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Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico

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Contaminants accumulated in passive samplers deployed in flooded cave systems in the Yucatan Peninsula in Mexico indicate contamination by domestic sewage, runoff and applications of pesticides to turf.

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A B S T R A C T

Intensive land development as a result of the rapidly growing tourism industry in the "Riviera Maya" region of the Yucatan Peninsula, Mexico may result in contamination of groundwater resources that eventually discharge into Caribbean coastal ecosystems. We deployed two types of passive sampling devices into groundwater flowing through cave systems below two communities to evaluate concentrations of contaminants and to indicate the possible sources. Pharmaceuticals and personal care products accumulated in the samplers could only have originated from domestic sewage. PAHs indicated contamination by runoff from highways and other impermeable surfaces and chlorophenoxy herbicides accumulated in samplers deployed near a golf course indicated that pesticide applications to turf are a source of contamination. Prevention and mitigation measures are needed to ensure that expanding development does not impact the marine environment and human health, thus damaging the tourism-based economy of the region.

1. Introduction

The geology of the Yucatan Peninsula in Mexico consists of highly-permeable karst limestone deposits. Rain water percolates rapidly through the porous substrate into the water table. The fresh groundwater of this coastal aquifer forms a distinct lens on top of intruding marine water. Along the Caribbean coast of the Yucatan Peninsula, flooded cave systems extending 8–12 km inland provide hydrological conduits that link the inland recharge areas to springs that discharge into the coastal zone (Smart et al., 2006). Sinkholes called "cenotes" provide access into these conduit cave systems.

The regional municipality of Solidaridad in the State of Quintana Roo along the "Riviera Maya" region of the Caribbean coast is a rapidly growing tourism and recreational area. Planned expansion of tourist numbers and intensive land development mean that the population is projected to increase at least 10-fold over the next 20 years (Municipalidad de Solidaridad, 2005). In larger urban municipalities and in hotel complexes where centralized sewage collection exists, the domestic sewage is currently pumped from municipalities and hotels into the saline water zone below the freshwater aquifer. As has been shown in the Florida Keys, USA, this waste disposal practice has the potential to contaminate the overlying freshwater aquifer and the coastal zone (Paul et al., 2000). However, only 32% of the population in the State of Quintana Roo and 14% of the population of the Municipality of Solidaridad is served by municipal wastewater treatment systems (Amigos de Sian Ka'an, unpublished data), so large amounts of domestic sewage are also deposited into septic tanks or pit latrines. In addition, there is potential for direct percolation of surface contaminants (e.g. spills, surface runoff, pesticides) to the freshwater aquifer by transport through the porous substrate or by direct inputs into cenotes.

Published water quality data are relatively scarce for the Yucatan Peninsula. High salinity as a result of salt water intrusion is the water quality parameter of most concern (Back and Hanshaw, 1970; Delgado et al., 2010). At sites near the coasts (~<10 km) the

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groundwater chemistry is dominated by sodium-chloride ions due to marine influences, but sites further inland are dominated by calcium-bicarbonate ions (Back and Hanshaw, 1970; Beddows et al., 2007). Where other water quality data have been reported, the concentrations of nitrogen and phosphorous compounds and fecal bacteriological loads are often borderline relative to drinking water standards in Mexico at sites distant from development, but near development, the groundwater is often highly contaminated with fecal coliforms and nitrate (Alcocer et al., 1998; Graniel et al., 1999; Pacheco et al., 2001). At the ecosystem level, the Meso-American Barrier Reef System has experienced >50% loss of coral cover over the last 20 years, which has been attributed to disease outbreaks that in turn are associated with eutrification of the coastal waters (Harvell et al., 2007). The P and N concentrations and isotopic ratios in turtle grass indicate groundwater sources of nutrients (Carruthers et al., 2005; Mutchler et al., 2007). These water quality data and the decline of the barrier reef clearly underline the need for monitoring approaches that are capable of identifying sources of anthropogenic compounds discharged into the aquifer and coastal waters.

Karst aquifers provide 25% of global drinking water supplies, and yet are highly susceptible to contamination (Ford and Williams, 2007). The Caribbean coastal zone of the Yucatan Peninsula is particularly at risk to contamination because of intensive tourism development and population growth. Groundwater velocities through the well-integrated flooded cave networks range from 0.5 to 2.5 km/day (Beddows, 2004). The potential exists for contaminants even from non-coastal sites to be rapidly discharged into coastal waters and onto the Meso-American Barrier Reef System. Within a coastal band along the Caribbean that extends approximately 10 km inland, the aquifer is tidally influenced, with significant variations in conduit velocity (Beddows, 2004). Long term monitoring over 2+ years has shown that the prominent semi-diurnal fluctuations in groundwater velocity (and therefore discharge) are overprinted by annual cycles tied to mean sea level (that do not relate to wet–dry seasons), and also short-lived storm events. *In situ* passive sampling approaches, such as used in this study, are therefore ideal for time-integrated monitoring in these highly dynamic systems.

The objective of this study was to evaluate whether contamination of the freshwater resources is currently occurring by monitoring selected groundwater discharge sites using passive sampling techniques. By monitoring for various classes of contaminants, inferences can be made about probable sources. Passive sampling techniques have proven useful as monitoring tools for a range of contaminants in the aquatic environment. For instance, semi-permeable membrane devices (SPMDs) have been used to monitor for hydrophobic compounds in aquatic environments (Huckins et al., 1997). We have deployed SPMDs in embayments, rivers and streams to monitor for various persistent contaminants (Bennett and Metcalfe, 2000; Metcalfe et al., 2000, 2008; O'Toole et al., 2006). More recently, a passive sampler has been developed for more water-soluble (i.e. hydrophilic) contaminants (Alvarez et al., 2004). We recently showed that the Polar Organic Chemical Integrative Sampler (POCIS) is a valuable monitoring technique for polar contaminants, such as pharmaceuticals, personal care products and endocrine disrupting compounds (Li et al., 2010a).

