Environmental Pollution xxx (2010) 1–7

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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

Chris D. Metcalfe [a,*], Patricia A. Beddows [b], Gerardo Gold Bouchot [c], Tracy L. Metcalfe [a], Hongxia Li [a], Hanneke Van Lavieren [d]

[a] Worsfold Water Quality Centre, Trent University, Peterborough, ON, K9J 7B8, Canada
[b] Department of Earth and Planetary Sciences, Northwestern University, Evanston, IL, USA
[c] Departemento de Recursos del Mar, CINVESTAV Unidad Merida, Yucatán, Mexico
[d] UN University Institute for Water, Environment and Health (UNU-INWEH), Hamilton, ON, Canada

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.

ARTICLE INFO

Article history:
Received 5 July 2010
Received in revised form
16 November 2010
Accepted 20 November 2010

Keywords:
Passive sampling
Pharmaceuticals
Herbicide
Karst
Coastal aquifers
Yucatan
Caribbean
Meso-American Barrier Reef System

ABSTRACT

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

* Corresponding author.
E-mail address: cmetcalfe@trentu.ca (C.D. Metcalfe).

0269-7491/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2010.11.031

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.

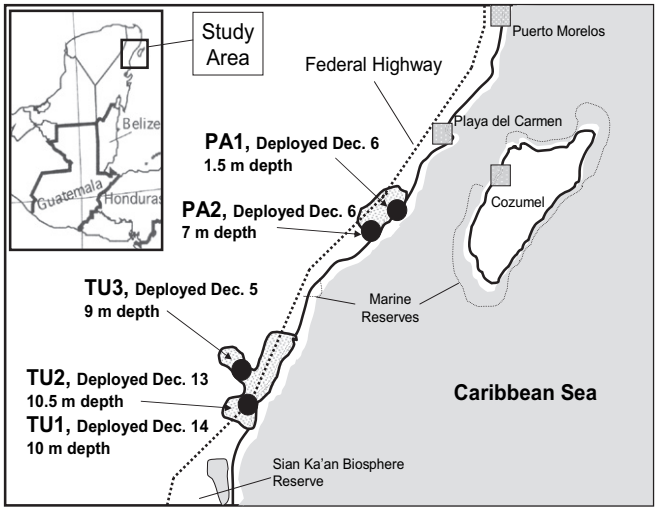

Fig. 1. Study area along the Caribbean coast of the Yucatan Peninsula in Mexico, showing the 5 sites for deployment of passive samplers in cave systems below the towns of Tulum (TU) and Puerto Aventuras (PA). The shaded areas around the deployment sites represent the approximate limits of the flooded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

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031

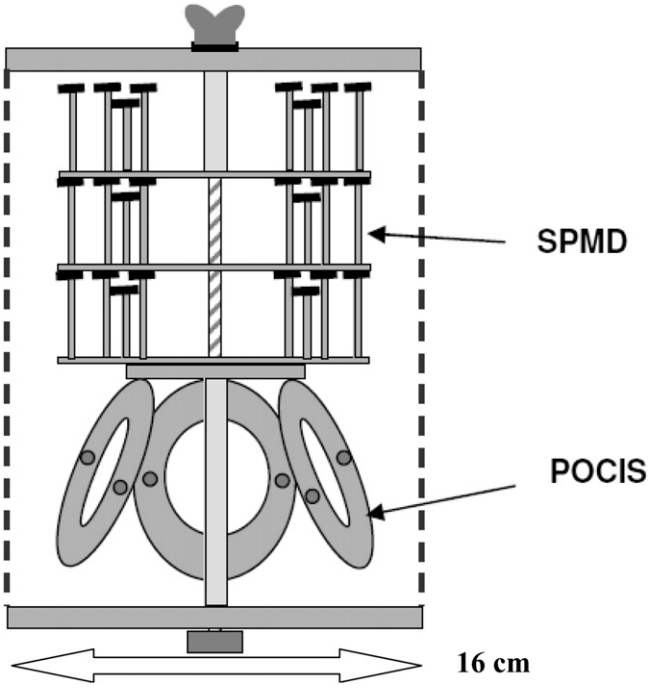

Fig. 2. Configuration of stainless steel cage used to deploy SPMD ($n = 3$) and POCIS ($n = 3$) passive samplers in cave systems in the study area.

Trip blanks were exposed to the air at the time of deployment only. The passive samplers were deployed at depths within the freshwater lens, and at least 2 m above the fresh–saline interface, except at PA2, which was periodically mixed with inland saline flow. In all locations, the groundwater flow direction is likely to be dominated by net coastward freshwater flow. The depths below sea level for the deployments are listed in Fig. 1. Freshwater temperatures in these aquifers at the deployment depths are consistently between 26 and 28 °C (Beddows et al., 2007).

Deployments occurred at these sites from December 5–14, 2008 (Fig. 1) and the samplers were retrieved 28–32 days after deployment (depending on the site) in January, 2009. The retrieved samplers were placed in coolers with cold packs and were transported within 48 h to the Marine Resources Institute at CINVESTAV in Merida, Mexico, where they were extracted into solvent.

