. In summer, diluted river water expended to the east side, resulting in fairly similar water ages for both sides of the river mouth. Although nutrients were higher during the summer season, lower chl-*a* concentrations indicated that reduced primary production might be caused by high SPM (low light penetration). The results obtained from this study will provide knowledge needed for effectively developing and managing the PRE.

Keywords: Pearl River Estuary; radium isotopes; water ages; nutrients



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P1.9 Assessing the role of Submarine Groundwater Discharge in the transport of Fukushima-derived radionuclides to the coastal ocean off Japan

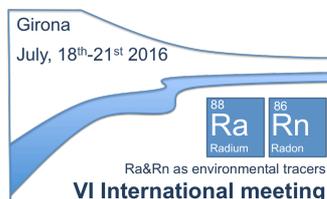
V. Sanial¹, K. Buesseler¹, M. Charette¹, N. Casacuberta², M. Castrillejo³, P. Henderson¹, X. Juan Diaz³, J. Kanda⁴, P. Masque^{3,5}, S. Nagao⁶, J. Nishikawa⁷, S. Ootaka⁸ and S. Pike¹

¹Woods Hole Oceanographic Institution, USA; ²Laboratory of Ion Beam Physics, ETH-Zürich, Switzerland; ³Universitat Autònoma de Barcelona, Spain; ⁴Tokyo University of Marine Science and Technology, Japan; ⁵School of Science, Edith Cowan University, Australia; ⁶Kanazawa University, Japan; ⁷Tokai University, Japan; ⁸Japan Atomic Energy Agency, Japan

On March 11, 2011, an earthquake followed by a tsunami triggered an unprecedented nuclear accident at the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) leading to large releases of radionuclides to the ocean, in particular the isotopes of cesium (¹³⁷Cs & ¹³⁴Cs). Though most of the Fukushima atmospheric fallout was believed to be over the ocean, fallout over land led to Cs enrichment in river runoff and contamination of surficial aquifers. Furthermore, groundwater has been reported to be infiltrating the FDNPP reactor buildings at several hundred tons/day and being transformed into highly contaminated radioactive wastewater; massive efforts attempt to store the wastewater in 1000's of tanks for further treatment. Over the past 5 years after the accident, Tokyo Electric Power Company (TEPCO) has acknowledged ongoing direct radionuclide inputs to the local aquifer with the potential for transport to the coastal ocean *via* submarine groundwater discharge (SGD).

Cs activities in the coastal ocean off Japan dropped by orders of magnitude within one month after the accident but have remained relatively constant over the past 5 years exceeding background values. That being said, we observed, and Japanese data confirm, a significant increase in Cs activities in the coastal ocean off Japan during September and October 2015. The higher Cs activities last fall were restricted within a radius of approximately 20 km from the FDNPP revealing a new source of radionuclides from the power plant area coincident with heavy typhoon rains. Our highest Cs activities in October 2015 were not found in the ocean, but in saline groundwater samples underlying coastal beaches 35 km south of the FDNPP. Thus, identifying the role played by SGD in the transfer of Cs from land to ocean appears to be crucial in understanding the variation of the Cs activities observed in the coastal ocean off Japan 5 years after the accident.

In addition to Cs isotopes, we performed radium isotopes analysis (²²³Ra, ²²⁴Ra, ²²⁶Ra and ²²⁸Ra) in seawater samples from 5 cruises conducted in the coastal ocean off Japan between May 2013 and October 2015. We further analyzed samples of groundwater and rivers collected in the surrounding area of the FDNPP. The Ra dataset will be used to quantify the flux of Cs associated with SGD. To do so, a Ra mass balance will be executed in the coastal ocean off Japan by estimating the different sources and sinks of Ra. A similar mass balance model will be constructed for tritium, which will allow us to estimate the terrestrial component of SGD.



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P1.10 SGD-driven metal fluxes offshore in a mining area estimated from Ra isotopes

Aaron Alorda-Kleinglass^a, Jordi Garcia-Orellana^{b,c}, Giada Trezzi^c, Valentí Rodellas^d,
Marc Cerdà-Domènech^e, Almudena Hierro^b, Antonio Tovar-Sanchez^f

^a Environmental Sciences degree – Universitat Autònoma de Barcelona (UAB)

^b Departament de Física, Universitat Autònoma de Barcelona (UAB)

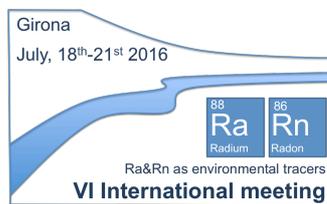
^c Institut de Ciència i Tecnologia Ambiental – Universitat Autònoma de Barcelona (UAB)

^d Centre de Reserche et d'Enseignement de Géosciences de l'Environnement (CEREGE).

^e GRC Geociències Marines Dept. d'Estratigrafia, Paleontologia i Geociències Marines Facultat de Geologia, Universitat de Barcelona.

^f IMEDEA (CSIC-UIB), Esporles, Mallorca, Islas Baleares, Spain

Portman Bay is located in Cartagena - La Unión Pb and Zn mining district, Murcia, Spain. 57 million tons of mine tailings had been deposited since 1957 to 1991, representing the most important environmental impact in the Mediterranean Sea. In this work, we studied the flux of metal fluxes from the mining deposits to the coastal sea driven by submarine groundwater discharge (SGD). Ra isotopes and dissolved metals have been collected in porewaters and in transects offshore in two samplings conducted in March 2015 and January 2016. Whilst long-lived Ra isotopes (²²⁸Ra and ²²⁶Ra) were almost constant along an offshore transect, significant gradients of short-lived Ra isotopes (²²³Ra and ²²⁴Ra) were observed, were used to calculate the SGD water and metal fluxes. Cd, Pb and Zn concentrations in seawater were comparable or even higher to the highest concentrations reported in the Mediterranean Sea, reaching up to seawater concentrations of 3.6 nM, 5.6 nM and 490 nM for Cd, Pb and Zn, respectively. Maximum metal fluxes of 8 ± 2 , 49 ± 10 and 663 ± 139 mol·day⁻¹ for Cd, Pb and Zn were calculated. These results highlight the importance of SGD in Portman Bay as a mechanism to transfer metals from the mining deposits to the coastal sea. Finding from this work also reveal that, after 30 years of the last dumping of mine tailings in the area there is still a significant flux of metals into the sea that can affect the biogeochemical cycles of the area.



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P1.11 Using Radon-222 as a tracer of groundwater discharge into a tropical lagoon: Discovery Bay, Jamaica

Debbie-Ann Gordon-Smith¹; Richard N. Peterson²; Leigha, E. Peterson²

¹University of the West Indies, Mona Jamaica

²Coastal Carolina University, USA

Submarine groundwater discharge (SGD) is now recognised as an important source of chemical species, such as nutrients and trace metals, to marine environments. Numerous SGD studies have been conducted off the coasts of large continents but only a few studies have been done on tropical islands, and even fewer studies have investigated SGD from small karstic islands. This paper presents the preliminary results obtained from a study investigating groundwater discharge into Discovery Bay, a small tropical lagoon on the north coast of Jamaica. Previous studies have attempted to quantify discharge into the bay using water balances and direct flow measurements but this study has been initiated to measure SGD using the naturally-occurring tracer ²²²Rn. The results of multiple surveys and time-series measurements of ²²²Rn within the bay will be presented and discussed alongside salinity/conductivity profiles and data from previous studies.

P1.12 A Ra/Rn study of submarine groundwater discharge in three locations on Java and Lombok, Indonesia

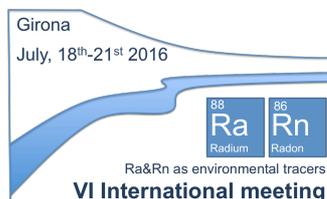
Till Oehler¹, Doni Putra², Hendra Bakti³, Rachmat Fajar Lubis³, Bernhard Schnetger⁴, Dini Adyasari¹, Nils Moosdorf¹

¹Leibniz Center for Tropical Marine Ecology (ZMT), Bremen, Germany ; ²Universitas Gadjah Mada, Geological Engineering Departement, Yogyakarta, Indonesia; ³Research Center for Geotechnology, Indonesian Institute of Sciences (LIPI), Bandung, Indonesia; ⁴Institute for Chemistry and Biology of the Marine Environment (ICBM), Oldenburg, Germany

Submarine groundwater discharge (SGD) occurs in many coastal regions. Indonesia has one of the longest coastlines in the world and consists of more than 17 000 islands, mostly of volcanic origin. Permeable volcanic rocks, as well as heavy rain fall might lead to a large freshwater SGD flux from these islands to the ocean. However, only few studies analyze SGD on Indonesia (e.g. Lubis et al., 2011). Radon and Radium are powerful chemical tracers for the detection and quantification of SGD in coastal areas. Here we present one of the first measurements of SGD via Radon and Radium isotopes from different geological settings in Indonesia. In November 2015 and March 2016 SGD was measured in a karstic area, a coral reef and on volcanic and carbonate sands on Java and Lombok Island. Radium isotopes (RaDeCC system) were measured in a karstic area in the southern part of Central Java, where freshwater enters the Indian Ocean via discrete submarine springs. In the northern part of Central Java continuous Radon measurements (Durrige, Rad7 and Rad Aqua) were performed on volcanic and carbonate sands, and in the northern part of Lombok continuous Radon measurements were performed in a coral reef in which submarine springs occur from a volcanic aquifer (fig. 1). At all visited sites in Indonesia higher Radon and Radium activities were correlated to lower salinities. Especially in volcanic aquifers extraordinarily high Radon concentrations were measured. In geologically young volcanic tropical islands such as Indonesia, Radon might thus be a powerful tracer for SGD.



Figure 1: A submarine groundwater spring in the northern part of Lombok. Within a coral reef submarine springs occur mostly along holes of up to ~20 meters in diameter and ~7 meters deep. In the background the island of Bali can be seen.



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P1.13 Novel Approaches in Radon Mass Balancing for Quantifying Groundwater Discharge into Surface Water Bodies

Eric Petermann¹ & Michael Schubert¹

¹Helmholtz Centre for Environmental Research – Dept. Groundwater Remediation

Apart from river and surface water runoff subsurface discharge of groundwater plays a key role in coastal water and matter budgets. Two major forms of submarine groundwater discharge (SGD) can be distinguished: (i) pure freshwater discharge from continental aquifers that are connected to the coastal sea driven by a positive hydraulic gradient (fresh SGD) and (ii) re-circulation of seawater that has penetrated permeable coastal sediments (recirculated SGD). Localization of SGD zones and quantification of SGD water fluxes is of high interest for coastal water management due to potential threats related to SGD, namely (i) the detrimental impact of discharging nutrient- or contaminant-laden groundwater on coastal seawater quality, and (ii) the loss of freshwater to the ocean.

