U/Th Series Radionuclides as Coastal Groundwater Tracers

P. W. Swarzenski

U.S. Geological Survey, 600 4th Street South, St. Petersburg, Florida 33701

Received April 7, 2006

Contents

1. Introduction

The study of coastal groundwater has recently surfaced as an active interdisciplinary area of research, driven foremost by its importance as a poorly quantified pathway for subsurface material transport into coastal ecosystems.[1−10] Key issues in coastal groundwater research include a complete geochemical characterization of the groundwater(s);[11−13] quantification of the kinetics of subsurface transport, including rock−water interactions;[14−18] determination of groundwater ages;[19−20] tracing of groundwater discharge into coastal waters using radiochemical fingerprints;[21−24] and an assessment of the potential ecological impact of such subsurface flow to a receiving water body.[25−29] For such applications, the isotopic systematics of select naturally occurring radionuclides in the U/Th series has proven to be particularly useful. These radionuclides (e.g., U, Th, Ra, and Rn) are ubiquitous in all groundwaters and are each represented by several isotopes with widely different half-lives and chemistries (Figure 1). As a result, varied biogeochemical processes occurring over a broad range of time scales can thus be studied.

In source rock, most U/Th series isotopes are in secular equilibrium; that is, the rate of decay of a daughter isotope is equal to that of its radiogenic parent, and so will have equal activities (in this context, the specific activity is simply a measure of the amount of radioactivity per unit amount).[20,30,31] In contrast, these nuclides exhibit strong fractionations within the surrounding groundwaters because of their respective physicochemical differences.[32,33] Disequilibria in U/Th series radionuclides can thus be used to identify distinct water masses, quantify release rates from source rocks,[34,35] assess groundwater migration rates,[36,37] and assess groundwater discharge rates in coastal waters. Large isotopic variations also have the potential for providing precise fingerprints for groundwaters from specific aquifers[38] and have been explored as a means for calculating groundwater ages and estuarine water mass transit times.[29,39−43]

The highly fractionated nature of U/Th series nuclides in groundwater[11,14,19,20,33,44−46] is illustrated by the range in some measured activities (Figure 2). Highest activities are typically observed for ^{222}Rn, reflecting the inert nature of this noble gas.[47−49] Groundwater ^{222}Rn ($t_{1/2} = 3.8$ days) activities are thus controlled only by rapid in situ decay (Table 1) and production within host rocks, without the added complications of reversible removal via adsorption or precipitation. Uranium, which is soluble as U(VI) in oxidizing waters, is present in intermediate activities in groundwaters that are moderated by redox-initiated removal onto aquifer rocks.[50] The alkaline earth Ra and, to a greater extent, the less soluble actinide Th are readily removed from groundwater by water−rock interactions and so are strongly depleted.[51,52] Both of these elements have very short-lived as well as longer-lived isotopes, and so their isotope compositions reflect processes over a range of time scales.

Peter W. Swarzenski received his education in chemical oceanography from the University of Colorado−Boulder as well as Louisiana State University and is currently a staff oceanographer at the U.S. Geological Survey office in St. Petersburg, FL. His specialty includes the use of U/Th series isotopes to examine a suite of coastal processes, including (1) submarine groundwater discharge, (2) river–ocean mixing and exchange processes across land–sea margins, and (3) coastal sediment dynamics. Currently he is involved in projects that address coastal groundwater fluxes into estuaries from Florida to California and abroad. Dr. Swarzenski is also involved in projects on the Louisiana shelf that address the delivery of sediment-hosted contaminants and historic hypoxia.

10.1021/cr0503761 CCC: $65.00
Published on Web 01/20/2007

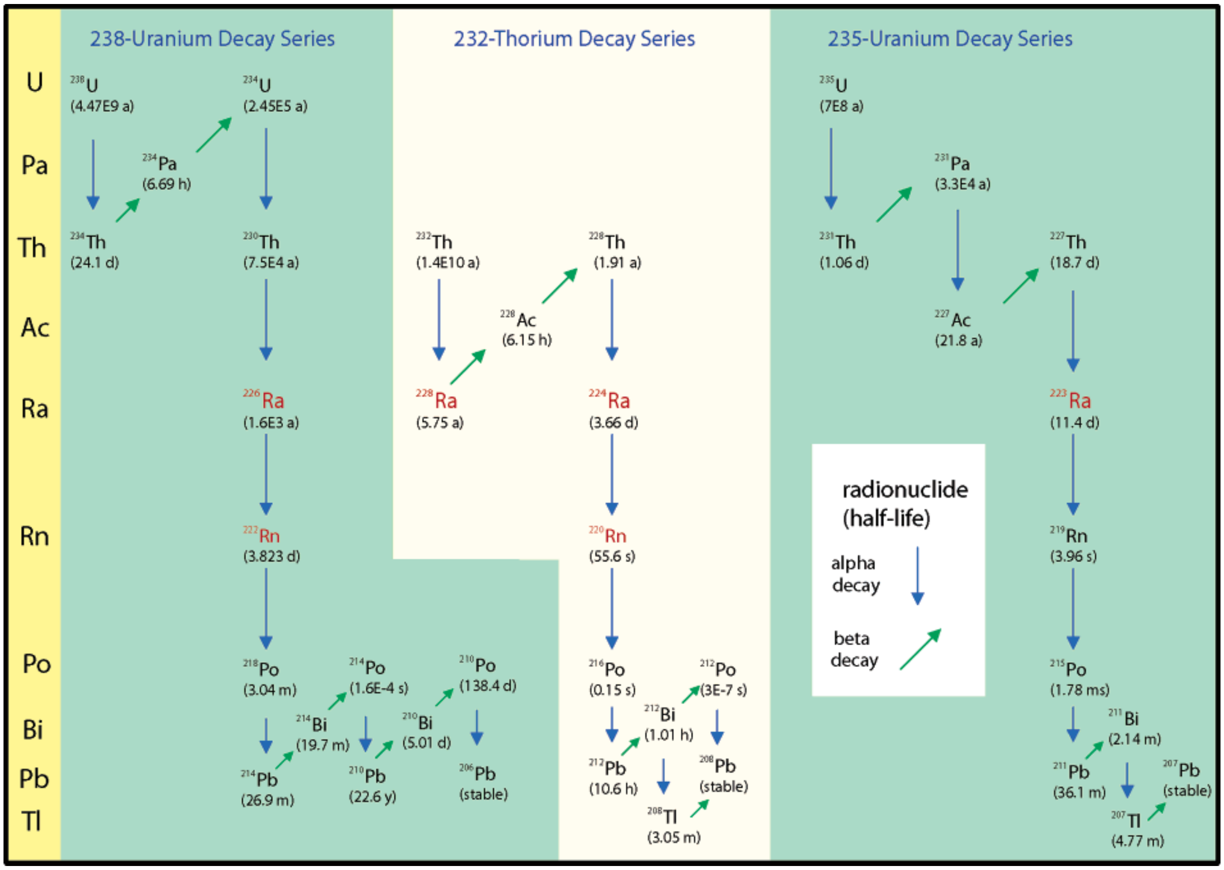

Figure 1. Schematic of the ^{238}U, ^{232}Th, and ^{235}U decay chains.