2.2. Sample preparation

2.2.1. SPMDs

After retrieval, each SPMD was cleaned with water and the contaminants were dialyzed into hexane according to methods previously described by Metcalfe et al. (2008). Residual triolein and co-extractives were removed from the dialysate by gel permeation chromatography (GPC) with BioBeads SX-3 (Bio-Rad Laboratories, Mississauga, ON, Canada) using one of two methods, depending on the target analytes. Extracts to be analyzed for PCBs, PBDEs, PAHs and organochlorine (OC) pesticides were cleaned up by GPC using dichloromethane as the mobile phase and the extract was subsequently fractionated by silica gel chromatography, as described previously (Metcalfe et al., 2008). Fraction I isolated by silica gel chromatography contained PCB congeners and some organochlorine pesticides (e.g. *p,p′*-DDE, aldrin). Fraction II isolated by silica gel chromatography contained organochlorine pesticides, PAHs and PBDEs. Extracts to be analyzed for synthetic musks, triclosan and alkylphenol surfactants were cleaned up by GPC using ethyl acetate as the mobile phase, according to the methods described by O'Toole et al. (2006). No further sample cleanup was required for analysis of these target analytes. The samples were evaporated to near-dryness using a vacuum centrifuge and transferred into an autosampler vial in 300 μL of iso-octane for analysis of the non-polar contaminants.

2.2.2. POCIS

The extraction procedures for POCIS were previously described by Li et al. (2010a). Briefly, each POCIS device was rinsed with water, the disc array disassembled, and the membranes detached from the stainless steel collars. The sorbent powder was carefully transferred into a glass chromatography column and a mixture of stable isotope internal standards was added to the top of the column. The sorbent was eluted with 50 ml of methanol and the eluate volume was then reduced to about 1 ml by rotary evaporation, and transferred into a conical centrifuge tube. Then, the extract was evaporated to near-dryness using a nitrogen stream and transferred into an autosampler vial in 300 μL of methanol for analysis of the polar contaminants.

The extracts from three POCIS samplers were pooled for analysis of chlorophenoxy herbicides. Each pooled extract was spiked with ^{13}C labelled 2,4-D and 2,4,5-T as internal standards, evaporated to near-dryness and reconstituted in 50 μL of methanol. The analytes were derivatized to methylated products using diazomethane reagent, as described by Woudneh et al. (2006). The derivatized sample was cleaned up using column chromatography with Florisil, followed by further cleanup by passing through an aminopropyl-bonded silica solid phase extraction (SPE) cartridge, as previously described by Woudneh et al. (2006).

2.3. Analysis

Table 1 summarizes the classes of compounds analyzed in the extracts prepared from SPMD and POCIS passive samplers, the analytical instrumentation used for these analyses and the references from the peer-reviewed literature that describe the analytical techniques. Briefly, the PCBs and the organochlorine pesticides in the SPMD extracts were analyzed by gas chromatography with an electron capture detector (i.e. GC-ECD). Also from the SPMD extracts, the PBDEs, synthetic musks and alkylphenols (after acetylation) were analyzed by gas chromatography with low resolution mass spectrometry (i.e. GC-LRMS). The individual PCB and PBDE congeners, the organochlorine pesticides, the alkylphenols and the synthetic musks analyzed are listed in Table 1. Note that decabromodiphenyl ether (BDE 209) was not included in the analysis of PBDEs because it is susceptible to degradation in the GC column (Covaci et al., 2003). A total of 15 "priority PAHs" identified by the US Environmental Protection Agency was analyzed by GC-LRMS (Table 1). The antibacterial compound, triclosan, in the SPMD extracts was analyzed by LC-MS/MS.

Except for the chlorophenoxy herbicides, all compounds in the POCIS extracts were analyzed by liquid chromatography with tandem mass spectrometry (i.e. LC-MS/MS), including a range of prescription and non-prescription pharmaceuticals, illicit drugs and stimulants (Table 1). The chlorophenoxy herbicides in the POCIS

Table 1
Contaminants monitored, their possible sources, and the instrumentation used to analyze extracts from passive samplers deployed in flooded cave systems in the study area along the Caribbean coast of the Yucatan Peninsula in Mexico. The references describing the analytical methods are also listed. The individual analytes are listed in the footnotes.

Compound class	Possible sources	Analytical instrument	Reference
SPMD extracts:			
PCBs[a]	Industry, runoff	GC-ECD	O'Toole et al., 2006
Organochlorine pesticides[b]	Agriculture	GC-ECD	O'Toole et al., 2006
PAHs[c]	Runoff, industry	GC-LRMS	Metcalfe et al., 2000
PBDEs[d]	Industry	GC-LRMS	Dodder et al., 2002
Synthetic musks[e]	Sewage	GC-LRMS	O'Toole and Metcalfe, 2006
Alkylphenols[f]	Industry, sewage	GC-LRMS	Hawrelak et al., 1999
Antibacterials[g]	Sewage	LC-MS/MS	Chu and Metcalfe, 2007
POCIS extracts:			
Chlorophenoxy herbicides[h]	Turf care	GC-HRMS	Woudneh et al., 2006
Stimulants[i]	Sewage	LC-MS/MS	Li et al., 2010a
Pharmaceuticals[j]	Sewage	LC-MS/MS	Li et al., 2010a
Illicit drugs[k]	Sewage	LC-MS/MS	Metcalfe et al., 2010

Individual analytes:

[a] PCB congeners 44, 49, 52, 87, 99, 101, 105, 110, 118, 138, 151, 153, 156, 170, 180, 194, 195, 209.

[b] 2,4- and 4,4-isomers of DDT, DDE and DDD, α-, β-, δ- and γ-isomers of HCH, *trans*- and *cis*-isomers of chlordane and nonachlor, endosulfan I and II, endosulfan sulfate, heptachlor and heptachlor epoxide, aldrin, dieldrin, endrin, endrin ketone and endrin aldehyde, methoxychlor, mirex, HCB.

[c] Naphthalene, acenaphthylene, acenapthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1]pyrene, dibenz[a,h]anthracene, benzo[g.h.i]perylene.