In this study, we present quantitative studies using a radon mass balance for determining SGD water fluxes was conducted at an identified SGD location. Methodological novelties comprise the calculation of radon mixing rate, radon degassing rate and SGD Rn endmember concentration. By applying an empirical relationship for the ratio fresh SGD/recirculated SGD proposed by Prieto and Destouni (2010) [Water Resour. Res., 41, W12427] in combination with the radon mass balance results we discriminated between the fresh and the recirculated SGD component. The results reveal mean fresh SGD rates of 3.7 mm/d (1.4 m³/d per m coastline) respectively 3.2 mm/d (1.2 m³/d per m coastline) for two study campaigns in May 2009 and in March 2014. The recirculated SGD water flux was estimated with a mean of 4.0 mm/d respectively a mean of 1.5 m³/d per m coastline for both campaigns. Uncertainty of water fluxes was quantified using stochastic simulations (Monte Carlo simulations). The fresh SGD rate estimate revealed significant uncertainty mainly caused by uncertainty of fresh SGD endmember Rn concentration, Rn mixing rate and Rn degassing rate. The plausibility of our results has been proven using a hydrological model for SGD water flux estimates. This approach supported the Rn based findings. The presented approaches for Rn parameter estimation and Rn flux calculation contribute to methodological progress in localizing and quantifying SGD and in determining the related uncertainty applying the environmental tracer radon. These approaches are transferable to other groundwater-surface water systems such as lakes or lagoons quantifying groundwater discharge.

P1.14 Identification of the submarine groundwater discharge locations around the tropical island of Mauritius

Yashvin Neehaul¹, Ulf Mallast², Daniel Marie¹, Jan Scholten³

¹ Mauritius Oceanography Institute, Avenue des Anchois, Albion, Mauritius (yneehaul@moi.intnet.mu).

² Department Catchment Hydrology, Helmholtz Centre for Environmental Research, Halle, Germany

³ Institute of Geosciences Kiel University, Kiel Germany

The tropical island of Mauritius relies heavily upon groundwater to meet potable water demand. As the island is of volcanic origin a considerable part of groundwater flows through subsurface fractures towards the sea. We conducted a multidisciplinary investigation to identify the locations of submarine groundwater discharge (SGD) around the island. Using Landsat satellite images 37 near-shore locations were identified showing seawater temperature anomalies which may indicate SGD. For further ground-truthing, temperature, salinity and radon were determined at these locations. Based on these measurements, 28 SGD locations could be confirmed. We present more detailed results from the areas La Prairie and Trou aux Biches showing the spatial distribution of the parameters investigated in relation to SGD.

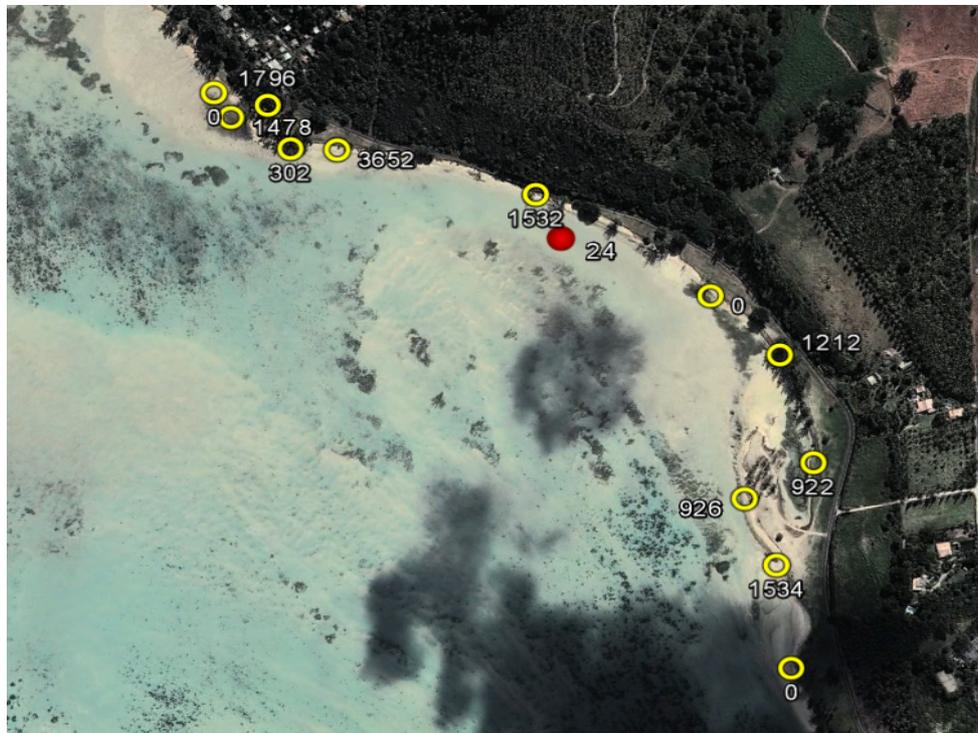
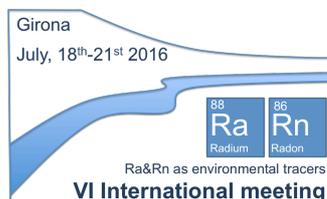


Figure 1: Measurement of ²²²Radon content at La Prairie in Bq/m³.



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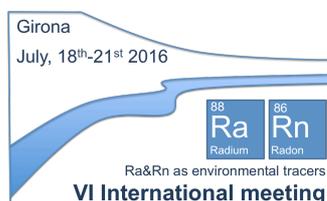
INLAND PROCESSES

T2.1 Investigating the Potential Risks of Hydraulic Fracturing Technology in the Marcellus Shale

Colin P. Casey¹, Jessica Balerna¹, Karen Knee¹, & Gabriel Santos²

¹American University, Washington, D.C. ²Federal University of the State of Rio de Janeiro

This project aimed to assess whether hydraulic fracturing (“fracking”) and activities associated with it could affect water quality in the Potomac River, Washington, DC’s water source. Much of the Potomac’s watershed overlies the Marcellus shale play in the states of Virginia, West Virginia, and Maryland; fracking development has already occurred in West Virginia but not in Maryland or in the parts of Virginia that are within the Potomac watershed. We measured specific conductance, pH, radium, and concentrations of dissolved metals that have been associated with fracking in samples from 73 river and stream sites in the Potomac watershed, distributed evenly among the three states, hypothesizing that West Virginia sites would demonstrate evidence of contamination. ²²⁴Ra activities were higher in West Virginia and Maryland than in Virginia, partially supporting our hypothesis. No significant differences in ²²³Ra were observed. Analysis of other Ra isotopes and other parameters is ongoing. Future work includes using strontium isotopes to distinguish fracking pollution from that originating from other sources, such as historical and current coal, oil and gas extraction, as well as combining water quality data with stream discharge to develop a simple model of pollutant loading from fracking within the Potomac watershed.



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T2.2 Characterization of Radium and Radon Isotopes in Hydraulic Fracturing Produced Water and Gas from the Marcellus Shale

A. Bardsley¹, D. Hammond¹, K. Jessen², T. Tsotsis², J. Xu²

¹Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089, USA

²Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089, USA

High volume hydraulic fracturing of unconventional deposits has expanded rapidly over the past decade in the US, with much attention focused on the Marcellus Shale gas reservoir in the northeastern US. We use naturally occurring radium isotopes and ^{222}Rn to explore changes in formation characteristics as a result of hydraulic fracturing. Gas and produced waters were analyzed from time series samples collected soon after hydraulic fracturing at two Marcellus Shale well sites in the Appalachian Basin, USA. Analyses of $\delta^{18}\text{O}$, Cl^- , and ^{226}Ra in early flowback fluid were consistent with two end member mixing between injected slick water and formation brine. All three tracers indicate that the ratio of injection water to formation brine declined with time across both time series. On a plot of water isotopes, $\delta^{18}\text{O}$ in formation brine-dominated fluid was enriched by approximately 3‰ relative to the Global Meteoric Water Line, indicating oxygen exchange with shale. Seven to 15 months following well stimulation, patterns of Cl^- and ^{226}Ra do not plot on previous mixing lines, evidence that water of different composition moved into the production region. Water isotopes also evolved over this time period, towards lighter isotopic values, suggesting that the increase in radium and chloride is not due to evaporation of the in situ fluid as gas is withdrawn. The ratio of $^{223}\text{Ra}/^{226}\text{Ra}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ in produced waters was quite low relative to shale samples. This indicates that most of the ^{226}Ra in the formation brine must be sourced from shale weathering or dissolution rather than emanation due to alpha recoil from the rock surface. During the first week of flowback, ratios of short lived isotopes ^{223}Ra and ^{224}Ra to longer lived radium isotopes changed modestly, suggesting rock surface area per unit of produced water volume did not change substantially. In gas samples, the $^{222}\text{Rn}/\text{CH}_4$ ratio in both wells dropped during the first 8-10 days following fracking. This may represent a loss of fluid from the formation relative to the gas that is present. Subsequent fluctuations in the $^{222}\text{Rn}/\text{CH}_4$ ratio may reflect radon added to the gas phase directly from shale emanation in addition to that from decay of ^{226}Ra in the formation fluid. Naturally occurring radium and radon isotopes show promise in elucidating sub-surface dynamics following hydraulic fracturing plays.



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T2.3 Coupling radium/radon, geophysical and hydrological approaches on a shallow lake to constrain water mass balance

Buquet Damien¹, Anschutz Pierre¹, Chaillou Gwenaëlle^{1,4}, Sirieix Colette², van Beek Pieter³, Bejannin Simon³, Souhaut Marc³, Naessens Fabien².