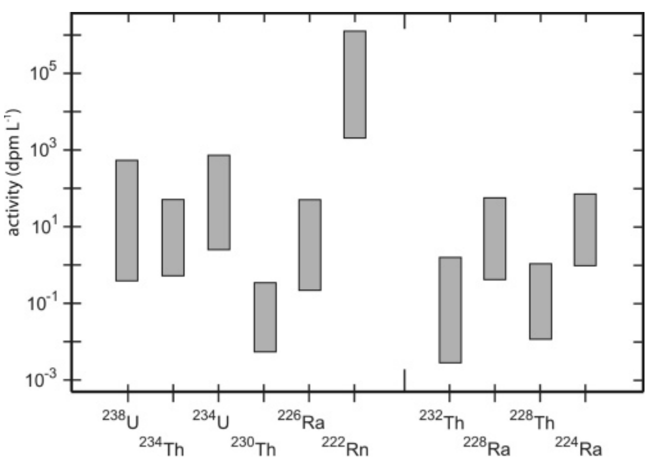

Figure 2. Comparison of select U/Th series radionuclide activities in select groundwater samples (after Porcelli and Swarzenski[18]). Data have been collated from Krishnaswami et al.,[14] Luo et al.,[162] and Tricca et al.[12]

Many studies have evaluated the behavior of select radionuclides in groundwater and surface water systems.[19,20,31] Recent advances in high-precision mass spectrometry[53,54] have opened new possibilities for more subtle interpretations in select long-lived U/Th series isotopes, such as U, Ra, Pa, and Th.[55] However, these techniques have yet to be fully developed, and as a consequence, such data remain largely scarce and underutilized. Although many different approaches have been developed to study radionuclide behavior in groundwater, all are based on principles of radioactive production and decay[19] and knowledge of source terms from weathering and recoil processes, as well as removal terms from the interaction with aquifer host rock surfaces by sorption and precipitation.[18]

Table 1. Select U/Th Series Radionuclides Useful for Coastal Groundwater Studies (After Porcelli and Swarzenski)[a]

radio-nuclide	$t_{1/2}$	factors controlling groundwater activities
^{238}U	4.47 × 10^{9} years	weathering, adsorption
^{234}Th	24.1 days	recoil, strong adsorption, decay
^{234}U	2.45 × 10^{5} years	weathering, adsorption
^{230}Th	7.57 × 10^{4} years	recoil, weathering, strong adsorption
^{226}Ra	1.60 × 10^{3} years	recoil, strong adsorption, decay, surface production
^{222}Rn	3.823 days	recoil, decay, surface production
^{210}Pb	22.6 years	recoil, strong adsorption, decay
^{232}Th	1.4 × 10^{10} years	weathering, strong adsorption
^{228}Ra	5.75 years	recoil, strong adsorption, decay, surface production
^{228}Th	1.91 years	recoil, strong adsorption, decay, surface production
^{224}Ra	3.66 days	strong adsorption, decay, surface production
^{220}Rn	55.6 s	recoil, decay, surface production
^{235}U	7.13 × 10^{8} years	weathering, adsorption
^{227}Th	18.7 days	recoil, strong adsorption, decay, surface production
^{223}Ra	11.7 days	recoil, strong adsorption, decay, surface production

[a] Adapted with permission from ref 18. Dpm is decays per minute (60 dpm = 1 Bq).

This review is structured to present first a brief description of the background, driving forces, scales, and ecological significance of submarine groundwater discharge. Following this, a description of the geochemistry and behavior of select

Figure 9. Near-continuous ^{222}Rn activities (dpm L^{-1}) measured using six Rn detectors plumbed in parallel in Biscayne Bay, Florida (from Swarzenski et al. *Novel Geophysical and Geochemical Techniques To Study Submarine Groundwater Discharge in Biscayne Bay, FL*; U.S. Geological Survey Fact Sheet 3117; Washington, DC, 2004).

as many as 12 readings per hour for typical coastal water Rn activities, with a precision of ∼12%. Figure 9, for example, shows results from such a nearly continuous ^{222}Rn survey conducted using six detectors in Biscayne Bay, Florida. Highest radon activities (∼11 dpm L^{-1}) relative to background values of 2−3 dpm L^{-1} were observed off Cutler Ridge, where Kohout[187] investigated subsurface freshwater/saltwater mixing dynamics and enhanced SGD.

Moore[4,40,41,188] developed an intriguing method to determine the apparent ages of freshened coastal water masses based on the activity ratio of the two short-lived Ra isotopes,^{223}Ra and ^{224}Ra. Assuming that the groundwater ^{224}Ra/^{223}Ra$_{gw}$ activity ratio remains constant and that the coastal water column activity ratio changes only by radioactive decay, then apparent coastal water mass ages can be calculated as

$$\left[\frac{_{xs}{}^{224}\mathrm{Ra}}{^{223}\mathrm{Ra}}\right]_{estu} = \left[\frac{^{224}\mathrm{Ra}}{^{223}\mathrm{Ra}}\right]_{gw} \frac{e^{-\lambda_{224}t}}{e^{-\lambda_{223}t}} \qquad (3)$$

where [$_{xs}{}^{224}$Ra/^{223}Ra]$_{estu}$ is the observed excess activity ratio in a coastal water, [^{224}Ra/^{223}Ra]$_{gw}$ is the average groundwater activity ratio, λ_{223} is the decay constant for ^{223}Ra (0.0608 day^{-1}), λ_{224} is the decay constant for ^{224}Ra (0.191 day^{-1}), and *t* is the calculated time elapsed between the groundwater activity ratio and the observed activity ratio. The ^{224}Ra/^{223}Ra activity ratio must therefore decrease by the apparent half-