[d] BDE congeners 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, 184, 191, 196, 197.

[e] HHCB, AHTN, musk xylene, musk ketone.

[f] Nonylphenol, octylphenol (after acetylation).

[g] Triclosan.

[h] 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, MCPP, MCPA, dicamba, dichlorprop, triclopyr.

[i] Caffeine and cotinine (nicotine metabolite).

[j] Acetaminophen, ibuprofen, naproxen, carbamazepine.

[k] Cocaine and benzoylecgonine (cocaine metabolite), amphetamine, methamphetamine, MDMA (ecstasy).

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031

extracts were methylated as described previously and then analyzed by gas chromatography with high resolution mass spectrometry (GC-HRMS).

3. Results and discussion

The SPMD and POCIS passive samplers accumulated selected classes of contaminants in nanogram (ng) amounts over the deployment period of approximately 1 month. The classes and the spatial distribution of the contaminants accumulated in the passive samplers indicate the possible sources of contamination. At site TU3 within the Aktun Ha cave system, none of the analytes were accumulated to detectable levels in the POCIS and SPMD samplers. This site, which is 8.6 km inland from the Caribbean coast is similar to all freshwater caves of this region, as it acts as a drainage conduit to the coastal zone (Beddows and Henrickson, 2007). The lack of contaminants in passive samplers deployed at this site indicates that there is little contamination originating from inland sources. Some contamination might have been expected as a result of leaching from the nearby Tulum municipal dump. However, fracture orientations, in addition to changes in hydraulic gradients, may divert the water on a flow path that is parallel to the coast. For instance, in the vicinity of TU3 and the Aktun Ha Cave system, groundwater could be channelled along the Holbox Fracture Zone, which passes near the sampling site at its southern terminus.

Pharmaceuticals used for human use, and caffeine and cotinine (i.e. metabolite of nicotine) were detected in ng amounts in POCIS samplers deployed at TU1, TU2, PA1 and PA2 (Fig. 3a). The human use pharmaceuticals that were detected included both prescription drugs (i.e. carbamazepine) and non-prescription drugs (i.e. acetaminophen, ibuprofen, naproxen). In addition, cocaine and its primary metabolite, benzoylecgonine (BE) were detected in small amounts in POCIS deployed at all four sites, as illustrated by the levels of "total cocaine" (i.e. cocaine plus BE) shown in Fig. 3a. The only possible source of these contaminants is treated or untreated sewage, as all of these compounds are excreted by humans in urine and feces. Human use pharmaceuticals, illicit drugs and stimulants have previously been detected in surface waters downstream of discharges from wastewater treatment plants (Metcalfe et al., 2004; Postigo et al., 2010) and pharmaceuticals and caffeine have also been detected in groundwater contaminated by septic plumes (Carrara et al., 2008; Seiler et al., 1999).

Chlorophenoxy herbicides were detected in POCIS samplers deployed at PA1 and PA2, but no herbicides were detected in POCIS deployed in the Tulum area (Fig. 3b). At PA1, 10 different herbicides were detected in the POCIS, but only six of these compounds were detected at PA2. Herbicides from the chlorophenoxy class are typically used to control broad leaf weeds on lawns and turf. Therefore, it is likely that the source of contamination in Puerto Aventuras was herbicide applications to lawns and turf, and in particular, to the turf on a 9-hole golf course that is located only a few meters from PA1. Suzuki et al. (1998) studied the persistence of several pesticides applied to golf courses in Japan and concluded that golf courses have a "high pollution potential for pesticides relative to agricultural areas". Herbicides from the chlorophenoxy class have a high potential for leaching from soils; especially in alkaline soils where the herbicides are primarily present in the water soluble, ionized form (Wu et al., 2009). Soil cover through the whole study area is very thin and patchy, with high-porosity limestone bedrock commonly exposed.

The SPMDs deployed at PA1, PA2, TU1 and TU2 accumulated detectable amounts of several personal care products, including synthetic musk compounds, triclosan and nonylphenol (Fig. 4a).

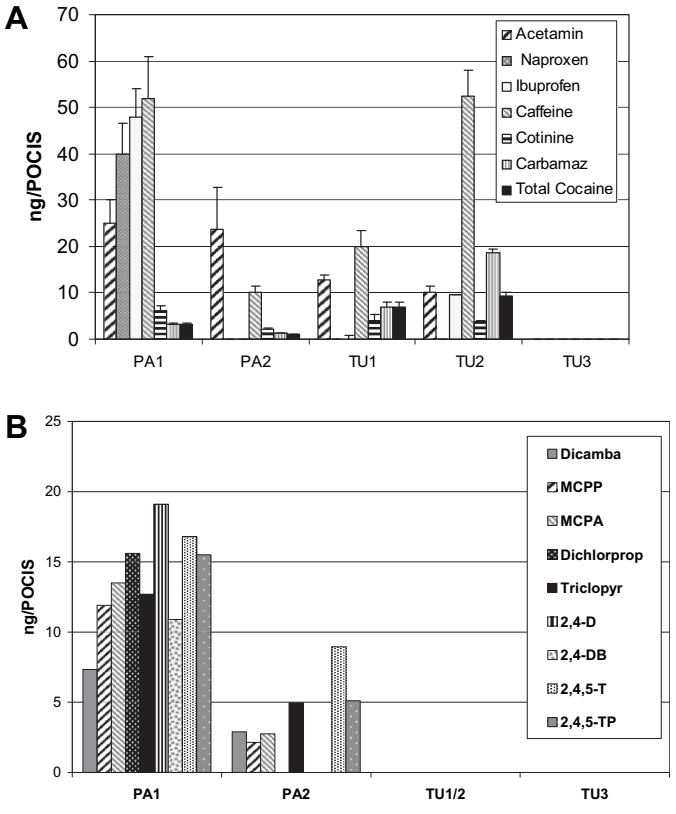

Fig. 3. Mean amounts (ng) of contaminants accumulated in POCIS samplers at the 5 deployment sites, including: A) human use drugs, and B) chlorophenoxy herbicides. The error bars for the drug data represent standard deviations about the mean ($n = 3$). The chlorophenoxy herbicides were analyzed in a single sample pooled from extracts from 3 POCIS samplers. Note that the extracts for sites TU1 and TU2 were combined for the analysis of chlorophenoxy herbicides.