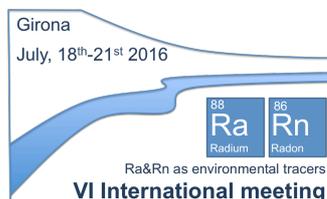
¹: EPOC, Université de Bordeaux, CNRS, Allée Geoffroy St Hilaire, CS 50023, 33615 Pessac Cedex, France

²: Laboratory I2M, Université de Bordeaux, Allée Geoffroy St Hilaire, CS 50023, 33615 Pessac Cedex, France

³: LEGOS, Observatoire Midi Pyrénées, 14 av. Edouard Belin, 31400 Toulouse, France

⁴: Canada Research Chair in the Geochemistry of Coastal Hydrogeosystems, Department of Biology, Chemistry and Geography, Université du Québec à Rimouski, G5L 3A1 Rimouski, Canada

Lake Groundwater Discharge (LGD) is recognized as a possible source of nutrients and may be involved in lakes eutrophication. We have studied the hydrological and biogeochemical processes occurring in the fresh-water Lake of Lacanau (20 km², SW France). The hydrological approach based on water mass balance was not sufficient to perform relevant calculation of LGD due to high uncertainties in stream flow measurements. We carried out LGD assessments in October 2015 and March 2016 to validate in the studied lake the different approaches commonly used to localise and quantify submarine groundwater discharges to coastal ocean. Measurements included radium (²²³Ra, ²²⁴Ra, ²²⁸Ra and ²²⁶Ra) and radon (²²²Rn) activity surveys in the lake water, surficial and groundwaters, a regional and annual water balance and Darcy estimations based on piezometric data around the lake. Additional hydrogeological data were obtained at local scale using a ground probing radar (GPR) to estimate the position of the water table near the lake shores. For the year 2014, groundwater fluxes calculated using Darcy law represented less than 2% of the total water fluxes with 46 m³.y⁻¹ per meter of shoreline. Surficial fluxes were very low during summer; groundwater fluxes reached 13% of the total fluxes during this period. Preliminary Rn results seem to support this seasonal variation of LGD contributions. Rn activities in groundwaters were 1200 ± 178 Bq/m³, N= 10. Rn activities were higher in March along the shoreline of the lake than during the dry period. Rn activities in surficial river waters were two orders of magnitude higher than the highest values measured in the lake, suggesting that the small rivers connected to the Lake could be major contributors to the volumetric budget of Rn of the lake. The localisation and quantification of LGD will certainly be improved with additional Rn and Ra results and GPR interpretations, which are in progress.



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T2.4 Validating ²²²Rn-based tracer method for assessing groundwater fluxes into rivers: case study from Meghna River, Bangladesh

Natasha Dimova¹ (ntdimova@as.ua.edu), P. Knappett², A. Hossain³, Z. G. Nichols¹, Daniel Montiel¹, K. Rhodes², P. Shuai², K. M. Ahmed³

¹Department of Geological Sciences, University of Alabama, Tuscaloosa, AL

²Department of Geology and Geophysics, Texas A&M University, College Station, TX

³University of Dhaka, Department of Geology, Dhaka, Bangladesh

In this paper we present results from a study whose main goal was to assess the contribution of groundwater to the discharge of a 10-km reach of a tidally-impacted river located in the Southeast Asia, the Meghna River in Bangladesh. To evaluate groundwater discharge to Meghna River we used three different approaches, namely: (1) Darcy's Law based on observed aquifer water levels, (2) differential gaging, and (3) mass-balance of ²²²Rn (a groundwater tracer). Complications in assessing groundwater discharge in this particular scenario arise from the fact that despite being about 200 km far from the coastline (Bay of Bengal), the river level and groundwater table at the researched location were greatly affected by daily tidal oscillations. To our knowledge, all listed approaches have previously been applied only to a steady flowing river. This may explain the large differences in groundwater discharge between the methods. Our results suggest that the radon-based mass-balance approach is perhaps the most adequate/realistic when inspecting water budgets in such systems. Water exchanged along the river-aquifer interface impacts the biogeochemistry and ecosystems within aquifers, rivers, and oceans in ways that are not well understood. However, there is evidence that these processes cause alteration of redox conditions favoring release of heavy metals (e.g. As) in local aquifers.

T2.5 Radon based SGD budgets of the Hawaiian Islands – spatial and long-term SGD trends and their biogeochemical implications

Henrietta Dulai

Department of Geology and Geophysics, School of Ocean, Earth, Science, and Technology, University of Hawaii

The Hawaiian Islands capture a range of geologic, land-use, climate, and population gradients. We study submarine groundwater discharge rates in multiple watersheds across these gradients. In this context we have been investigating the significance of SGD as a terrestrial nutrient pathway to the coastal zone and the origin of nutrients in coastal groundwater. I will present selected studies where variability of groundwater fluxes were monitored on longer time scales using radon measured by autonomous gamma-spectrometers. The instruments collected tidally and seasonally variable data through several processes that affect SGD, yet we have never had direct observations on their effect: tsunami, tropical cyclones, wind and precipitation anomalies, as well as the El-Nino period of 2015-2016.

Our analysis of watersheds, some of which host the largest coral reefs on the islands, revealed that SGD in the form of total (fresh+brackish) groundwater discharge was 1-4 times larger than surface inputs. Corresponding dissolved inorganic nutrient fluxes were also dominated by SGD (Figure 1) and their effect on the coastal ecosystem was evaluated.

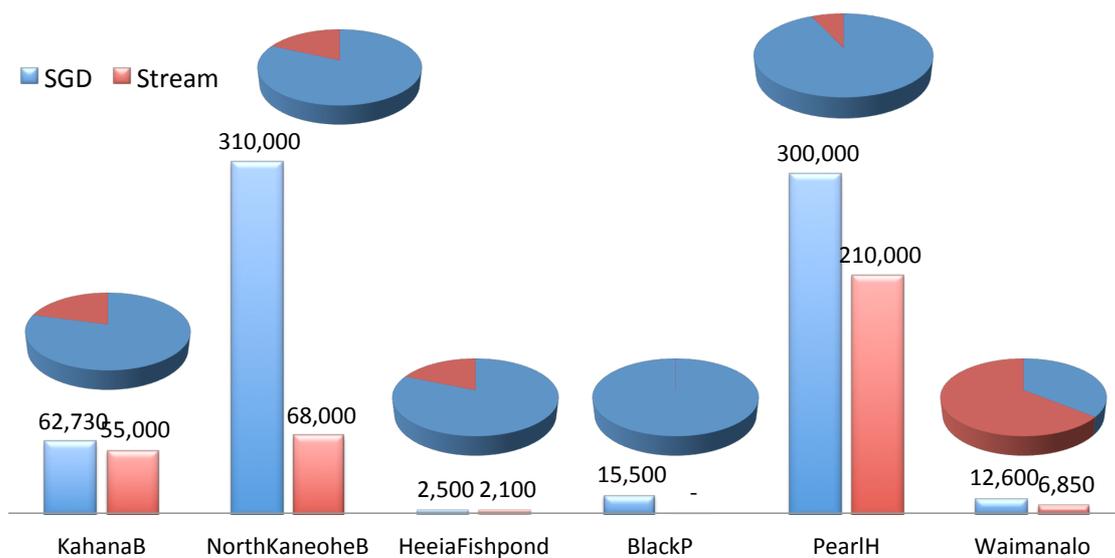


Figure 1: Submarine groundwater discharge (blue bars) and stream (red bars) discharge (m³/d) and corresponding nitrogen fluxes (pie charts, same color code) on the island of Oahu.

T2.6 Radon Helps Determine the Role of Groundwater in a Flood-Pulse System: Tonle Sap Lake, Cambodia

William C. Burnett¹, Gullaya Wattayakorn², Supitcha Chanyotha², Khamfeuang Sioudom³, Veasna Kum⁴

¹ Florida State University, USA; ² Chulalongkorn University, Thailand; ³ National University of Laos; ⁴ Ministry of Environment, Cambodia

Tonle Sap Lake (Cambodia), a classic example of a “flood pulse” system, is the largest lake in SE Asia, and is reported to have one of the highest freshwater fish productions anywhere. During the dry season (November–April) the lake drains through a tributary to the Mekong River. The flow in the connecting tributary completely reverses during the wet monsoon (May–October), adding huge volumes of water back to the lake, increasing its area about six fold. The lake is likely phosphorus limited and we hypothesized that groundwater discharge may represent an important source of P and other nutrients. To address this question, we surveyed hundreds of kilometers of the lake for natural ²²²Rn (radon), temperature, conductivity, GPS coordinates and water depth while underway. All major inorganic nutrients and phosphorus species were evaluated as well. Results showed that there were radon hotspots, all at the boundaries between the permanent lake and the floodplain, indicating likely groundwater inputs (Fig. 1). A radon mass balance model indicates that the groundwater flow to Tonle Sap Lake is about 10.3 km³/yr, about 25% as large as the floodwaters entering from the Mekong River during the wet monsoon. Our results suggest that the groundwater-derived dissolved inorganic phosphorus (DIP) contribution to Tonle Sap is more than 30% of the average inflows from all natural sources. Since the productivity of the lake appears to be phosphorus limited, this finding suggests that the role of groundwater is significant for Tonle Sap Lake and perhaps for many other flood pulse systems worldwide.

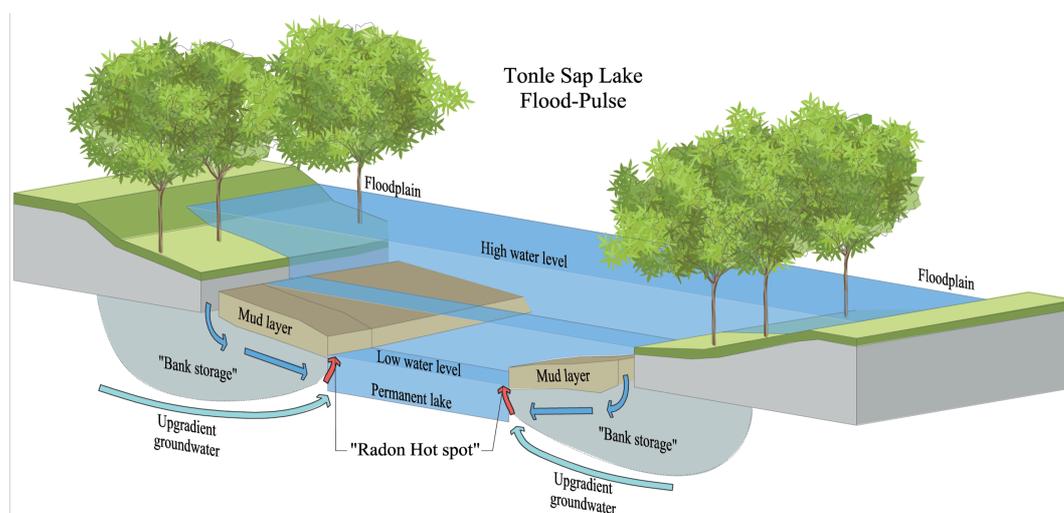
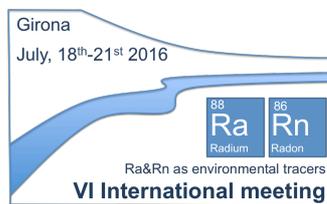


Figure 1. Conceptual drawing illustrates our view of groundwater/surface water interactions in Tonle Sap Lake. Subsurface water, a mixture of terrestrially derived groundwater and re-circulated lake water, discharges mainly along the boundary between the permanent lake and floodplain.