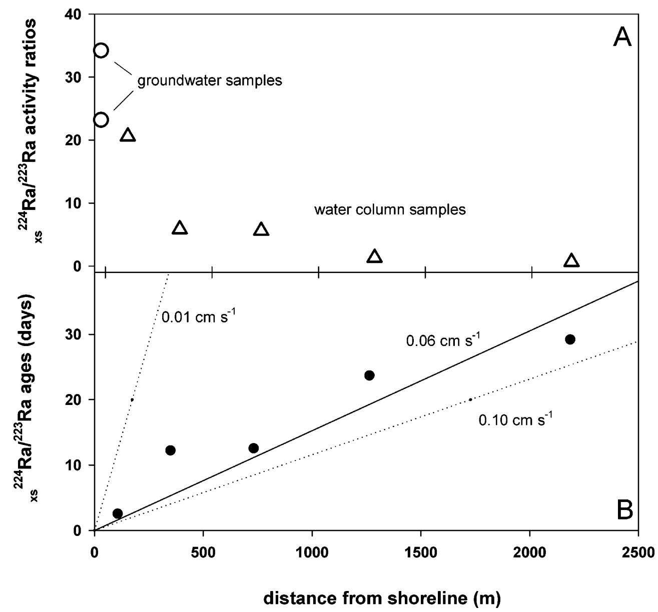

Figure 10. (A) ^{224}Ra/^{223}Ra activity ratios as a function of distance (m) along a shore-perpendicular transect from the mean high-water line at Santa Barbara beach, California, offshore. (B) Apparent ages of coastal waters off Santa Barbara, CA, as derived using ^{224}Ra/^{223}Ra activity ratios. From (B), water mass mixing velocities can be derived (i.e., 0.06 cm s^{-1}).

life of 5.4 days, so that older waters will have lower ^{224}Ra/^{223}Ra activity ratios. Ages calculated with ^{223,224}Ra are based on exponential decay laws rather than linear mixing and, thus, should be reported as apparent, not true, ages. Nonetheless, they do reflect a relative time history of dynamic coastal water masses that cannot be readily obtained using other techniques. These activity ratios may also be useful in identifying and quantifying groundwater-borne water from coastal water masses. Figure 10A shows $_{xs}{}^{224}$Ra/^{223}Ra activity ratios (AR) in two groundwater samples (average AR = 28.72) and five surface water column samples in the waters off Santa Barbara, CA. In these surface waters, this activity ratio decreased systematically with an increase in distance from shore. The $_{xs}{}^{224}$Ra/^{223}Ra activity ratio of the most inshore sample was closest to the average groundwater AR value, which suggests that the source of groundwater is most proximal to the shoreline. The most offshore sample had an $_{xs}{}^{224}$Ra/^{223}Ra AR of 0.64. Solely on the basis of these AR values, there appears to be little evidence coastal groundwater, with a unique isotopic composition, is being discharged beyond ∼700 m. As expected, the Ra-derived apparent ages of surface waters increased with increasing distance from the shoreline (Figure 10B). Given the sensitivity of this Ra technique, waters within the harbor proper are roughly 2 days old and approach an age of 30 days at the most distal site. A plot of distance from shoreline versus $_{xs}{}^{224}$Ra/^{223}Ra AR suggests that the coastal waters directly off Santa Barbara are being mixed at an average, apparent velocity of ∼0.6 cm s^{-1}.

Results from a 30-min averaged time-series experiment (^{222}Rn inventory, dpm m^{-2}, plotted as a function of time, min) in Santa Barbara harbor are shown in Figure 11. Where systematic increases in the ^{222}Rn inventory were observed, a linear regression was used to calculate respective ^{222}Rn fluxes (dpm m^{-2} min^{-1}). If one assumes that these observed fluxes are due solely to advection of Rn-rich coastal groundwater (the activity of ^{222}Rn in two shallow, coastal well samples ranged from 600 to 1000 dpm L^{-1}), one can

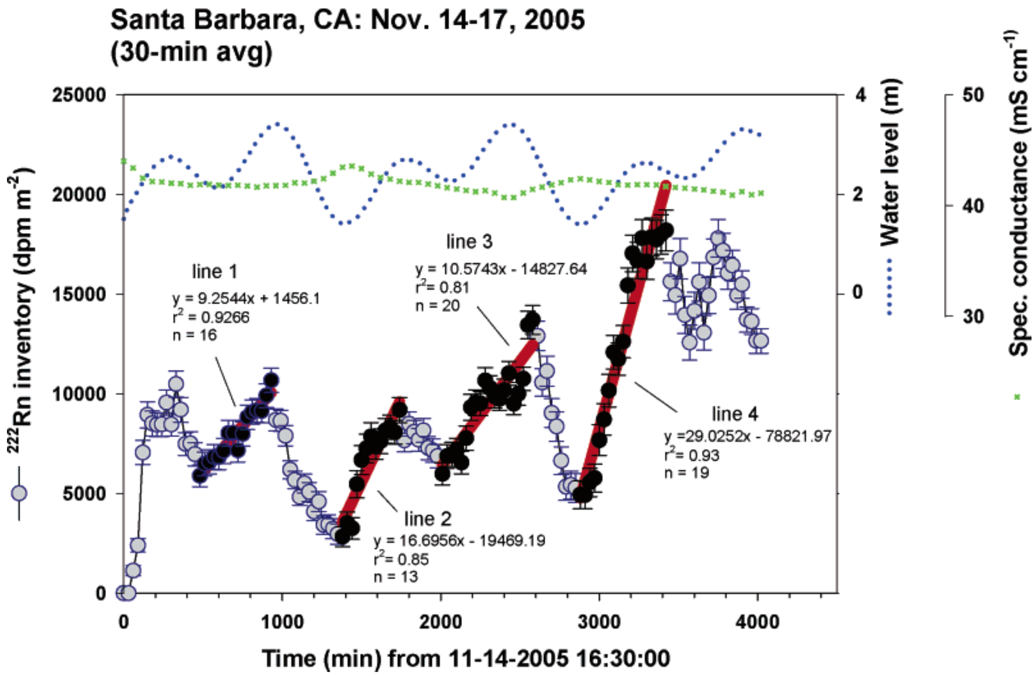

Figure 11. Three-day time series of ^{222}Rn inventories (dpm m^{-2}) as a function of time (min) elapsed within surface waters of the Santa Barbara, CA, harbor. Also shown are harbor surface water level (m) and specific conductance (mS cm^{-1}) values. Dark circles denote respective points used for the linear regressions that yield ^{222}Rn fluxes (dpm m^{-2} min^{-1}). See text for further detail on the derivation of first-order submarine groundwater discharge rates from such ^{222}Rn fluxes.

estimate a range of first-order SGD by dividing the fluxes by the measured groundwater activities. Such an approach yielded average SGD rates in Santa Barbara harbor that ranged from 2 to 6 cm day^{-1}.