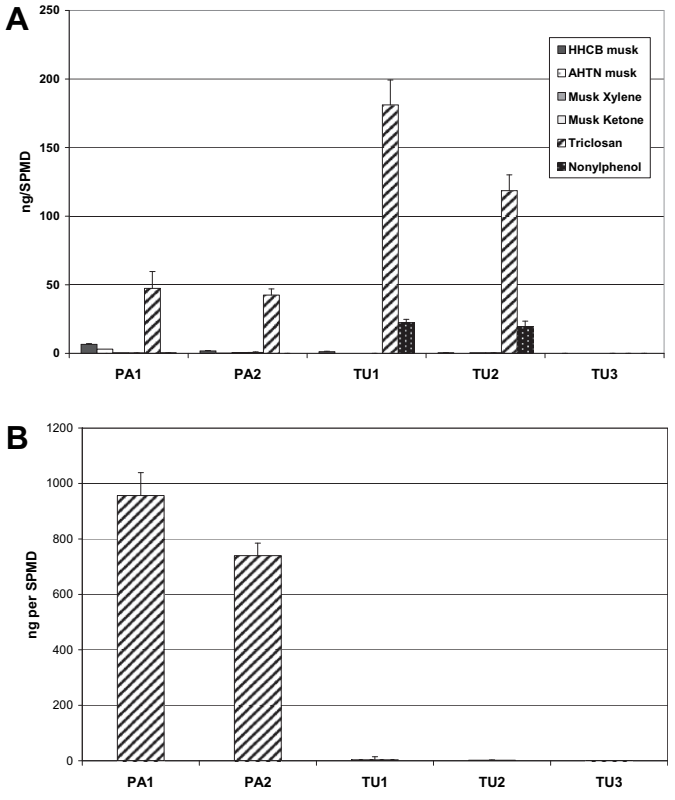

Fig. 4. Mean amounts (ng) of contaminants accumulated in SPMD samplers at the 5 deployment sites, including: A) personal care products, and B) total PAHs. The error bars represent standard deviations about the mean ($n = 3$).

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031

Two synthetic musks from the nitro-musk class, musk ketone and musk xylene were only present in amounts above detection limits in the SPMDs deployed at PA2 (i.e. mean of 1.3 and 1.2 ng, respectively). The polycyclic musk, HHCB was detected in the highest amount in the SPMDs deployed at PA1 (i.e. mean of 6.6 ng), but was also detected at PA2 and TU1. Another polycyclic musk, AHTN was only detected in the SPMDs deployed at PA1 (i.e. mean of 3.2 ng). The antibacterial compound, triclosan was detected in amounts >40 ng in SPMDs deployed at PA1, PA2, TU1 and TU2, with the largest amounts accumulated in the SPMDs deployed in the caves below Tulum (Fig. 4a). Nonylphenol, which is a microbial degradation product of nonylphenol ethoxylate surfactants that are used in a variety of household products was detected in amounts >15 ng in SPMDs deployed at Puerto Aventuras, but was not detected in SPMDs deployed in caves below Tulum (Fig. 4a). Octylphenol was not detected in extracts from any of the SPMDs. Domestic sewage is the most likely source of these personal care products, since these compounds have been widely detected in surface waters and in groundwater impacted by sewage (Bennett and Metcalfe, 2000; Kolpin et al., 2004; Carrara et al., 2008; Chalew and Halden, 2009). Since these personal care products all have log K_{ow} values >3.5, there is potential for bioaccumulation of these compounds by aquatic organisms if they are discharged into the coastal zone (Adolfsson-Erici et al., 2002; O'Toole and Metcalfe, 2006; Nakata et al., 2007).

PAHs were accumulated by SPMDs deployed at both sites in Puerto Aventuras, but were not detected in the caves below Tulum (Fig. 4b). Of the 15 PAHs monitored, the compounds detected in the highest proportions from the SPMD extracts were relatively water-soluble compounds, including naphthalene (>10%), phenanthrene (>30%), pyrene (>10%) and benz[a]anthracene (>20%). There are a variety of possible sources of PAHs in the environment, including atmospheric deposition, industrial discharges, oil spills and urban runoff. Since PAHs were not detected in SPMDs deployed at the reference site, TU3, atmospheric deposition is an unlikely source. As there is no industry at Puerto Aventuras, the most likely source of the PAHs is urban runoff. There is likely to be runoff of hydrocarbons from diesel particulates and spilled engine oils deposited along the federal highway just outside of Puerto Aventuras (Fig. 1). The conclusion that road runoff was the source of PAHs is supported by the mean fluorene/pyrene ratios of 0.87 and the mean phenanthrene/anthracene ratios of 17.8 observed in the extracts from SPMDs deployed at PA1 and PA2. Much higher ratios are indicative of PAHs from atmospheric sources, and lower ratios indicate contamination from fuel oil (Kose et al., 2008).