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T2.7 Applying radon to investigate freshwater ecosystem processes

Karen Knee

Department of Environmental Science, American University, Washington, DC, USA

Radon has often been used to investigate submarine groundwater discharge and mixing in coastal waters, but its application to freshwater aquatic ecosystems has been more limited. This presentation discusses two such applications. The first is to denitrification in agricultural streams. In many watersheds, especially those in the eastern United States, only a small fraction of net anthropogenic nitrogen inputs (NANI) can be accounted for by river and stream discharge. The remainder, known as the “missing N”, has two possible fates: (1) storage within the watershed and (2) transformation into biogenic nitrogen gases, followed by evasion to the atmosphere. One promising approach to determining the fate of the “missing N” is to quantify biogenic nitrogen gases escaping from stream surfaces within a watershed. Radon is an effective tracer of both groundwater input and gas exchange in agricultural streams, and, when combined with other measurements, it can be used to quantify the N_2 flux out of the stream and the N_2 mass balance. The second application is to the ecohydrology of urban hypotelminorheic habitats. Hypotelminorheic habitats occur at the outlets of shallow perched aquifers and are an important component of the Washington, DC area’s urban biodiversity. They harbor cave-adapted amphipods including the DC area’s only endangered species. However, very little is known about their hydrology. Since these habitats often have very high dissolved Rn activities (40,000 Bq/m³ or higher), I decided to investigate whether Rn could shed light on the residence time of water in the perched aquifer and the size of the recharge area, factors which could influence the habitats’ susceptibility to damage from urban pollutants. Residence times of 1.2-5.4 days were estimated, and these estimates were supported by observations of lag times between precipitation events and increases in seep discharge. Combining empirical estimates of the perched aquifer’s hydraulic conductivity with these residence time estimates, it was estimated that water traveled on the order of ~200 m between infiltration and discharge, providing a preliminary idea of the area that would need to be protected for effective conservation of these habitats.

P2.1 Change of radon exhalation from a volcanic tuff placed in a closed-loop circuit at increasing kerosene content. Implications for soil NAPLs contamination.

De Simone G.¹, Pompilj F.¹, Lucchetti C.¹, Galli G.², Tuccimei P.¹

¹ Università “Roma Tre”, Dipartimento di Scienze, Roma, Italy

² Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 1, Roma, Italy

Soil radon is employed to trace NAPLs (Non-Aqueous Phase Liquids) contamination because radon is very soluble in these substances and its activity concentration is strongly reduced at surface (80 cm depth), as shown by monitoring surveys across a polluted area. The use of it for quantitative assessment is not generally taken, because soil radon concentration is directly related to many factors which may affect it simultaneously, with diverging results. This is why specific experiments under controlled conditions have been carried out to isolate the effect of increasing kerosene content on radon exhalation rate and activity concentration in a closed-loop circuit. The test configuration consists of: i) an accumulation chamber (a modified pressure cooker) where 650 g of a dried volcanic tuff are placed; ii) vinyl tubing to connect the chamber to a radon monitor in a closed-loop array; iii) a RAD7 radon monitor (DurrIDGE Co.) located in a laboratory oven set at 43 °C; a thermo-refrigerating bath hosting the accumulation chamber, set at 35°C to keep the exhalation temperature at constant condition. A temperature difference of 8 °C is chosen to avoid condensation effects on the surface of the silicon detector in the RAD7. No desiccant (drierite) is used because it would absorb kerosene vapors and part of radon released by the tuff and then dissolved in the vapors, masking the results. The effect of water molecules in the RAD7 volume on the efficiency of the electrostatic collection-based silicon detector is corrected on the basis of proper equations. Several tests have been carried out at increasing kerosene content (0, 5, 10, 15, 20, 25 mL) to quantify correlated radon exhalation and concentration changes. At the end of each experiment (24-hour long), the amount of kerosene vapor has been measured using the Dräger tubes for petroleum hydrocarbons and the MiniRae Lite photo-ionization detector manufactured by Extratech for total Volatile Organic Carbon (VOC). The experimental outcomes show that radon exhalation and concentration (namely ²²⁰Rn) in the 5.3 L circuit grow at increasing volumes of added kerosene because radon is largely dissolved in kerosene vapors. At 20 mL of added kerosene, corresponding to approximately 300 ppm of petroleum vapors, the partition equilibrium of radon between vapor and liquid kerosene is reached. This outcome can be applied to natural systems only when the NAPL spill is recent and the investigation is restricted to areas located very close to the polluted volume of soil. In this case, an increase of radon is expected, rather than a deficit. However, this effect is supposed to be negligible in natural systems because films or blobs of residual kerosene irregularly dispersed in the soil pores entrap natural radon at depth, pinpointing an area of negative concentration to be compared to a meaningful background site. The introduction of the drierite emphasizes the radon deficit and is useful for qualitative assessment.



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P2.2 Interpreting groundwater Radon-222 data in the Alt Empordà regional hydrogeological system (NE Catalonia)

Josep Mas-Pla^{1,2}, Joan Bach³, Anna Menció², Carles Roqué², David Soler², Manel Zamorano², Merce Boy-Roura¹ and David Brusi².

¹Institut Català de Recerca de l'Aigua, josep.mas@udg.edu

²Grup de Recerca GAiA, Centre de Recerca Geocamb, Dept. de Ciències Ambientals, Universitat de Girona, anna.mencio@udg.edu

³Unitat de Geodinàmica Externa i Hidrogeologia, Dept. de Geologia, Univesitat Autònoma de Barcelona, joan.bach@uab.cat

The radioactive isotope radon-222 (²²²Rn) is a useful tracer in regional flow systems, whose use has spread in recent years. Because of its very short half-life (3.82 days), the presence of an activity in ²²²Rn in groundwater shows the influence of areas with a high production of this isotope within the aquifer, or the existence of geological features such as fault zones.

The hydrogeological system of the Alt Empordà (NE Catalonia) comprises different aquifers with distinct lithological formations: igneous and metamorphic rocks of Paleozoic, Mesozoic carbonate rocks, clastic formations, carbonate and evaporite Paleogene, and partially consolidated detritic deposits of Neogene and Quaternary. Tectonics plays a decisive role in the geological structure of the aquifer system, with Paleogene compressive overlaps in the eastern Pyrenees, and Neogene extensional faults that have led to the present depression of the Alt Empordà.

This study describes the hydrogeological characteristics of this system based on hydrochemical and isotopic data, including those of ²²²Rn. Depending on the hydrogeologic conceptual model, two groups of groundwater samples are distinguished based on their ²²²Rn activities: samples below 10 Bq/L are associated with the background activity of the Neogene sediments, and those with higher activities (~ 30 Bq/L) are related to the proximity of the ²²²Rn production zones (igneous rocks or sediments derived from them) or to fault zones that allow a rapid rise of groundwater originally in contact with these lithologies in the Paleozoic basement. Consistently with other isotopic data ($\delta^{18}\text{O}$, δD , tritium), ²²²Rn activities highlight the importance of fracture zones in the regional flow as an efficient groundwater recharge of the Neogene and Quaternary aquifers which concentrate most of the human groundwater exploitation.

This study is funded by project CGL2014-57215-C4-2-R.

P2.3 Radon-in-water time-series modelling from radon-in-air records

Eric Petermann¹ & Michael Schubert¹

¹Helmholtz Centre for Environmental Research – Dept. Groundwater Remediation

Radon-in-water concentration time-series that are detected by means of radon-in-air detectors usually demonstrate a distinct response delay between radon-in-water concentration and the related radon-in-air records. This response delay results in recorded radon-in-air time-series that are not fully reflecting short-term radon-in-water fluctuations. The response delay is due to (i) the water/air transfer kinetics of radon and (ii) the delayed decay equilibrium between ^{222}Rn and its progeny ^{218}Po , which is actually being measured by most radon-in-air monitors. In the discussed study we designed a laboratory experiment with a defined radon-in-water input function, recorded the radon-in-air response signal and analyzed the two time-series. Radon-in-air records showed a delay of ~ 10 min relative to the radon-in-water concentrations. However, for reconstructing the original radon-in-water signal based on the detected radon-in-air time-series we developed an algorithm considering all delay causing parameters. It was shown that the applied algorithm allows reconstructing the input signal without any time delay and with correct concentrations for all concentration fluctuations lasting longer than about 10 min. In conclusion we can state that the developed algorithm allows a precise determination of radon-in-water concentration time-series based on radon-in-air records even if short-term fluctuations occur. Possible applications include a more precise localization of groundwater discharge into surface water bodies.

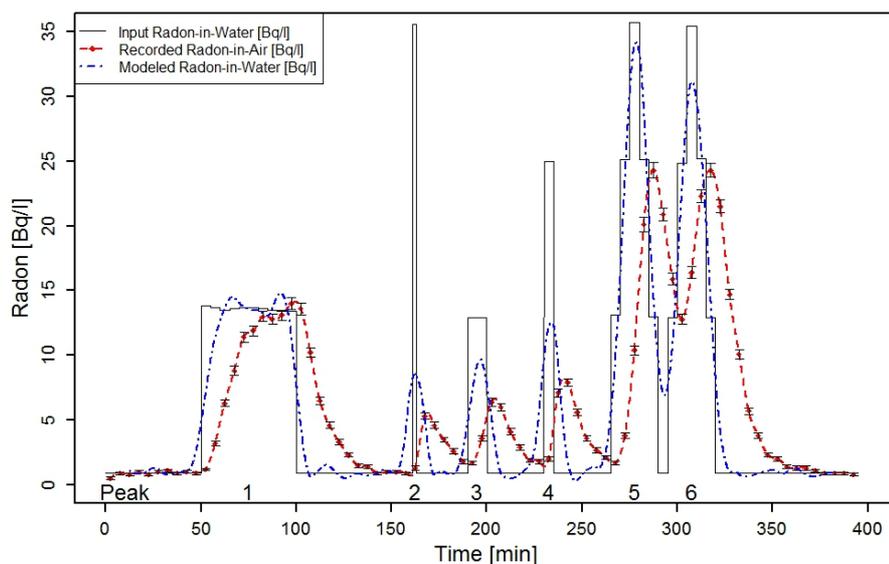


Fig.: Radon-in-water concentrations (input signal) compared to the recorded radon-in-air concentrations and the modeled radon-in-water concentrations. The modeled radon-in-water concentrations are well in accordance with the input radon-in-water signal. Independently from magnitude or duration of the input signal, the modeled radon-in-water concentration peaks are consistent with the input signal anomalies regarding the respective onsets. For a better comparison with radon-in-water concentrations, the radon-in-air concentrations were corrected for water/air partitioning of radon.