5. Future Studies

Recent studies of submarine groundwater discharge into coastal waters indicate that select long-lived and short-lived U/Th series isotopes show great promise as new tools to directly examine and quantify fluid exchange processes across the sediment−water interface. As new detection methods and further field validation strategies develop, for example, in situ ^{222}Rn monitors[90] and delayed counting techniques, coastal scientists will be able to realistically identify and quantify SGD and associated fluxes into receiving coastal water bodies. Where previous studies have reported exchange rates based solely on information derived from single cores or benthic flux chambers under one small “footprint”, these new U/Th series methods can uniquely provide more synoptic, large-scale information. Often, it is these larger scale results that resource managers seek.

Ideally, a thorough SGD study should begin with a reconnaissance survey that includes geophysical streaming resistivity and nearly continuous ^{222}Rn work to identify sites of enhanced fluid exchange across the sediment−water interface. Once such sites are established, direct measurements of this exchange via autonomous seepage meters and numerical modeling efforts to link coastal observations to a larger hydrogeologic framework should complement the use of U/Th series geochemical tracers. In concert, such an approach provides a powerful diagnostic suite of tools for regional scale SGD investigations.

Considerable advances continue to be made in the application of radionuclide tracers in coastal aquifer studies. Clearly, further studies are required to examine, for example, precise mechanisms of Rn and Ra release during subsurface fresh water/seawater mixing and tidally driven water level fluctuations, to further constrain the controlling processes both on land and in the sea, and to refine the analytical methods (e.g., development of diffusion coils to concentrate Rn in water samples would eliminate the use of pumps and water/air exchangers). Although the use of Ra and Rn as quantitative coastal groundwater tracers has matured considerably during the past decade, placing these results and interpretations into a broader framework that covers a wide range of hydrogeologic settings may eventually yield a realistic typology of submarine groundwater discharge.

6. Acknowledgments

The preparation of this paper would not have been possible without the support and assistance of many colleagues. I am particularly grateful to ongoing collaborations with W. C. Burnett (FSU) and his past and present students, who have unraveled many novel U/Th series tracer methods to interpret and quantify rates of coastal groundwater discharge. Jason Greenwood, Chris Reich, Marci Marot, and Brian Blake-Collins assisted in the field and laboratory. Theresa Burress assisted in the editing of the manuscript. I gratefully recognize the continued support from the U.S. Geological Survey Coastal and Marine Geology Program. Reviews by Richard Poore (USGS) and two anonymous reviews are greatly appreciated. The use of trade, firm, and brand names is for identification purposes only and does not constitute endorsement by the U.S. government.

7. References

(1) Burnett, W. C. *EOS* **1999**, *80*, 13.
(2) Burnett, W. C.; Cable, J. E.; Corbett, D. R. In *Land and Marine Hydrogeology*; Taniguchi, M., Wang, K., Gamo, T., Eds.; Elsevier: Amsterdam, The Netherlands, 2003; pp 25−43.
(3) Church, T. M. *Nature* **1996**, *380*, 579.
(4) Moore, W. S. *Nature* **1996**, *380*, 612.
(5) Moore, W. S. *Mar. Chem.* **1999**, *65*, 111.