Of the remaining target classes listed in Table 1, the PCBs and PBDEs were not detected in SPMDs in amounts above the limits of detection (i.e. <1 ng). Among the organochlorine pesticides, only dieldrin, p,p-DDE and p,p-DDT were detected in the samplers deployed at PA1 in mean amounts of 5.9, 3.3 and 2.1 ng per SPMD, respectively, which are only slightly above the limits of detection. None of the organochlorine pesticides were detected at any other sites. There appear to be no active inputs of these persistent halogenated compounds in the study area.

It is possible to use passive sampler data to estimate the time-weighted average concentrations of contaminants in the aqueous phase, if passive sampling rates, R_s (L/d) are known for the individual compounds. For SPMDs, sampling rates vary widely with water temperature and flow rate (Booij et al., 2002; Huckins et al., 1997), but POCIS appear to have more consistent sampling rates over a range of environmental conditions (Li et al., 2010a, 2010b). Fortunately, the water temperatures within the cave systems in the study area only vary by 1–2 °C, although the rates of water flow may vary considerably over time (Beddows, 2004). Table 2 shows the estimated concentrations of selected compounds in water at either TU1 or PA1, as calculated from the sampling rates (R_s). The sampling rates were determined in laboratory experiments conducted at water temperatures close to those in the cave systems (i.e. 26–28 °C), except for nonylphenol (Table 1). Because of the variability in sampling rates under field conditions, these concentrations can be considered estimates only. The data shown in Table 2 show that the estimated concentrations of these compounds in water were all in the low ng/L (i.e. part per trillion) range.

Table 2
Estimated concentrations of selected compounds in water (ng/L) at TU1 or PA1 calculated from the mean amounts (ng) accumulated in the SPMD or POCIS passive samplers deployed over 28 d at TU1 and 32 d at PA1 and the sampling rates, R_s (L/d) determined experimentally for these compounds at the temperature (°C) specified in brackets. The sources of the sampling rate data are listed in the footnotes.

Compound class	Compound	Site	Mean amount ng	R_s L/d (°C)	Estimated conc. ng/L
SPMD:					
PAHs	Phenanthrene	PA1	339.4	5.0 (26)[a]	2.12
Synthetic musks	HHCB	PA1	6.6	6.8 (25)[b]	0.03
Antibacterials	Triclosan	TU1	181.2	7.9 (25)[b]	0.81
Alkylphenols	Nonylphenol	TU1	22.4	7.4 (10)[c]	0.11
POCIS:					
Pharmaceuticals	Ibuprofen	PA1	47.9	0.35 (25)[d]	4.27
Pharmaceuticals	Naproxen	PA1	39.8	0.39 (25)[d]	3.19
Stimulants	Caffeine	PA1	52.0	0.13 (25)[d]	12.50
Illicit drugs	Cocaine and BE	TU1	6.8	0.13 (25)[b]	1.87
Chloroph. herbicides	2,4-D	PA1	19.1	0.25 (17)[e]	2.39

Sources of R_s data:
[a] Huckins et al. (1999).
[b] R_s values reported here for the first time. Experiments to determine the sampling rates for musks were conducted as described by Li et al. (2010a).
[c] Harman et al. (2008).
[d] Li et al. (2010a).
[e] R_s for 2,4-D was not specifically measured, but this R_s is typical of a range of values reported for ionic herbicides by Mazzella et al. (2007).

These low concentrations are not surprising, considering the large volumes of water that pass through these cave systems. Hanshaw and Back (1980) calculated an average discharge for the entire coastline of the Yucatan Peninsula of 8.6×10^6 m^3 per year per kilometre. However, Beddows (2004) showed that discharge from coastal caletas can be two orders of magnitude higher. Discharge in caleta Xel Ha summed to 3.0×10^8 m^3/year, which is 9.4 m^3/s, while discharge in caleta Casa Cenote summed to 1.4×10^8 m^3/year, which is 4.4 m^3/s (Beddows, 2004). Discharge in freshwater caves at inland sites will be lower than the discharge at coastal sites, which combine the waters from a number of inland cave flow paths. Beddows (2004) estimated discharge in Heaven's Gate cenote, situated 3.2 km inland to be 3.1×10^7 m^3/year, which is 1.0 m^3/s (Beddows, 2004). Thus, cumulative discharges of contaminants over time can be substantial. For instance, water containing a chemical at a concentration of 10 ng/L discharged at a rate of 10 m^3/s would release 3 kg per year of the chemical into the coastal environment.

The cenote at site PA1 with an effective cross-sectional flow area of approximately 0.5 m^2 is typical of the thousands of small cenotes in the area., Considering a time-weighted average caffeine concentration of 10 ng/L and a discharge for PA1 of 10^5–10^6 m^3/year, this equates to an annual loading of 3–30 cups of coffee (at 100 mg caffeine per cup) flowing through this small, but urbanized site. The 2005 census of Puerto Aventuras identified 2000 permanent residents, which omits the large transient population in this well established tourist development.