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P2.4 Monte Carlo modelling of NaI scintillation detector for continuous underground radon monitoring

Gustavo Haquin^{1,2}, Tamir Kamai³, Hovav Zafir⁴, Danielle Ilzyer², Moriel Pinchasi⁵ and Noam Weisbrod¹

¹ Zuckerberg Institute for Water Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sde Boker, Israel

² Radiation Safety Division, Soreq Nuclear Research Center, Yavne, Israel

³ Soil, Water and Environmental Sciences, Agricultural Research Organization - Volcani Center, Beit Dagan, Israel

⁴ Geological Survey of Israel, Jerusalem, Israel

⁵ Nuclear Licensing and Safety Office, Israel Atomic Energy Commission, Tel Aviv, Israel

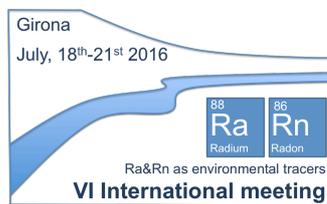
Continuous underground radon monitoring in boreholes, tunnels and springs is widely performed since several decades. Geophysical and environmental radon monitoring demand ruggedized detectors able to resist harsh conditions that may exist in the field. Radon signals in tunnels and boreholes measured using NaI gamma counting are more sensitive by 2-3 orders of magnitude than alpha counting beside of being more reliable and easy to use.

As the gamma radiation is emitted by radon decay products RDP in the soil solid phase, source-detector distance, soil radon emanation rate, scattering and attenuation of photons in the surrounding materials, considerably impact the overall counting efficiency.

Monte Carlo simulations allow estimation of the photon flux in the detector volume accordingly to the geometrical and physical characteristics of the measuring setup.

The purpose of this work is to model underground radon gamma signals using the Monte Carlo code MCNP4C. The results of the characterization of radon signals measured using NaI scintillation detectors in a laboratory column containing grinded phosphate rock are presented. The constant background level of each detector in the column and the volume of soil in the column that contributes to the radon gamma signal were determined and compared to measured values. An optimization of the detector energy window showed that photons with energy lower than 500 keV do not significantly increase the accuracy of the measurement. This may be attributed to the strong influence of the density of the materials surrounding the detector to the number of low energy photons from scattering events.

Preliminary results of the characterization of the measured gamma radon signal in boreholes in the field will also be presented.



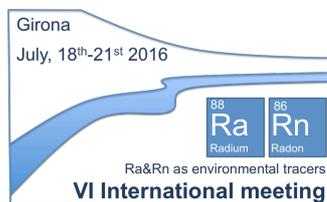
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P2.5 On the use of ²²²Rn as activity indicator for fault zones: the experience of UAB

Moreno^a, V., Bach^b, J., Zarroca^b, M., Font^a, Ll., Linares^b, R., Roqué^c, C.

^aUnitat de Física de les Radiacions, Dpt. de Física, Ed. Cc, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain; ^bUnitat de Geodinàmica Externa i d'Hidrogeologia, Dpt. de Geologia, Ed. Cs, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain; ^cGeodinàmica Externa, Dpt. de Ciències Ambientals, Universitat de Girona, 17071 Girona, Spain.

Since 2005 the radon group of UAB has been measuring soil ²²²Rn in different fault zones of Spain, with the aim of using this gas as an indicator of the potential seismic activity of faults. Our first studies consisted on analyzing data from integrated and continuous soil radon measurements using passive and active detectors along profiles perpendicular to the main faults. Later we incorporated additional analysis as punctual soil radon, thoron and CO₂ measurements, the electrical resistivity tomography technique (ERT) and radionuclide content of soil materials, which aided to improve significantly the data analysis. The first studied fault area is the Amer Fault, located in the north-east of Catalonia. This normal fault has shown recent seismic activity. In this region soil radon measurements exhibit a wide range of values, [1-150] kBq·m⁻³, and a very marked seasonal variation. In addition, average radon concentrations close to the main fault are higher, showing greater dispersion where the heterogeneity of the materials covering the fault affects significantly radon transport. Measured soil radon concentrations do not correlate with ²²⁶Ra content measured from the soil samples collected at the radon measurement points. A detailed study has been conducted for 4 years at the area where we recorded the highest average values (>60 kBq·m⁻³) and seasonal variation. A moderate correlation (r²=0.7) between daily mean values of soil radon and atmospheric temperature has been observed. The second studied region is located at the Central Pyrenees, where radon has been measured along a 5 km-long profile, which intersects two parallel normal faults: the North Maladeta Fault and the Tredós Fault, also considered potentially seismically active. The highest radon values, up to 75 kBq·m⁻³, have been recorded at the points where the profile intersects the faults. Additionally, in this region, groundwater shows anomalous high radon levels, up to 345 kBq·m⁻³. The third study site is the Alhama de Murcia Fault area, located at the eastern sector of the Béticas System mountain ranges, and which is considered the Iberian fault with the greatest seismic potential. There we analyzed two of the four different compressional fault segments characterized by different activity rates. In both monitored segments, average radon levels obtained are rather low: [5-12] kBq·m⁻³ on the El Saltador Lorca profile and [1-22] kBq·m⁻³ on the Alcantarilla profile; and no significant radon maxima near the main fault are observed. These results could be explained due to the different rock stress patterns observed in compressional faults as opposed to normal faults. As a conclusion, fault zones can present a wide range of geological characteristics that can lead to very different radon levels and dynamics. Important spatial and temporal soil radon variations can occur, even in the same region, so they should be taken into account when punctual soil radon measurements are just performed. To achieve clear conclusions about fault potential seismic activity, besides radon measurements, additional analysis becomes necessary.



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P2.6 Temporal Radon and Radium variations in the Lez karstic spring (South of France)

A. Molina Porras^{a,c,*}, J.L. Seidel^a, M. Condomines^b,

^a UMR HydroSciences, Montpellier Univ., France (jean-luc.seidel@umontpellier.fr); ^b UMR Géosciences, Montpellier Univ., France (condomines@gm.univ-montp2.fr); ^c University of Costa Rica, Costa Rica
(* corresponding author : arnold.molinaporras@ucr.ac.cr)

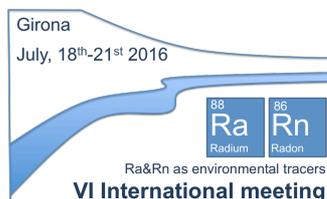
The Lez spring is the main perennial outlet of the Mediterranean Lez karst aquifer (South of France) and is characterized by a complex mixing of different types of water (shallow and deep mineralized fluxes), according to the hydrological conditions and an intense pumping regime (Batiot-Guilhe et al., 2015). The physico-chemical parameters and the mineralization of the Lez spring present large variations during the hydrological cycle. In particular, mineralized peaks appear during the recharge periods with water enriched in Cl, Sr, SO₄ Mg, Li, Ba and B. This mineralization suggests the involvement of evaporites or brines at depth. These waters, probably stored in a deep compartment (>1500m), reach the surface in significant amounts by a piston flow effect, detected by a short electrical conductivity peak (EC >850 μS/cm). But this hypothesis still needs to be confirmed.

The objective of this work was to study the radium quartet (²²⁸Ra, ²²⁶Ra, ²²⁴Ra and ²²³Ra) and radon (²²²Rn) temporal behaviour in the Lez spring and in other springs and wells of the Lez aquifer in combination with water chemistry, hydrological parameters and geological context in order to better characterize the origin of the different water masses and the dynamics of this karstic main outlet. Ra isotopes were measured by gamma spectrometry using MnO₂-fibers to concentrate radium, and radon was measured with an AlphaGUARD device coupled to an AquaKIT system.

²²⁸Ra and ²²⁶Ra activities in the Lez spring are correlated with EC. (²²⁸Ra/²²⁶Ra) ratios (0,68±0,04; n=15) are higher than those from the surrounding springs and wells (0,58±0,05; n=8) during the dry and most of the wet season, except when the mineralization peak occurs, with a (²²⁸Ra/²²⁶Ra) ratio decreasing to 0.6. (²²⁸Ra/²²⁶Ra) ratios in the Lez spring appear anti-correlated with EC. No such correlation is apparent for the ratios involving short-lived isotopes ²²⁴Ra and ²²³Ra. (²²⁴Ra/²²⁸Ra) of the Lez waters are always close to 1, but higher values (up to 1.65) are observed in a nearby spring, suggesting a possible derivation of ²²⁴Ra from ²²⁸Th adsorbed at shallow depth below the surface. Concerning radon, the model proposed by Savoy et al. (2011) for Rn behaviour in karstic springs (the higher the flood, the higher the radon concentration) is respected at the Lez spring during flood events, but the presence of higher Rn activities in the surrounding springs and wells during dry periods opens the possibility that, in some cases, higher radon activities could be due to shallow lateral inflows rather than rain water infiltration through the soil or epikarst fillings.

Batiot-Guilhe, C., Ladouche, B., Seidel, J. L., & Maréchal, J. C. (2015). Caractérisation hydrochimique et qualité des eaux de l'aquifère karstique du Lez. *Karstologia*, **62**, 23-32.

Savoy, L., Surbeck, H., & Hunkeler, D. (2011). Radon and CO₂ as natural tracers to investigate the recharge dynamics of karst aquifers. *Journal of Hydrology*, **406**(3), 148-157.



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P2.7 Ra isotopes as tracers of saline water from the potash mining industry

A. Hierro⁽¹⁾; J. García-Orellana^(1,2); V. Rodellas⁽³⁾; R. Espínola⁽⁴⁾; A. Folch⁽⁵⁾; F. Ribera⁽⁶⁾; N. Otero⁽⁷⁾; A. Soler⁽⁷⁾

⁽¹⁾ Departament de Física, Universitat Autònoma de Barcelona, Campus UAB, 08193 Bellaterra, Spain

⁽²⁾ Institut de Ciència i Tecnologia Ambientals (ICTA), Universitat Autònoma de Barcelona, Campus UAB, 08193 Bellaterra, Spain

⁽³⁾ Centre de Reserche et d'Enseignement de Géosciences de l'Environnement (CEREGE), Aix-Marseille Université, France

⁽⁴⁾ Water Catalan Agency

⁽⁵⁾ Hydrogeology Group, Dept. of Geotechnical Engineering and Geo-Sciences Universitat Politècnica de Catalunya

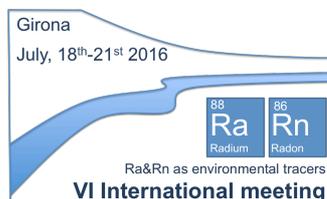
⁽⁶⁾ Fundación Centro Internacional de Hidrología Subterránea (FCIHS).