(6) Shaw, T. J.; Moore, W. S.; Kloepfer, J.; Sochaski, M. A. *Geochim. Cosmochim. Acta* **1998**, *62*, 3047.
(7) Taniguchi, M. *Geophys. Res. Lett.* **2002**, *29*, 10.1029/2002GL014987.
(8) Taniguchi, M.; Burnett, W. C.; Cable, J. E.; Turner, J. V. *Hydrol. Proc.* **2002**, *16*, 2115.
(9) Younger, P. L. *Nature* **1996**, *382*, 121.
(10) Zektser, I. S.; Loaiciga, H. A. *J. Hydrol.* **1993**, *144*, 405.
(11) Hussain, N. *Geophys. Res. Lett.* **1995**, *22*, 1521.
(12) Tricca, A.; Wasserburg, G. J.; Porcelli, D.; Baskaran, M. *Geochim. Cosmochim. Acta* **2001**, *65*, 1187.
(13) Zukin, J. G.; Hammond, D. E.; Ku, T. L.; Elders, W. A. *Geochim. Cosmochim. Acta* **1987**, *51*, 2719.
(14) Krishnaswami, S.; Graustein, W. C.; Turekian, K. K.; Dowd, F. *Water Resour. Res.* **1982**, *6*, 1663.
(15) Rama, P. S.; Moore, W. S. *Geochim. Cosmochim. Acta* **1984**, *48*, 395.
(16) Suksi, J.; Rasilainen, K.; Casanova, J.; Ruskeeniemi, T.; Blomqvist, R.; Smellie, J. A. T. *J. Contam. Hydrol.* **2001**, *47*, 187.
(17) Torgerson, T.; Turekian, K. K.; Turekian, V. C.; Tanaka, N.; DeAngelo, E.; O'Donnell, J. *Cont. Shelf Res.* **1996**, *16*, 1545.
(18) Porcelli, D.; Swarzenski, P. W. *Rev. Mineral. Geochem.* **2003**, *52*, 317.
(19) Osmond, J. K.; Cowart, J. B. In *Uranium-Series Disequilibrium: Application to Environmental Problems*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, U.K., 1982; pp 202−245.
(20) Osmond, J. K.; Cowart, J. B. In *Uranium-Series Disequilibrium*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, U.K., 1992; pp 290−334.
(21) Krest, J. M.; Moore, W. S.; Gardner, L. R. *Global Biogeochem. Cycles* **2000**, *14*, 167.
(22) Swarzenski, P. W.; Reich, C. D.; Spechler, R. M.; Kindinger, J. L.; Moore, W. S. *Chem. Geol.* **2001**, *179*, 187.
(23) Yang, H-S.; Hwang, D.-W.; Kim, G. *Mar. Chem.* **2002**, *78*, 1.
(24) Moore, W. S.; Krest, J.; Taylor, G.; Roggenstein, E.; Joye, S.; Lee, R. *Geophys. Res. Lett.* **2002**, *29*, 10.1029/2002GL014923.
(25) Johannes, R. E. *Mar. Ecol. Prog. Ser.* **1980**, *3*, 365.
(26) Valiela, I.; D'Elia, C. *Biogeochemistry*; Groundwater Inputs to Coastal Waters, Special Issue 10; Springer: Berlin, Germany, 1990.
(27) Simmons, G. M., Jr. *Mar. Ecol. Prog. Ser.* **1992**, *84*, 173.
(28) Kim, G.; Swarzenski, P. W. In *Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis*; Liu, K.-K., Atkinson, L., Quinones, R., Talaue-McManus, L., Eds.; Springer-Verlag: New York, 2006.
(29) Swarzenski, P. W.; Orem, W. G.; McPherson, B. F.; Baskaran, M.; Wan, Y. *Mar. Chem.* **2006**, *101*, 248−265.
(30) Bourdon, B.; Turner, S.; Lundstrom, C.; Henderson, G. *Rev. Mineral. Geochem.* **2003**, *52*, 1.
(31) Gascoyne, M. In *Uranium-Series Disequilibrium*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, U.K., 1992; pp 34−61.
(32) Hussain, N.; Krishnaswami, S. *Geochim. Cosmochim. Acta* **1980**, *44*, 1287.
(33) Ivanovich, M. *Radiochim. Acta* **1991**, *52/53*, 257.
(34) Henderson, G. M.; Slowey, N. C.; Naddad, G. A. *Earth Planet. Sci. Lett.* **1999**, *169*, 99.
(35) Webster, I. T.; Hancock, G. J.; Murray, A. S. *Geochim. Cosmochim. Acta* **1995**, *59*, 2469.
(36) Copenhaver, S. A.; Krishnaswami, S.; Turekian, K. K.; Epler, N.; Cochran, J. K. *Geochim. Cosmochim. Acta* **1993**, *57*, 597.
(37) Roback, R. C.; Johnson, T. M.; McLing, T. L.; Murrell, M. T.; Luo, S. D.; Ku, T. L. *Geol. Soc. Am. Bull.* **2001**, *113*, 1133.
(38) Moore, W. S. *Biogeochemistry* **2003**, *66*, 75.
(39) Charette, M. A.; Buesseler, K. O.; Andrews, J. E. *Limnol. Oceanogr.* **2001**, *46*, 465.
(40) Moore, W. S. *Cont. Shelf Res.* **2000a**, *20*, 1993.
(41) Moore, W. S. *J. Geophys. Res.* **2000b**, *105*, 22117.
(42) Kelly, R. P.; Moran, S. B. *Limnol. Oceanogr.* **2002**, *47*, 1796.
(43) Swarzenski, P. W.; Reich, C.; Kroeger, K.; Baskaran, M. Ra and Rn isotopes as natural tracers of submarine groundwater discharge in Tampa Bay, FL. *Mar. Chem.* **2007**, in press.
(44) Osmond, J. K.; Cowart, J. B. In *Environmental Tracers in Subsurface Hydrology*; Cook, P., Herczeg, A., Eds.; Kluwer Academic Publishers: Boston, MA, 2000; pp 290−333.
(45) Banner, J. L.; Chen, J. H.; Wasserburg, G. J.; Moore, C. H. *Earth Planet. Sci. Lett.* **1990**, *101*, 296.
(46) Ku, T.-L.; Luo, S.; Leslie, B. W.; Hammond, D. E. In *Uranium-Series Disequilibrium*; Ivanovich, M., Harmon, R. S., Eds.; Clarendon Press: Oxford, U.K., 1992; pp 631−668.
(47) King, P. T.; Michel, J.; Moore, W. S. *Geochim. Cosmochim. Acta* **1982**, *46*, 1173.
(48) Cable, J. E.; Burnett, W. C.; Chanton, J. P.; Weatherly, G. L. *Earth Planet. Sci. Lett.* **1996**, *144*, 591.