The probable sources of the contaminants that were detected in flooded caves at PA include runoff from highways and other impermeable surfaces (Kose et al., 2008; Yang et al., 2010) and pesticide applications to lawns and turf. Pesticides and fertilizers

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031

applied to golf courses have impacted the marine environment along the coast of the Gulf of Mexico in Florida, USA (Lewis et al., 2001, 2002). Domestic sewage was the probable source of caffeine, pharmaceuticals, illicit drugs and personal care products detected in the flooded caves below both TU and PA. Domestic sewage could have contaminated these freshwater resources from pit latrines, septic plumes and leaking sewer lines (Carrara et al., 2008). Injection of treated wastewater into salt water aquifers and subsequent transport of sewage constituents into the overlying freshwater aquifer could also have contributed to the contamination (Paul et al., 2000). Finally, it is common practice in this region of Mexico to use wastewater to irrigate lawns and turf. Treated domestic wastewater is used to irrigate the golf course at Puerto Aventuras. Since this golf course is an older recreational facility, there is no impermeable liner installed below the surface substrate to restrict leaching into the aquifer. A study of irrigation of crops with municipal wastewater in Colorado, USA indicated that several pharmaceuticals persist in soils and show high potential for leaching into groundwater (Kinney et al., 2006). Therefore, irrigation with wastewater could have been the source of the contamination by pharmaceuticals and personal care products that was detected in the cave systems at PA. Since sewage is also a source of pollution from nutrients and pathogens, these data point to other potential impacts of sewage, including nutrient loading in the coastal zone and exposure of human populations to bacterial, viral and parasitic pathogens. In this region of Mexico, there is widespread use of reverse osmosis systems for treatment of drinking water, but this technology is unlikely to remove all microcontaminants (Kimura et al., 2004). The data provided in this study raises some concerns about the potential for human exposure from the consumption of contaminated drinking water.

4. Conclusions

The planned growth of urban and tourism development in this region of Mexico will benefit from the adoption of mitigation strategies and Beneficial Management Practices (BMPs) to ensure that pollution does not pose a serious threat to the coastal ecosystems and human health, and thereby affect the economy. Several BMPs have already been recommended for protection of natural resources in a guideline for sustainable development of the area (SEMARNAT, 2006). Impermeable liners should be installed beneath golf courses and other areas that are extensively covered with turf in order to restrict the leaching of contaminants, nutrients and pathogens into the underlying aquifer. Lined and impermeable drainage canals, retention ponds and treatment systems should be installed to deal with the runoff in areas where liners have been installed. To avoid contamination from the domestic sewage produced by cities, towns and resorts, it is essential to develop and maintain adequate wastewater treatment infrastructure. The practice of injection of sewage into the salt water aquifer should be discontinued, as it has been in areas of Florida, USA that have karst geology. Finally, care must be taken to avoid contamination of the aquifer as a result of runoff from highways, roads, parking lots and the tarmac at airports. Protection of the remaining mangrove ecosystems is necessary to provide an additional buffer against coastal pollution. Other environmental stressors, such as climate change may also contribute to the deteriorating quality and quantity of freshwater resources. It is well established that saline intrusion into groundwater lenses and coastal aquifers resulting from a combination of sea-level rise and over-abstraction is already posing a threat to the quality and availability of freshwater supplies in the Caribbean region (Singh, 1997).

There are several obstacles to overcome in order to implement an effective management strategy for this region of the Yucatan Peninsula. There is a general lack of expertise and equipment for monitoring or tracking sources of pollution, and there are few administrative links between those responsible for water and coastal management and the researchers that generate the data. Land and water management in the region is fragmented, and is often ineffective in the face of pressure to develop the tourism and recreational industry. Integrated approaches to water management are required that are built upon participation by all stakeholders, including the private sector, government and the communities. The stakeholders can help to define problems, identify appropriate BMPs and monitor the effectiveness of management strategies. Without these integrated approaches, the tourism-based economy of the Maya Riviera region will not be sustainable over the medium to long term.

Acknowledgements

This work was conducted as part of the Caribbean Coastal Pollution Project of UNU-INWEH through support from the Canadian POPs Trust Fund of the Canadian International Development Agency (CIDA) and managed by the World Bank. Passive sampler extracts were analyzed for chlorophenoxy herbicides by Axys Analytics Inc. and we thank John Struger and Sean Backus of Environment Canada in Burlington, ON for arranging for these analyses. We are extremely grateful to the cave divers who deployed the passive samplers; Robert Schmittner, Dennis Weeks and Jeff Clark. Many thanks also to Ken Drouillard at the University of Windsor for the analysis of PBDEs, Simon Richards of Karst-Engineering Inc. for his advice on sources of contamination, and Alejandra Fregoso Dominguez and Albert Franquesa Rinos of Amigos de Sian Ka'an for their cooperation and advice.

References

Adolfsson-Erici, M., Pettersson, M., Parkkonen, J., Sturve, J., 2002. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. Chemosphere 46, 1485–1489.

Alcocer, J., Lugo, A., Marin, L.E., Escobar, E., 1998. Hydrochemistry of waters from five cenotes and evaluation of their suitability for drinking-water supplies, northeastern Yucatan, Mexico. Hydrogeol. J. 6, 293–301.

Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., 2004. Development of a passive, *in situ*, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23, 1640–1648.

Back, W., Hanshaw, B.B., 1970. Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. J. Hydrol. 10, 330–368.

Beddows, P.A., Henrickson, M.R., 2007. When the survey is not enough; temperature, salinity, and dye tracing reveal flow paths. National Cave and Karst Management Symposium, pp. 1–6.

Beddows, P.A., Smart, P.L., Whitaker, F.F., Smith, S.L., 2007. Decoupled fresh-saline groundwater circulation of a coastal carbonate aquifer: spatial patterns of temperature and specific electrical conductivity. J. Hydrol. 346, 18–32.

Beddows, P.A., 2004. Groundwater Hydrology of a Coastal Conduit Carbonate Aquifer: Caribbean Coast of the Yucatan Peninsula, Mexico. PhD thesis, University of Bristol, U.K., 303 p.