⁽⁷⁾ Grup de Mineralogia Aplicada i Geoquímica de Fluids, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Geologia, Universitat de Barcelona.

The middle section of the Llobregat and Cardener Rivers (Catalonia, NW Mediterranean Sea) is characterized by important potash mining. This activity produces large salt mine tailings that are usually stored at the surrounding of the mining sites, frequently with no waterproofing. Groundwater in this area presents high salinity (up to 21g Cl⁻ · L⁻¹), however, the origin of this salinity is controversial since it could be either attributed to the natural groundwater interaction with evaporitic formations or a consequence of potash mine tailings leaching. The hypothesis of this work is that Ra isotopes could help elucidating the origin of groundwater salinity. The disequilibrium between Ra isotopes provides relevant information on groundwater transit time, which is a valuable tool in order to determine the origin of salinity.

The results of ²²⁴Ra/²²⁸Ra and ²²³Ra/²²⁶Ra have allowed to distinguish two main groups of samples: i) samples with high ratios (up 7.97 for ²²⁴Ra/²²⁸Ra and 3.0 for ²²³Ra/²²⁶Ra) reveal short transit times and consequently a possible anthropogenic influence in the groundwater salinity from the mining tailings, and ii) samples with high ²²⁶Ra concentrations (up 700 Bq·m⁻³) and low ratios (²²⁴Ra/²²⁸Ra and ²²³Ra/²²⁶Ra values between 0.5 - 2.0 and around 0.046, respectively) indicate longer groundwater residence times suggesting a salt enrichment linked to natural interaction with evaporitic layers. These results are in good agreement with stable S isotopes values (δ³⁴S_{S04}), which show a distinctive isotopic signature: natural saline formations have a δ³⁴S_{S04} ranging from +11‰ to +14‰, and anthropogenic mine tailings have a δ³⁴S_{S04} ranging from +18‰ to +21‰).

In conclusion, Ra isotopes provide key information on groundwater transit time, which in combination with stable isotopes, helps to distinguish the origin of salinity in groundwater from potash mining areas.



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P2.8 Measurement of radium 226 and 228 in lake sediment pore waters by direct gamma spectrometry

Reyss, J. L.¹, Mangeret, A.², Garcia, M.², Stetten, L.^{2,3}, Seder-Colomina, M.², Morin, G.³, Thouvenot, A.⁴, Souhaut, M.⁵, van Beek, P.⁵

¹Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, F-91198, Gif-sur-Yvette, France

²Institut de Radioprotection et de Sureté Nucléaire, PRP-DGE, BP 17, 92262 Fontenay-aux-Roses

³Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR 7590 CNRS-UPMC-IRD-MNHR, 4 place Jussieu, 75252 Paris Cedex 6, France

⁴Université de Clermont-Ferrand, Athos Environnement, 63171 Aubière cedex

⁵LEGOS, Université de Toulouse, CNRS-IRD-CNES, 14 avenue Edouard Belin, Toulouse F-31400, France

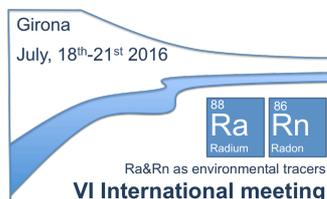
Uranium extraction activities took place from 1946 to 2001 and induced production of large quantities of radionuclide-enriched materials. Previous studies revealed that river and lake sediments downstream from former uranium mines constitute important long-term sources of natural radionuclides, including radium. Accumulation of radium isotopes in fresh sediment may be governed by several processes (adsorption onto particles, coprecipitation, diffusion...). However, very few studies investigated the fate of radium in modern sedimentary deposits, especially immediately after sediment deposition in lakes.

In order to better understand the radium distribution in these systems, we measured long-lived ²²⁶Ra ($T_{1/2}=1600$ y) and ²²⁸Ra ($T_{1/2}=5,75$ y) nuclides in lake sediment porewaters by non destructive gamma-spectrometry. The pore waters were extracted from the sediment in an anaerobic glove bag using microporous samplers. The water volume (14 to 33mL) was then reduced to 4 mL by evaporation at 70°C prior to analysis.

The main results of this study reveals that ²²⁶Ra vertical profile in porewaters extracted from the top 70 cm of the core mimics that of Fe and Ba distributions, increasing from 0.031 ± 0.003 Bq.L⁻¹ in surface to about 0.50 Bq.L⁻¹ at 40 cm depth. Deeper, the ²²⁶Ra activity remains constant within a one sigma counting statistic counting error.

The use of a very low background, high efficiency Germanium detector settled in the Underground Laboratory of Modane allowed, for the first time, measurement of ²²⁸Ra together with ²²⁶Ra in porewaters. The ²²⁸Ra vertical profile differs from that of ²²⁶Ra: it increases from 0.015 ± 0.005 Bq.L⁻¹ in surface to 0.160 ± 0.20 Bq.L⁻¹ at 40cm depth and decreases to 0.120 Bq.L⁻¹ at 65cm depth. The interpretation of both profiles may provide information on the mobility of Ra in porewaters and on the origin of Radium isotopes released from the sediment.

Assuming that the Ra isotopes have a similar behavior during the diagenetic process we plotted the ²²⁸Ra/²²⁶Ra ratio versus depth down core. The exponential decrease with increasing depth may thus be interpreted by the radioactive decay of ²²⁸Ra with time.



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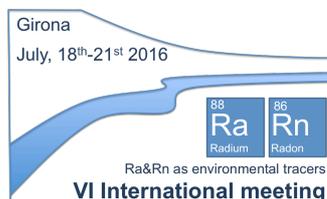
P2.9 Combining radon and carbon dioxide in small rivers to constrain hotspots of CO₂ degassing

Deirmendjian Loris¹, Voltz Baptiste¹, Chaillou Gwénaëlle², Abril Gwénaël¹

¹ UMR CNRS 5805 EPOC, Environnements et Paléoenvironnements océaniques et côtiers, Université de Bordeaux, France.

² Canada Research Chair in geochemistry of coastal hydrogeosystems, Département Biologie, Chimie, Géographie, Université du Québec à Rimouski, Qc, Canada.

River systems play a crucial role in the global carbon cycle. In regions where aquifers sustain rivers, the inputs of high pCO₂ groundwater significantly contribute to the water-to-air flux of CO₂ even if groundwater discharge rates are often low. Here, we combined in situ pCO₂ and radon (²²²Rn, a tracer for short-term processes at the groundwater-surface water interface) survey to quantify the role of rich CO₂ groundwater in the formation of hotspots of CO₂ degassing in the Leyre River, a lowland watershed in south-western France (~2141.4). Observations were performed along the watercourse in January and February 2016, a period of aquifer recharging and water table rising. In addition, a detailed survey was carried out along a 2.5 km-long headwater with 6 single stations to discretize the mode (e.g. point-source versus disseminated seepage) and locations of discharge. In groundwater end-members, CO₂ and ²²²Rn concentrations were one to two orders of magnitude higher than in surficial waters, showing that groundwater discharge influences the CO₂ distribution in the watershed. Our preliminary results highlight the role of headwaters as hotspots of CO₂ emission during the aquifer recharge: the concentrations of both CO₂ and ²²²Rn decreased from first order streams (~4235 ppm, ~2669 Bq/m³) to downstream (~2000 ppm, ~321 Bq/m³). The behavior of CO₂ and ²²²Rn along the headwater suggests that groundwater inflows were probably further upstream of our sampling points. A simple model based on ²²²Rn groundwater end-member decay matched well our observations. Our result reveal that the estimated transit time must be at least 5.4 d. Because the mean velocity deduced from stream flow measurements in the 2.5 Km-long section is ~0.5 m/s, the transit time is about 1.3h, indicating that ²²²Rn distribution is not only the result of radioactive decay. A ²²²Rn mass balance model will be presented and a special interest will be given to degassing processes over the transit.



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OCEAN PROCESSES

T3.1 ²²⁷Ac along GEOTRACES Transects in the Deep South Pacific and Preliminary Results for the Arctic

Doug Hammond¹, Matt Charette², Willard Moore³, Paul Henderson², Virginie Sanial^{2,4}, Lauren Kipp², Robert Anderson⁵, Francois Primeau⁶

¹Univ. Southern Calif., Los Angeles, CA, ² Woods Hole Oceanog. Inst., Woods Hole, MA ³ Univ. South Carolina, Columbia, SC, ⁴ LEGOS/CNRS, Observatoire Midi-Pyrénées, Toulouse, France, ⁵ Lamont-Doherty Earth Obs., Palisades, NY, ⁶ U.C. Irvine, Irvine, CA

²²⁷Ac (22 yr half life) diffuses from sediment and is mixed vertically and horizontally as it decays, providing a distribution that can be used to infer transport rates for other solutes in the deep ocean. Profiles were collected during the fall of 2013 at 19 stations along the US Peru-Tahiti GEOTRACES transect by pumping water through acrylic cartridges impregnated with MnO₂, to trap Ac Th, and Ra. Two cartridges were deployed in series to estimate extraction efficiency for each sample. Supported activity in the water column has been determined through measurement of its ²³¹Pa parent.

Profiles of excess ²²⁷Ac indicate several features of transport that are important across this transect: 1) Apparent vertical mixing rates from 1-D fits decrease as the water column stratification becomes more pronounced; 2) Integrated excess ²²⁷Ac in the water column increases with increasing distance from the East Pacific Rise (EPR), indicating that either the source function changes, or lateral diffusion dominates vertical diffusion as the EPR is approached, a result of increasing stratification in the waters near the ridge crest; 3) Most profiles show elevated activities near 2500-2600 m depth (sigma-theta 27.72), just below the ³He anomaly, indicating a source of ²²⁷Ac in the hydrothermal plume that can be traced as far as 152°W. The observed decrease can be used to estimate a 1-D horizontal velocity equivalent to about 0.4 cm/s, requiring about 40 years to travel from the EPR to 152°W. Comparison of the measurements below 2000 m to profiles generated with a whole ocean model (Devries and Primeau, 2011) that incorporates transport coefficients based on 14C, CFC, Temperature and salinity shows general agreement if the benthic source of ²²⁷Ac is uniform. However, there are some modest differences that suggest either the source function is not uniform, or deep benthic mixing rates differ slightly from the model parameters.