(49) Krishnaswami, S.; Bhushan, R.; Baskaran, M. *Chem. Geol.* **1991**, *87*, 125.
(50) Short, S. A.; Lowson, R. T. *Geochim. Cosmochim. Acta* **1988**, *52*, 2555.
(51) Dickson, B. L. In *The Environmental Behavior of Radium*; IAEA Technical Reports Series 310; International Atomic Energy Agency: Vienna, Austria, 1990; Vol. 1, pp 335−372.
(52) Lieser, K. H.; Hill, R. *Radiochim. Acta* **1992**, *56*, 141.
(53) Povinec, P. P.; La Rosa, J.; Lee, S.-H.; Mulsow, S.; Osvath, I.; Wyse, E. *J. Radioanal. Nucl. Chem.* **2001**, *248*, 713.
(54) Goldstein, S. J.; Stirling, C. H. *Rev. Mineral. Geochem.* **2003**, *52*, 23.
(55) Volpe, A. M.; Olivares, J. A.; Murrell, M. T. *Anal. Chem.* **1991**, *63*, 913.
(56) Burnett, W. C.; Bokuniewicz, H.; Huettel, M.; Moore, W. S.; Taniguchi, M. *Biogeochemistry* **2003**, *66*, 3.
(57) Bear, J. A., Cheng, H. D., Sorek, S., Ouuzar, D., Herrera, I., Eds. *Seawater Intrusion in Coastal Aquifers—Concepts, Methods and Practices*; Kluwer: Dordrecht, The Netherlands, 1999.
(58) Todd, D. K. *Groundwater Hydrology*, 2nd ed.; Wiley: New York, 1980.
(59) Henry, H. R. In *Sea Water in Coastal Aquifers*; Cooper, H. H., Jr., Kohout, F. A., Henry, H. R., Glover, R. E., Eds.; U.S. Geological Survey Water Supply Paper 1613-C; Washington, DC, 1964; pp C35−C70.
(60) Vanek, V. *J. Hydrol.* **1993**, *151*, 317.
(61) Destouni, G.; Prieto, C. *Biogeochemistry* **2003**, *66*, 171.
(62) Taniguchi, M.; Turner, J. V.; Smith, A. *Biogeochemistry* **2003**, *66*, 111.
(63) Smith, L.; Zawadzki, W. *Biogeochemistry* **2003**, *66*, 95.
(64) Stieglitz, T. *Mar. Pollut. Bull.* **2005**, *51*, 51.
(65) Valiela, I.; Bowen, J. L.; Kroeger, K. D. *Appl. Geochem.* **2002**, *17*, 935.
(66) Valiela, I.; Foreman, K.; LaMontagne, M.; Hersh, D.; Costa, J.; Peckol, P.; DeMeo-Anderson, B.; D'Avanzo, C.; Babione, M.; Sham, C.; Brawley, J.; Lajtha, K. *Estuaries* **1992**, *15*, 443.
(67) Giblin, A. E.; Gaines, A. G. *Biogeochemistry* **1990**, *10*, 309.
(68) Harvey, J. W.; Odum, W. E. *Biogeochemistry* **1990**, *10*, 217.
(69) Oberdorfer, J. A.; Valentino, M. A.; Smith, S. V. *Biogeochemistry* **1990**, *10*, 199.
(70) Reay, W. G.; Gallagher, D. L.; Simmons, G. M. *Water Resour. Bull.* **1992**, *28*, 1121.
(71) Nixon, S. W.; Ammerman, J. W.; Atkinson, L. P.; Berounsky, V. M.; Billen, G.; Boicourt, W. C.; Boynton, W. R.; Church, T. M.; Ditoro, D. M.; Elmgren, R.; Garber, J. H.; Giblin, A. E.; Jahnke, R. A.; Owens, N. J. P.; Pilson, M. E. Q.; Seitzinger, S. P. *Biogeochemistry* **1996**, *35*, 141.
(72) Charette, M. A.; Sholkovitz, E. R. *Geophys. Res. Lett.* **2002**, *29*, 1444.
(73) Talbot, J. M.; Kroeger, K. D.; Rago, A.; Allen, M. C.; Charette, M. A. *Biol. Bull.* **2003**, *205*, 244.
(74) Slomp, C. P.; Van Cappellen, P. V. *J. Hydrol.* **2004**, *295*, 64.
(75) Glover, R. E. In *Sea Water in Coastal Aquifers*; Cooper, H. H., Jr., Kohout, F. A., Henry, H. R., Glover, R. E., Eds.; U.S. Geological Survey Water Supply Paper 1613-C; Washington, DC, 1964; pp C32−C35.
(76) Bokuniewicz, H. J. *Estuar. Coast. Mar. Sci.* **1980**, *10*, 437.
(77) Riedl, R.; Huang, N.; Machan, R. *Mar. Biol.* **1972**, *13*, 210.
(78) Vacher, H. L. *Geol. Soc. Am. Bull.* **1988**, *100*, 580.
(79) Bokuniewicz, H. J.; Pavlik, B. *Biogeochemistry* **1990**, *10*, 257.
(80) Corbett, D. R.; Chanton, J.; Burnett, W.; Dillon, K.; Rutkowski, C.; Fourqurean, J. *Limnol. Oceanogr.* **1999**, *44*, 1045.
(81) Li, L.; Barry, D. A.; Stagnitti, F.; Parlange, J.-Y. *Water Resour. Res.* **1999**, *35*, 3253.
(82) Chanton, J. P.; Burnett, W. C.; Taniguchi, M.; Dulaiova, H.; Corbett, D. R. *Biogeochemistry* **2003**, *66*, 187.
(83) Hubbert, M. K. *J. Geol.* **1940**, *48*, 785.
(84) Freeze, R. A.; Cherry, J. A. *Groundwater*; Prentice Hall: Englewood Cliffs, NJ, 1979.
(85) Zektzer, I. S.; Ivanov, V. A.; Meskheteli, A. V. *J. Hydrol.* **1973**, *20*, 1.
(86) Zektser, I. S. *Groundwater and the Environment: Applications for the Global Community*; Lewis Publishers: Boca Raton, FL, 2000.
(87) Kohout, F. A. *Hydrology* **1966**, *26*, 391.
(88) Manheim, F. T.; Paull, C. K. *J. Hydrol.* **1981**, *54*, 95.
(89) Meybeck, M.; Helmer, R. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **1989**, *75*, 283.
(90) Burnett, W. C.; Taniguchi, M.; Oberdorfer, J. *J. Sea Res.* **2001**, *46*, 109.
(91) Swarzenski, P. W.; Bratton, J.; Crusius, J. *Submarine Groundwater Discharge and Its Role in Coastal Processes and Ecosystems*; U.S. Geological Survey Open-File Report 2004-1226; Washington, DC, 2004.