Bennett, E.R., Metcalfe, C.D., 2000. The distribution of degradation products of alkylphenol ethoxylates near sewage treatment plants in the lower Great Lakes. Environ. Toxicol. Chem. 19, 784–792.

Booij, K., Smedes, F., van Weerlee, E.M., 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. Chemosphere 46, 1157–1161.

Carrara, C., Ptacek, C.J., Robertson, W.D., Blowes, D.W., Moncur, M.C., Sverko, E., Backus, S., 2008. Fate of pharmaceutical and trace organic compounds in three septic system plumes, Ontario, Canada. Environ. Sci. Technol. 42, 2805–2811.

Carruthers, T.J.B., van Tussenbroek, B.I., Dennison, W.C., 2005. Influence of submarine springs and wastewater on nutrient dynamics of Caribbean seagrass meadows. Estuar. Coast. Shelf Sci. 64, 191–199.

Chalew, T.E.A., Halden, R.U., 2009. Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban. J. Am. Water Res. Assoc. 45, 4–13.

Chu, S., Metcalfe, C.D., 2007. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1164, 212–218.

Covaci, A., Voorspoels, S., De Boer, J., 2003. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples – a review. Environ. Int. 29, 735–756.

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031

Delgado, C., Pacheco, J., Cabrera, A., Batllori, E., Orellana, R., Bautista, F., 2010. Quality of groundwater for irrigation in tropical karst environment: the case of Yucatan, Mexico. Agric. Water Manag. 97, 1423–1433.

Dodder, N., Strandberg, B., Hites, R.A., 2002. Concentrations and spatial variations of polybrominated diphenyl ethers in fish and air from the North-Eastern United States. Environ. Sci. Technol. 36, 146–151.

Ford, D.C., Williams, P., 2007. Karst Hydrogeology and Geomorphology, second ed. John Wiley and Son, NY, USA, 526 p.

Graniel, C.E., Morris, L.B., Carrillo-Rivera, J.J., 1999. Effects of urbanization on groundwater resources of Merida, Yucatan, Mexico. Environ. Geol. 37, 303–312.

Hanshaw, B.B., Back, W., 1980. Chemical mass-wasting of the northern Yucatan Peninsula by groundwater dissolution. Geology 8, 222–224.

Harman, C., Tolefsen, K.-E., Boyum, O., Thomas, K., Grung, M., 2008. Uptake rates of alkylphenols, PAHs nd carbazoles in semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS). Chemosphere 72, 1510–1516.

Harvell, D., Jordan-Dahlgren, E., Merkel, S., Rosenberg, E., Raymundo, L., Smith, G., Weil, E., Willis, B., 2007. Coral diseases, environment drivers, and the balance between coral and microbial associates. Oceanography 20, 172–195.

Hawrelak, M., Bennett, E., Metcalfe, C., 1999. The environmental fate of the primary degradation products of alkylphenol ethoxylate surfactants in recycled paper sludge. Chemosphere 39, 745–752.

Huckins, J.N., Petty, J.D., Lebo, J.A., Orazio, C.E., Prest, H.F., Tillitt, D.E., Ellis, G.S., Johnson, B.T., Manuweera, G.K., 1997. Semipermeable membrane devices (SPMDs) for the concentration and assessment of bioavailable organic contaminants in aquatic environments. In: Ostrander, G. (Ed.), Techniques in Aquatic Toxicology. Lewis Publ., Boca Raton, FL, USA, pp. 625–655.

Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., Echols, K.R., 1999. Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. Environ. Sci. Technol. 33, 3918–3923.

Kimura, K., Toshima, S., Amy, G., Watanabe, Y., 2004. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. J. Memb. Sci. 245, 71–78.

Kinney, C.A., Furlong, E.T., Werner, S.L., Cahill, J.D., 2006. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environ. Toxicol. Chem. 25, 317–326.

Kolpin, D.W., Skopec, M., Meyer, M.T., Furlong, E.T., Zaugg, S.D., 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants in streams during different flow conditions. Sci. Total Environ. 328, 119–130.

Kose, T., Yamamoto, T., Anegawa, A., Mohri, S., Ono, Y., 2008. Source analysis for polycyclic aromatic hydrocarbon in road dust and urban runoff using marker compounds. Desalination 226, 151–159.

Lewis, M.A., Boustany, R.G., Dantin, D.D., Quarles, R.L., Moore, J.C., Stanley, R.S., 2002. Effects of a coastal golf complex on water quality, periphyton and seagrass. Ecotoxicol. Environ. Saf. 53, 154–162.

Lewis, M.A., Foss, S.S., Harris, P.S., Stanley, R.S., Moore, J.C., 2001. Sediment chemical contamination and toxicity associated with a coastal golf course complex. Environ. Sci. Technol. 20, 1390–1398.

Li, H., Helm, P., Metcalfe, C., 2010a. Sampling for pharmaceuticals, personal care products, and endocrine disrupting substances using the passive polar sampler (POCIS): temperature effects, predictive relationships and application to monitoring in the Great Lakes. Environ. Toxicol. Chem. 29, 751–762.

Li, H., Vermiersson, E., Helm, P., Metcalfe, C.D., 2010b. A controlled field evaluation of water flow rate effects on sampling of pharmaceuticals, personal care products and endocrine disruptor substances using polar organic chemical integrative samplers (POCIS). Environ. Toxicol. Chem. 29, 2461–2469.