Analyses of samples collected during the US Arctic transect from Alaska to the North Pole are in progress. Preliminary results will be presented for comparison.

DeVries, T. and F. Primeau (2011) Dynamically and observationally constrained estimates of water-mass distributions and ages in the global ocean. *Journal of Physical Oceanography* 41 (12), 2381-2401



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T3.2 $^{224}\text{Ra}/^{223}\text{Ra}$ distribution in the benthic boundary layers of the continental slopes off Peru and Mauritania.

J. Scholten^a, P. Reichert^b, V. Liebetrau^c, B. Gasser^d, J. C. Miquel^d, A. Eisenhauer^c

^a Institute of Geosciences, Kiel University, Germany (js@gpi.uni-kiel.de)

^b Collaborative Research Center 754 (SFB754), Kiel, Germany

^c GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany

^d IAEA-EL Environment Laboratories, Monaco

Sediments in oxygen minimum zones (OMZ) may be an important sink and source for nutrients influencing the bioproductivity in the mixed layer. The benthic-pelagic solute fluxes are difficult to obtain. So far the most established methods to quantify this exchange are modelling of sediment pore water profiles, i.e. determining fluxes by a gradient-diffusion approach and benthic incubation chamber experiments. In this presentation we describe another method using the distribution of radium isotopes ^{224}Ra (half-life: 3.66 days) and ^{223}Ra (half-life: 11.4 days) between the surface sediments and the water column above. Our investigations concentrated on two continental slopes, off Peru (transect at 12 °S) and off Mauritania (transect at 18° N). Both continental margins are characterized by well-developed OMZ with water column oxygen concentrations less than 20 $\mu\text{mol/l}$ (Peru) and between 60 $\mu\text{mol/l}$ -120 $\mu\text{mol/l}$ (Mauritania).

For sampling of radium close to the sediment-water interface we used Mn-fibers which were attached to benthic landers. These landers were moored for ~ 24 hours at the sea floor in water depths between 65 m and 1025 m off Peru, and in water depths between 53 m and 1100 m off Mauritania. Radium sampling in the water column above the landers was conducted using in-situ filtration pumps equipped with Mn-cartridges. ^{223}Ra and ^{224}Ra were measured on-board the ship using a delayed coincidence counting system (RaDeCC).

Radium distributions indicated, both spatially and temporarily, a highly dynamic mixing environment of the water column above the seafloor along the Peruvian and Mauritanian continental slopes. Based on the $^{224}\text{Ra}/^{223}\text{Ra}$ distributions two mixing environments were observed: (i) Rapid near bottom mixing on time scales of a few days that (ii) differed from the water column above. $^{224}\text{Ra}/^{223}\text{Ra}$ -derived benthic nutrient fluxes at selected locations off Peru were within the same range as flux estimates based on microstructure and benthic chamber measurements.



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T3.3 Radium isotopes as tracers of water mass movement in the Western Arctic Ocean

Lauren Kipp^{1,2}, Matthew Charette¹, Willard Moore³, Paul Henderson¹, Doug Hammond⁴

¹Woods Hole Oceanographic Institution, Woods Hole, MA, USA

²Massachusetts Institute of Technology, Cambridge, MA, USA

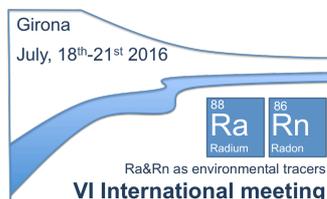
³University of South Carolina, Columbia, SC, USA

⁴University of Southern California, Los Angeles, CA, USA

We will present preliminary results of radium isotopes (^{226}Ra , ^{228}Ra , ^{224}Ra) measured on the recent US GEOTRACES Arctic Transect (GN01). Surface and water column samples were collected in the Makarov and Canada Basins between Dutch Harbor, Alaska, and the North Pole, greatly increasing the sampling resolution of Ra isotopes in the Western Arctic Ocean. As analyses of the water column samples are ongoing, we will focus on results from the high-resolution surface samples collected on this transect, and compare results to historical data collected in the Arctic.

Initial findings show that the highest ^{228}Ra activities (~ 20 dpm 100L^{-1}) and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (~ 2) are located near the North Pole, suggesting that the source of the water mass located at the Pole differs from that of the water below approximately 85°N . Similar activity ratios were observed by Rutgers van der Loeff et al. (2003) in the Kara and Laptev Seas, indicating that the water near the Pole may have been transported from these shelf seas, perhaps via the Transpolar Drift. Activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ and $^{228}\text{Th}/^{228}\text{Ra}$ will be used to help quantify the timescale of transport.

Rutgers van der Loeff, M., Kuhne, S., Wahsner, M., Holtzen, H., Frank, M., Ekwurzel, B., Mensch, M., Rachold, V., 2003. ^{228}Ra and ^{226}Ra in the Kara and Laptev seas. *Cont. Shelf Res.* 23, 113–124. doi:10.1016/S0304-4203(98)00070-X



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T3.4 Quantifying Shelf-Ocean Fluxes of Trace Elements and Isotopes Using Radium-228

M. Charette¹, P.J. Lam², M. Lohan³, and E.Y. Kwon⁴

¹Woods Hole Oceanographic Institution, USA

²University of California-Santa Cruz, USA

³University of Southampton, UK

⁴Seoul National University, Korea

Continental shelves and shelf seas play a central role in the global carbon cycle, however, their importance with respect to trace element and isotope (TEI) inputs to ocean basins is less well understood. Here, we present a proof-of-concept for a new method to estimate shelf TEI fluxes using ^{228}Ra ($T_{1/2}=5.75$ y), which is continuously supplied to the shelf from coastal aquifers, sediment porewater exchange, and rivers. The approach takes advantage of the global inverse model of Kwon et al. [2014], which focused on isolating the flux ^{228}Ra via submarine groundwater discharge to the ocean, but at its root was designed to estimate the total ^{228}Ra flux from all shelf sources required to balance the upper ocean ^{228}Ra inventory and decay. The model ^{228}Ra flux has the advantage of integrating the shelf source of ^{228}Ra over annual to decadal timescales, which averages out seasonal variability that hampers the use of nearshore ^{228}Ra gradients to estimate shelf ^{228}Ra fluxes directly. Model-derived shelf ^{228}Ra fluxes were combined with shelf TEI/ ^{228}Ra ratios measured during the U.S. GEOTRACES GA03 cruises to quantify TEI fluxes to the North Atlantic Ocean. The results from this new approach agree well with previous estimates for shelf Co, Fe, Mn, and Zn inputs to the North Atlantic and exceed published estimates of atmospheric deposition by factors of ~2-50.

Kwon, E.Y., G. Kim, F. Primeau, W.S. Moore, H. Cho, T. DeVries, J.L. Sarmiento, M.A. Charette, and Y. Cho. (2014) Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model. *Geophysical Research Letters*, **41**, 8438-8444.

T3.5 Shelf sediment trace metal fluxes to overlying waters and the open ocean

Amber Annett^{1,2}, Walter Geibert³, Antony Birchill⁴, Maeve Lohan^{4,5}, Will Homoky⁶,
Jessica Klar⁵, Peter Statham⁵, Dagmara Rusiecka⁵, Alex Thomas², Eric Achterberg^{5,7}

¹Now at: Rutgers University, New Jersey, USA; ²University of Edinburgh, Edinburgh, UK; ³Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany; ⁴University of Plymouth, Plymouth UK; ⁵University of Southampton, Southampton, UK; ⁶University of Oxford, Oxford, UK; ⁷GEOMAR Centre for Ocean Research, Kiel, Germany

Continental shelf sediments represent a major source of trace metals to the open ocean, playing an important role in cycling of the micronutrient iron (Fe). However, considerable uncertainties remain concerning the magnitude and variability of this source, including the seasonal variation in flux of Fe from sediments, the influence of sediment type, and time scale of subsequent offshore advection.

This study used naturally occurring isotopes of the radioactive element radium (Ra) to investigate sedimentary flux. Like Fe, Ra can accumulate in sediment pore waters and both elements can be released to the overlying water column by resuspension events and diffusion. Each of the four Ra isotopes decay at different known rates, facilitating the use of Ra as a tracer of source, transport into the overlying water column, and subsequent advection over multiple time and length scales.

We measured Ra and Fe concentrations across spring, summer and autumn above the Celtic Sea shelf and in pore waters, at sites spanning a range of sediment lithologies from mud to sand. Sediment incubations were used to study the coupled release of Fe and Ra from different sediment types, which can explain much of the regional Ra distribution. Off-shelf transport was assessed by 2D sections across the shelf break (Fig. 1), indicating speeds of 5.9 - 8.0 km·d⁻¹ for an intermediate nepheloid layer (INL) at ~400 m depth. We show that INLs identified in this study are enriched in Fe, manganese and cobalt, and further discuss seasonal variation in inventories and transport to explore the implications for release of Fe and other trace metals from continental shelf sediments on a larger scale.

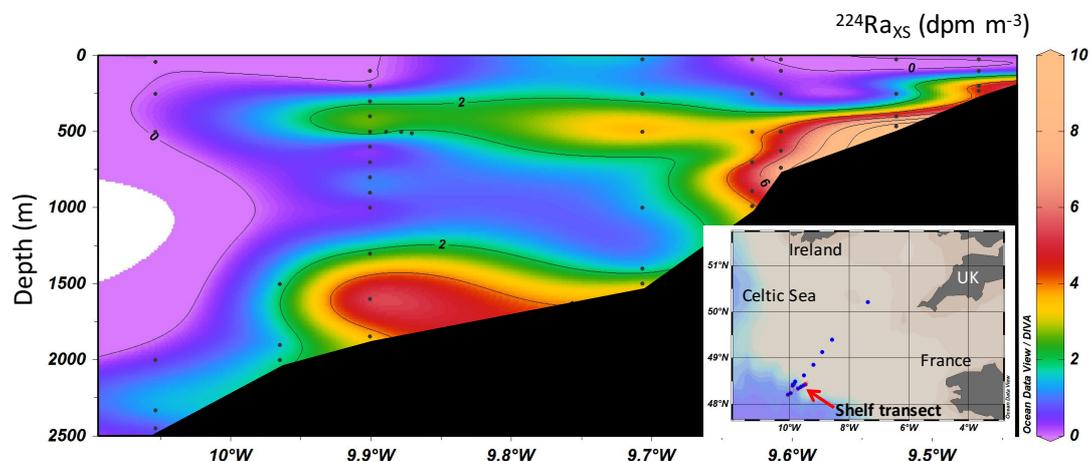
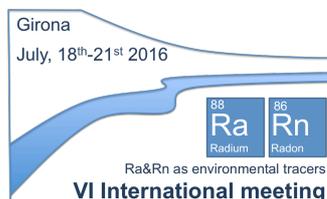


Figure 1: ²²⁴Ra-excess with depth along a Northeast Atlantic shelf-break transect in November 2014. Black dots indicate sampling depths; contour lines are drawn every 2 dpm·m⁻³. Inset map shows transect location in the Celtic Sea.