(92) Bugna, G. C.; Chanton, J. P.; Young, J. E.; Burnett, W. C.; Cable, P. H. *Geochim. Cosmochim. Acta* **1996**, *60*, 4735.
(93) LaRoche, J.; Nuzzi, R.; Waters, R.; Wyman, K.; Falkowski, P. G.; Wallace, D. W. R. *Global Change Biol.* **1997**, *3*, 397.
(94) Hwang, D. W.; Kim, G.; Lee, Y.-W.; Yang, H.-S. *Mar. Chem.* **2005**, *96*, 61.
(95) Hu, C.; Muller-Karger, F.; Swarzenski, P. W. *Geophys. Res. Lett.* **2006**, *33*, L11601, doi:10.1029/2005GL025449.
(96) Valiela, I.; Costa, J.; Foreman, K.; Teal, J. M.; Howes, B.; Aubrey, D. *Biogeochemistry* **1990**, *10*, 177.
(97) Bokuniewicz, H. J. *Estuaries* **1992**, *15*, 458.
(98) Capone, D. G.; Bautista, M. F. *Nature* **1985**, *313*, 214.
(99) Capone, D. G.; Slater, J. M. *Biogeochemistry* **1990**, *10*, 277.
(100) Lapointe, B.; O'Connell, J. D.; Garrett, G. S. *Biogeochemistry* **1990**, *10*, 289.
(101) D'Elia, C. F.; Webb, D. K. L.; Porter, J. W. *Bull. Mar. Sci.* **1981**, *31*, 903.
(102) Lee, D. R. *Limnol. Oceanogr.* **1977**, *22*, 140.
(103) Cable, J. E.; Burnett, W. C.; Chanton, J. P.; Corbett, D. R.; Cable, P. H. *Estuar. Coast. Shelf Sci.* **1997**, *45*, 367.
(104) Libelo, E. L.; MacIntyre, W. G. *Hydrogeol. J.* **1994**, *2*, 49.
(105) Michael, H. A.; Lubetsky, J. S.; Harvey, C. F. *Geophys. Res. Lett*. **2003**, *30*, 10.1029/GL016000.
(106) Shaw, R. D.; Prepas, E. E. *J. Hydrol.* **1990**, *119*, 105.
(107) Cherkauer, D. S.; McBride, J. M. *Ground Water* **1988**, *26*, 165.
(108) Paulsen, R. J.; Smith, C. F.; O'Rourke, D.; Wong, T. *Ground Water* **2001**, *39*, 904.
(109) Rosenberry, D. O.; Morin, R. H. *Ground Water* **2004**, *42*, 68.
(110) Sholkovitz, E. R.; Herbold, C.; Charette, M. A. *Limnol. Oceanogr. Methods* **2003**, *1*, 17.
(111) Taniguchi, M.; Burnett, W. C.; Smith, C. F.; Paulsen, R. J.; O'Rourke, D.; Krupa, S.; Christoff, J. L. *Biogeochemistry* **2003**, *66*, 35.
(112) Taniguchi, M.; Fukuo, Y. *Ground Water* **1993**, *31*, 675.
(113) Taniguchi, M.; Iwakawa, H. *J. Groundwater Hydrol.* **2001**, *43*, 271.
(114) Swarzenski, P. W.; Charette, M.; Langevin, C. *An Autonomous, Electromagnetic Seepage Meter To Study Coastal Groundwater/Surface Water Exchange*; U.S. Geological Survey Open-File Report 2004-1369; Washington, DC, 2004.
(115) Martin, J. M.; Hartl, K. M.; Corbett, R. D.; Swarzenski, P. W.; Cable, J. E. *J. Sediment. Res.* **2003**, *73*, 128.
(116) Swarzenski, P. W.; Porcelli, D.; Andersson, P. S.; Smoak, *J. Rev. Mineral. Geochem.* **2003**, *52*, 577.
(117) Cornett, R. J.; Risto, B. A.; Lee, D. R. *Water Resour. Res.* **1989**, *25*, 1815.
(118) Cable, J. E.; Martin, J.; Swarzenski, P.; Lindenburg, M.; Steward, J. *Ground Water* **2004**, *42*, 1011.
(119) Webster, I. T.; Norquay, S. J.; Ross, F. C.; Wooding, R. A. *Estuar. Coast. Shelf Sci.* **1996**, *42*, 171.
(120) Langmuir, D. *Geochim. Cosmochim. Acta* **1978**, *42*, 547.
(121) Chalov, P. I.; Merkulova, K. I. *Geochem. Int.* **1968**, *5*, 391S.
(122) Bonotto, D. M.; Andrews, J. N. *Chem. Geol. (Isot. Geosci. Sect.)* **1993**, *103*, 193.
(123) Fleischer, R. L.; Raabe, R. O. *Geochim. Cosmochim. Acta* **1978**, *42*, 973.
(124) Greeman, D. J.; Rose, A. W. *Chem. Geol.* **1996**, *129*, 1.
(125) Fleischer, R. L. *Science* **1980**, *207*, 979.
(126) Fleischer, R. L. *Geochim. Cosmochim. Acta* **1982**, *46*, 2191.
(127) Fleischer, R. L. *Geochim. Cosmochim. Acta* **1988**, *52*, 1459.
(128) Andrews, J. N.; Ford, D. J.; Hussain, N.; Trevedi, D.; Youngman, M. J. *Geochim. Cosmochim. Acta* **1989**, *53*, 1791.
(129) Dabous, A. A.; Osmond, J. K. *J. Hydrol.* **2001**, *243*, 242.
(130) Dran, J.-C.; Langevin, Y.; Petit, J.-C. *Chem. Geol.* **1988**, *70*, 126.
(131) Hussain, N.; Lal, D. *Proc. Indian Acad. Sci., Earth Planet. Sci.* **1986**, *95*, 245.
(132) Rosholt, J.; Shields, W. R.; Garner, E. L. *Science* **1963**, *139*, 224.
(133) Michel, J. *Geochim. Cosmochim. Acta* **1984**, *48*, 1249.
(134) Copenhaver, S. A.; Krishnaswami, S.; Turekian, K. K.; Shaw, H. *Geophys. Res. Lett.* **1992**, *19*, 1383.
(135) Ivanovich, M.; Tellam, J. H.; Longworth, G.; Monaghan, J. J. *Radiochim. Acta* **1992**, *58/59*, 423.
(136) Ivanovich, M.; Fröhlich, K.; Hendry, M. J. *Appl. Geochem.* **1991**, *6*, 405.
(137) Charette, M. A.; Sholkovitz, E. R. *Geochim. Cosmochim. Acta* **2005**, *70*, 811.
(138) Swarzenski, P. W.; Baskaran, M. Uranium distributions in the coastal waters and pore waters of Tampa Bay, Florida. *Mar. Chem.* **2006**, *102*, (3-4), 252.
(139) Yanase, N.; Payne, T. E.; Sekine, K. *Geochem. J.* **1995**, *29*, 31.
(140) Kronfeld, J.; Vogel, J. C.; Talma, A. S. *Earth Planet. Sci. Lett.* **1994**, *123*, 81.