We deployed SPMD and POCIS passive samplers in flooded cave systems beneath the communities of Tulum and Puerto Aventuras in the Riviera Maya region of Mexico. The samplers were deployed for a period of approximately one month at 5 locations judged to have potential for groundwater contamination. Extracts from the SPMD and POCIS samplers were analyzed for contaminants that are representative of a range of sources of contamination, including pharmaceuticals and personal care products (PPCPs) that are indicative of sewage contamination, current use herbicides that are indicative of contamination from lawn and turf care, and non-polar compounds that are indicative of industrial and urban contamination sources. The presence or absence of these indicator compounds in the passive samplers was used to identify the probable sources of these contaminants. Once sources are identified, prevention and mitigation measures can be proposed to reduce contamination of the coastal zone.

2. Methods and materials

2.1. Passive sampler deployment

The methods used to prepare the SPMD passive samplers were described in detail by O'Toole et al. (2006). Briefly, the SPMDs were prepared in a Class A clean room at Trent University from sealed polyethylene strips containing 1 mL of 95% triolein (Sigma–Aldrich, Mississauga, ON, Canada) spiked with a recovery standard, PCB congener 203. The SPMDs were placed in solvent washed jars and frozen at −10 °C until shipped for deployment. POCIS samplers of the "pharmaceutical" configuration (i.e. with Oasis HLB solid sorbent) were purchased from Environmental Sampling Technology (St. Joseph, MO, USA). "Trip blank" POCIS and SPMDs were also transported to the field area and exposed to the air at each deployment site.

The samplers were deployed at the five sites illustrated in Fig. 1 near the communities of Puerto Aventuras (PA) and Tulum (TU). Puerto Aventuras is divided into two areas, a coastal community with condominiums, a hotel, restaurants, an entertainment area, marina and a 9-hole golf course, and an inland residential community located on the western side of the highway (Fig. 1). Site PA1 was located in a small, shallow cenote in the middle of the business district of Puerto Aventuras and site PA2 was located in a cave system that discharges into the Chac Ha Lal caleta (i.e. embayment) just south of Puerto Aventuras coastal development. The water in PA1 was observed to be cool and transparent, indicating groundwater flow and connectivity with the local conduit networks. While the full extent of the cave systems at PA1 and PA2 are unknown, there is an extensive system of inland caves (Chac Mool system) and grottos (Grotte des Aluxes) in the area, indicating a high degree of hydrogeological connectivity. Tulum is a growing community that provides retail and entertainment services to the rapidly growing tourist region south of Playa del Carmen (Fig. 1). Sites TU1 and TU2 were located in the Ak Tulum and Herradura caves, respectively, which are extensive cave systems that pass beneath the town of Tulum. Site TU3 is the cave system Aktun Ha (Car Wash cenote) situated at 8.7 km from the Caribbean coast and approximately 6 km to the northwest of Tulum. This location was selected as a potential reference site because there is no significant urban development inland, although the historical landfill for Tulum is located approximately 1.5 km inland of the upper reaches of this cave system.

Three SPMDs and three POCIS passive samplers were placed in cages made of stainless steel. As illustrated in Fig. 2, the SPMDs ($n = 3$) were stretched around a series of stainless steel posts, and the POCIS ($n = 3$) were bolted into place on stainless steel mounting brackets. Two cages were then deployed at each site by certified cave divers by attaching them with plastic ties to rock features in the caves, or in one case (i.e. PA1), by suspending the cage on a weighted rope into the cenote.

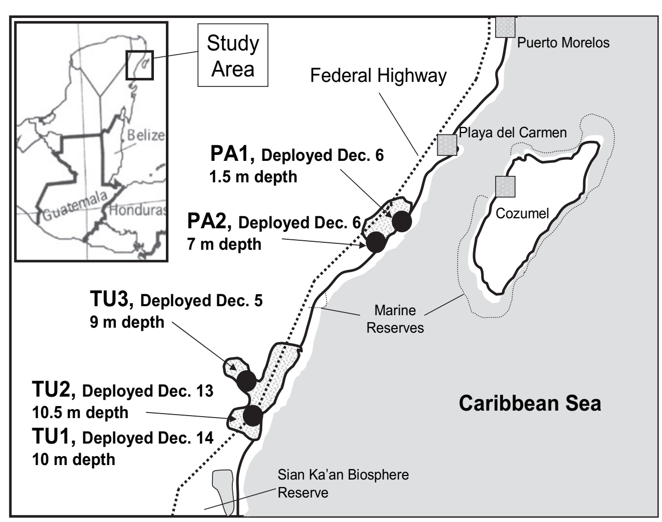

Fig. 1. Study area along the Caribbean coast of the Yucatan Peninsula in Mexico, showing the 5 sites for deployment of passive samplers in cave systems below the towns of Tulum (TU) and Puerto Aventuras (PA). The shaded areas around the deployment sites represent the approximate limits of the flooded cave systems in the region. Note the locations of the Sian Ka'an Biosphere reserve and the marine reserves in the region.