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T3.6 Long-lived Ra isotopes by counting or by mass spectrometry: What's the better method?

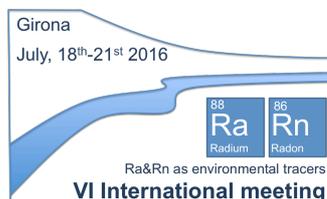
Walter Geibert

Alfred Wegener Institute, Bremerhaven, Germany

The radium isotopes ^{226}Ra and ^{228}Ra have traditionally been determined by counting methods, mostly by gamma counting, or via their shorter-lived daughter isotopes. With increasing sensitivity of mass spectrometers, in particular ICP-MS, attempts have been made to measure ^{226}Ra and ^{228}Ra via mass spectrometry. While the more abundant (in terms of atoms) ^{226}Ra is relatively well established and several datasets have been published, only a few analyses have been published for ^{228}Ra . ICP-MS methods, if fully developed, promise improved precision and therefore an extended applicability of radium isotopes. However, there are still a number of unresolved issues that prevent mass spectrometric techniques from being used more widely.

Complications often arise from (1) pre-concentration methods, often including manganese dioxide, and strontium or barium salts. (2) Separation of adsorbers and carriers from the Ra-containing solution (3) Availability of a ^{228}Ra -spike for isotope dilution methods and (d) Sensitivity of the mass spectrometer, which also needs to allow controlling possible interferences.

Here I will give an overview of the pros cons of counting vs. mass spectrometry, and discuss possible ways to address some of the key problems for radium measurements via ICP-MS.



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P3.1 Short lived Ra isotopes in the investigation of the influence of the Congo River on the South Atlantic Ocean

Lucia H. Vieira¹, Eric P. Achterberg¹, and Jan Scholten³

¹GEOMAR - Helmholtz Centre for Ocean Research Kiel, Germany.

³University of Kiel, Kiel, Germany

The circulation patterns of water masses in the SE Atlantic Ocean make of that region one of the highest productive areas of the world ocean. The Benguela is unique because it is bounded at both equatorward and poleward ends by warm-water systems, and it is fed by a mixture of saline Indian Ocean water - from the Agulhas Current - and fresher Subantarctic surface water - from ACC. In addition, the Benguela forms an important eastern boundary upwelling system. The region receives elemental inputs from eolian, benthic and riverine sources, such as that from the Congo River, which, in turn, has the second highest discharge ($39,866 \text{ m}^3 \cdot \text{s}^{-1}$). This large volume of water produces a vast fresh water plume reaching 700–800 km into the South Atlantic (Hopkins et.al., 2013). However, little is known about the elemental fluxes from the Congo River. Radium isotopes were employed in this study to trace the freshwater plume of the Congo River into the ocean and study the distribution and behavior of trace metals and isotopes (TEIs) in surface and deep waters of the Angola Basin. Radium isotopes were used as tracers because of their conservative behavior in seawater. Here we present the distribution of short-lived radium isotopes, ^{224}Ra and ^{223}Ra , which were measured onboard the ship using four Delayed Coincidence Counters (RaDeCC). The surface samples were obtained by filtering about 200 L of seawater over Mn-fibers, and samples from depth, including from the bottom depth, were obtained using in-situ pumps. This study is part of the international GEOTRACES program and the cruise carried out between November 21st to December 28th, 2015 onboard the German Research Vessel Meteor. The sampling took place on two east-west transects. The long lived radium isotopes (^{226}Ra and ^{228}Ra) will be determined by Element 2 HR-ICPMS.

References:

Hopkins, J., Lucas, M., Dufau, C., Sutton, M., Stum, J., Lauret, O., Channelliere, C. 2013. Detection and variability of the Congo River plume from satellite derived sea surface temperature, salinity, ocean colour and sea level. *Remote Sensing of Environment* 139 (2013) 365–385

P3.2 Radium isotopes (^{226}Ra & ^{228}Ra) along the GEOVIDE transect in the North Atlantic Ocean (GEOTRACES GA01)

Emilie Le Roy¹, Virginie Sanial², Matt Charette², Paul Henderson², Marc Souhaut¹, François Lacan¹, Pieter van Beek¹

¹LEGOS, Observatoire Midi-Pyrénées, Toulouse, France

²Woods Hole Oceanographic Institute Woods Hole, Woods Hole, MA 02543, USA

In this study, we report activities of radium isotopes (^{226}Ra , $T_{1/2}=1602$ y; ^{228}Ra , $T_{1/2}=5,75$ y) determined along the GEOTRACES (GA01) section conducted in the North Atlantic (May-July 2014; Lisbon, Portugal-St John, Canada).

To determine ^{226}Ra activities, relatively small volumes of seawater were collected at each station (one Niskin bottle per sample), passed through Mn-fibers and analyzed using the radon emanation technique. This method allowed us to build vertical profiles of ^{226}Ra activities with a relatively high vertical resolution (up to 22 depths per station, using a single rosette at each station). Apart from the ^{226}Ra section, the ^{226}Ra data will allow us to determine the yield of Ra fixation onto the Mn-cartridges that were mounted onto *in situ* pumps in order to determine vertical profiles of ^{228}Ra along the same transect.

We will present Ra activities obtained in contrasting biogeochemical regions of the North Atlantic: the Iberian margin, the West European Basin, Reykjanes Ridge, the Irminger Sea, the Greenland margin and the Labrador Sea. These regions strongly differ in terms of boundary inputs, biogeochemistry and deep water formation. Finally, we will also report ^{226}Ra activities determined in suspended particles along this section.

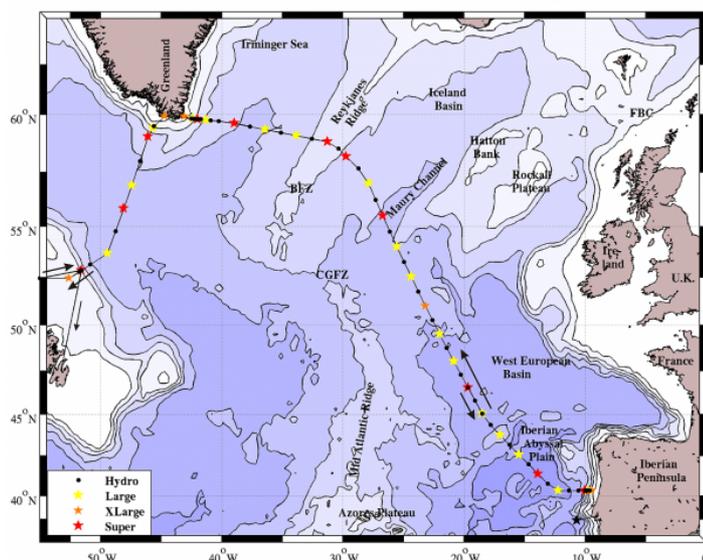
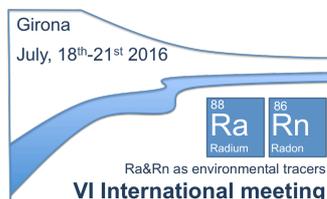


Figure 1: Geovide section conducted in the North Atlantic (GEOTRACES, GA01).



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P3.3 The radium quartet (^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra) in the plume of the Amazon river

Van Beek, Pieter¹; Souhaut, Marc¹; Moore, Willard²; De Oliveira, Joselene³; Seyler, Patrick⁴; Jeandel, Catherine¹

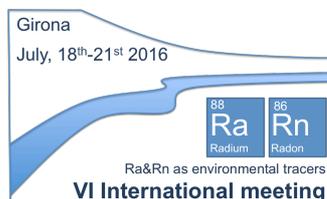
¹Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (LEGOS), Toulouse, France.

²Department of Earth and Ocean Sciences, University of South Carolina, Columbia, USA

³Laboratório de Radiometria Ambiental, Centro de Metrologia das Radiações, IPEN, São Paulo, Brasil

⁴now at Hydrosiences (HSM), Montpellier, France

We report radium activities (^{223}Ra , ^{224}Ra , ^{226}Ra , ^{228}Ra) that were determined in the Amazon estuary and in the plume of the Amazon river that extends off the coasts of Brazil and French Guyana into the Atlantic Ocean. This study reports activities that were determined in the framework of two different projects that took place in years 1989-91 (AMASSEDS) and later in years 2007-08 (AMANDES project). The Ra isotopes that are released into the dissolved phase when the freshwaters of the Amazon river enter into the saline waters of the Atlantic Ocean can be used to trace the fate of the Amazon plume off the Brazilian coast. We used the $^{224}\text{Ra}/^{223}\text{Ra}$ and $^{224}\text{Ra}/^{228}\text{Ra}$ ratios of water samples collected along the Amazon plume to estimate the transit time of the waters entering into the Atlantic Ocean and to provide information on the residence time of these waters on the Brazilian continental shelf.



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P3.4 The MARiS database: operation, radium data summary and future development

Paul J. Morris, Iolanda Osvath, Paul McGinnity, Hussein Ramadan

IAEA, Environment Laboratories, 98000 Monaco

The MARiS (MARine Information System) database is an open-access database of radionuclides in the World's oceans that is hosted and maintained by the IAEA (International Atomic Energy Agency). With currently over 173,500 marine radioactivity measurements, representing more than 60 different radionuclides or radionuclide ratios in seawater, biota, seabed sediments, and suspended matter, the database is unique in the context of the marine environment. MARiS provides an open-access data resource for scientists, policymakers and the general public that can be used for radiological environmental assessments, spatial and temporal change investigations, contamination event analysis, and can provide data to validate models. The MARiS database is compiled from an IAEA in-house database called GLOMARD (GLOBAL MARine Radioactivity Database), which is the primary repository for marine radioactivity measurements curated by the IAEA. Through the MARiS website, data can be searched for using various criteria, for example ocean region, matrix, isotope, date or depth.

Here, we will present an introduction to the MARiS database, the approach to our database governance, and how to search and downloaded data. A summary of the radium data contained in MARiS will be presented to inform the radium community of this open-access resource. Furthermore, the IAEA would like to raise awareness of MARiS as an archival tool for marine radionuclide data that is available to all IAEA Member States. Finally, an overview of database and website development will be presented.