(141) Hodge, V. F.; Johannesson, K. H.; Stetzenbach, K. J. *Geochim. Cosmochim. Acta* **1996**, *60*, 3197.
(142) Chen, J. H.; Edwards, R. L.; Wasserburg, G. J. *Earth Planet. Sci. Lett.* **1986**, *80*, 241.
(143) Langmuir, D.; Herman, J. *Geochim. Cosmochim. Acta* **1980**, *44*, 1753.
(144) Lauria, D. C.; Almeida, R. M. R.; Sracek, O. *Environ. Geol.* **2004**, *47*, 11.
(145) Dearlove, J. L. P.; Longworth, G.; Ivanovich, M.; Kim, J. I.; Delakowitz, B.; Zeh, P. *Radiochim. Acta* **1991**, *52*/*53*, 83.
(146) Kim, J. I.; Zeh, P.; Delakowitz, B. *Radiochim. Acta* **1992**, *58*/*59*, 147.
(147) Sun, H.; Semkow, T. *J. Hydrol.* **1998**, *205*, 126.
(148) Moore, W. S.; Arnold, R. *J. Geophys. Res.* **1996**, *101*, 1321.
(149) Benes, P. In *The Environmental Behavior of Radium*; IAEA Technical Reports Series 310; International Atomic Energy Agency: Vienna, Austria, 1990; Vol. 1, pp 373−418.
(150) Bollinger, M. S.; Moore, W. S. *Geochim. Cosmochim. Acta* **1993**, *57*, 2203.
(151) Rama, P. S.; Moore, W. S. *Geochim. Cosmochim. Acta* **1996**, *60*, 4645.
(152) Hancock, G. J.; Webster, I. T.; Ford, P. W.; Moore, W. S. *Geochim. Cosmochim. Acta* **2000**, *21*, 3685.
(153) Langmuir, D.; Reise, A. C. *Geochim. Cosmochim. Acta* **1985**, *49*, 1593.
(154) Langmuir, D.; Melchoir, D. *Geochim. Cosmochim. Acta* **1985**, *49*, 2423.
(155) Gnanapragasam, E. K.; Lewis, B. A. *Geochim. Cosmochim. Acta* **1991**, *59*, 5103.
(156) Hammond, D. E.; Zukin, J. G.; Ku, T. L. *J. Geophys. Res.* **1988**, *93*, 13175.
(157) Moise, T.; Starinsky, A.; Katz, A.; Kolodny, Y. *Geochim. Cosmochim. Acta* **2000**, *64*, 2371.
(158) Morawska, L.; Phillips, C. R. *Geochim. Cosmochim. Acta* **1992**, *57*, 1783.
(159) Miller, R. L.; Kraemer, T. F.; McPherson, B. F. *Estuar. Coast. Shelf Sci.* **1990**, *31*, 439.
(160) Crotwell, A. M.; Moore, W. S. *Aquat. Geochem.* **2003**, *9*, 191.
(161) Davidson, M. R.; Dickson, B. L. *Water Resour. Res.* **1986**, *22*, 34.
(162) Luo, S. D.; Ku, T. L.; Roback, R.; Murrell, M.; McLing, T. L. *Geochim. Cosmochim. Acta* **2000**, *64*, 867.
(163) Sturchio, N. C.; Bohlke, J. K.; Markun, F. J. *Geochim. Cosmochim. Acta* **1993**, *57*, 1203.
(164) Martin, P.; Akber, R. A. *J. Environ. Radioact.* **1999**, *46*, 271.
(165) Wilkening, M. *Radon in the Environment*; Studies in Environmental Science 40; Elsevier: Amsterdam, The Netherlands, 1990.
(166) Semkow, T. M. *Geochim. Cosmochim. Acta* **1990**, *54*, 425.
(167) Suksi, J.; Ruskeeniemi, T.; Lindberg, A.; Jaakkola, T. *Radiochim. Acta* **1991**, *52*/*53*, 367.
(168) Tadolini, T.; Spizzico, M. *Hydrogeol. J.* **1998**, *6*, 450.
(169) Howard, A. J.; Simsarian, J. E.; Strange, W. P. *Health Phys.* **1995**, *69*, 936.
(170) Rama, P. S.; Moore, W. S. *Nucl. Geophys.* **1990**, *4*, 475.
(171) Andrews, J. N.; Wood, D. F. *Trans. Inst. Min. Metall.* **1972**, *B81*, 198.
(172) Burnett, W. C.; Cowart, J. B.; Deetae, S. *Biogeochemistry* **1990**, *10*, 237.
(173) Burnett, W. C.; Cable, J. E.; Corbett, D. R.; Chanton, J. P. *Proceedings of the International Symposium on Groundwater Discharge in the Coastal Zone*; Land−Ocean Interactions in the Coastal Zone (LOICZ); Moscow, Russia, 1996; pp 22−28.
(174) Ellins, K. K.; Roman-Mas, A.; Lee, R. *J. Hydrol.* **1990**, *115*, 319.
(175) Cable, J. E.; Bugna, G. C.; Burnett, W. C.; Chanton, J. P. *Limnol. Oceanog.* **1996**, *41*, 1347.
(176) Moore, W. S.; Shaw, T. J. *J. Geophys. Res.−Oceans* **1998**, *103*, 21543.
(177) Corbett, D. R.; Dillon, K.; Burnett, W.; Chanton, J. *Limnol. Oceanogr.* **2000**, *45*, 1546.
(178) Hussain, N.; Church, T.; Kim, G. *Mar. Chem.* **1999**, *65*, 127.
(179) Kim, G.; Hwang, D. W. *Geophys. Res. Lett*. **2002**, *29*, 10.1029/2002GL015093.
(180) Burnett, W. C.; Chanton, J.; Christoff, J.; Kontar, E.; Krupa, S.; Lambert, M.; Moore, W.; O'Rourke, D.; Paulsen, R.; Smith, C.; Smith, L.; Taniguchi, M. *EOS* **2002**, *83*, 117.
(181) Burnett, W. C.; Dulaiova, H. *J. Environ. Radioact.* **2003**, *69*, 21.
(182) Garrison, G. H.; Glenn, C. R.; McMurtry, G. M. *Limnol. Oceanogr.* **2003**, *48*, 920.
(183) Charette, M. A.; Buesseler, K. O. *Limnol. Oceanogr.* **2004**, *49*, 376.
(184) Moore, W. S.; Wilson, A. M. *Earth Planet. Sci. Lett.* **2005**, *235*, 564.
(185) Burnett, W. C., Chanton, J. P., Kontar, E., Eds. *Biogeochemistry*; Submarine Groundwater Discharge, Special Issue 66 (1−2); Springer: Berlin, Germany, 2003.
(186) Dulaiova, H.; Peterson, R.; Burnett, W. C. *J. Radioanal. Nucl. Chem.* **2005**, *263*, 361.
(187) Kohout, F. A. *J. Geophys. Res.* **1960**, *65*, 2133.
(188) Moore, W. S. *Proc. Indian Acad. Sci.* **1998**, *4*, 343.

CR0503761