Mazzella, N., Dubernet, J.-F., Delmas, F., 2007. Determination of kinetic and equilibrium regimes in the operation of polar organic chemical integrative samplers. Application to the passive sampling of the polar herbicides in aquatic environments. J. Chromatogr. A 1154, 42–51.

Metcalfe, C.D., Tindale, K., Li, H., Rodayan, A., Yargeau, V., 2010. Illicit drugs in Canadian municipal wastewater and estimates of community drug use. Environ. Pollut. 158, 3179–3185.

Metcalfe, T.L., Dillon, P.J., Metcalfe, C.D., 2008. Transport of toxic substances from golf courses into watersheds in the Precambrian Shield region of Ontario, Canada. Environ. Toxicol. Chem. 27, 811–818.

Metcalfe, C.D., Miao, X.-S., Hua, W., Letcher, R., Servos, M., 2004. Pharmaceuticals in the Canadian environment. In: Kümmerer, K. (Ed.), Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks, second ed. Springer-Verlag, pp. 67–87.

Metcalfe, T.L., Metcalfe, C.D., Bennett, E.R., 2000. Distribution of toxic organic contaminants in water and sediments in the Detroit River. J. Great Lakes Res. 26, 55–64.

Municipalidad de Solidaridad., 2005. Programa director de desarrollo urbano del centro de población Tulum. 2002-2026. Actualizacion Marzo de 2005. www.solidaridad.gob.mx.

Mutchler, T., Dunton, K.H., Townsend-Small, A., Fredriksen, S., Rasser, M.K., 2007. Isotopic and elemental indicators of nutrient sources and status of coastal habitats in the Caribbean Sea, Yucatan Peninsula, Mexico. Estuar. Coast. Shelf Sci. 74, 449–457.

Nakata, H., Sasaki, H., Takemura, A., Yoshioka, M., Tanabe, S., Kannan, K., 2007. Bioaccumulation, temporal trend, and geographical distribution of synthetic musks in the marine environment. Environ. Sci. Technol. 41, 2216–2222.

O'Toole, S., Metcalfe, C.D., Crane, I., Gross, M., 2006. Release of persistent organic contaminants from carcasses of Lake Ontario Chinook salmon (*Oncorhynchus tshawytscha*). Environ. Poll. 140, 99–110.

O'Toole, S., Metcalfe, C.D., 2006. Synthetic musks in fish from urbanized areas of the lower Great Lakes, Canada. J. Great Lakes Res. 32, 361–369.

Pacheco, J., Marín, L., Cabrera, A., Steinich, B., Escolero, O., 2001. Nitrate temporal and spatial patterns in 12 water-supply wells, Yucatan, Mexico. Environ. Geology. 40, 708–715.

Paul, E., McLaughlin, M.R., Griffin, D.W., Lipp, E.K., Rose, J.B., 2000. Rapid movement of wastewater from on-site disposal systems into surface waters in the Lower Florida Keys. Estuaries 23, 662–668.

Postigo, C., de Alda, M.J.L., Barceló, D., 2010. Drugs of abuse and their metabolites in the Ebro River basin: occurrence in sewage and surface water, sewage treatment plants removal efficiency, and collective drug usage estimation. Environ. Int. 36, 75–84.

Seiler, R.L., Zaugg, S.D., Thomas, J.M., Howcroft, D.L., 1999. Caffeine and pharmaceuticals as indicator of waste water contamination in wells. Ground Water 37, 405–410.

SEMARNAT., Nov. 2006. Reflexiones y acciones para el desarrollo turístico sostenible, derivadas de la Evaluación de Impacto Ambiental en el caribe Mexicano: Sistema ambiental Punta Bete – Punta Maroma. Secretaría de Medio Ambiente y Recursos Naturales, 112 p.

Singh, B., 1997. Climate-related global changes in the southern Caribbean: Trinidad and Tobago. Glob. Planet. Change 15, 93–111.

Smart, P.L., Beddows, P.A., Coke, J., Doerr, S., Smith, S., Whitaker, F.F., 2006. Cave development on the Caribbean coast of the Yucatan Peninsula, Quintana Roo, Mexico. In: Harman, R.S., Wicks, C. (Eds.), Perspectives on Karst Geomorphology, Hydrology and Geochemistry - A Tribute Volume to Derek C. Fords and William B. White. Geol. Soc. America Special Paper 404, pp. 105–128.

Suzuki, T., Kondo, H., Yaguchi, K., Maki, T., Suga, T., 1998. Estimation of leachability and persistence of pesticides at golf courses from point-source monitoring and model to predict pesticide leaching to groundwater. Environ. Sci. Technol. 32, 920–929.

Woudneh, M.B., Sekela, M., Tuominen, T., Gledhill, M., 2006. Isotope dilution high-resolution gas chromatography/high resolution mass spectrometry method for analysis of selected acidic herbicides in surface water. J. Chromatogr. A 1133, 293–299.

Wu, X.-W., Shan, K.-Z., Kong, D.-Y., Xue, Y.-H., 2009. Adsorption and leaching behavior of herbicide, 2-4-dichlorophenoxy acetic acid in soils. J. Agro-Environ. Sci. 28, 691–695.

Yang, Y., Van Metre, P.C., Mahler, B.J., Wilson, J.T., Ligouis, B., Razzaque, M.M., Schaefer, D.J., Werth, C.J., 2010. Influence of coal-tar sealcoat and other carbonaceous materials on polycyclic aromatic hydrocarbon loading in an urban watershed. Environ. Sci. Technol. 2010, 1217–1223.

Please cite this article in press as: Metcalfe, C.D., et al., Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, Environmental Pollution (2010), doi:10.1016/j.envpol.2010.11.031