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Contamination by organochlorine pesticides in the aquifer of the Ring of Cenotes in Yucatán, México

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Abstract

Banned or restricted organochlorine pesticides in many countries worldwide are still in use in developing countries for agricultural and livestock activities, as well as for vector control in public health campaigns. The present study was conducted to map estimated concentrations of organochlorine pesticides in a karstic region in the Yucatan Peninsula, Mexico, known as ‘Ring of Cenotes’. Water samples from 20 sinkholes (‘cenotes’) were collected during the dry and rainy seasons in 2010–11, analysed by gas chromatography and maps of pesticide concentrations were produced using geographical information system. Results show the presence of banned pesticides, all of them exceeding the limits stated by the Mexican Official Norm. The number and concentration of pesticides during the dry season were qualitatively and quantitatively higher than in the rainy season. The spatial distribution of pesticide concentrations shows that causes of pesticide pollution in the aquifer of the Ring of Cenotes are multifactorial.

Introduction

Karst aquifers supply 25% of drinking water in the world (Ford & Williams 2007), but their preservation is constantly threatened, particularly in developing countries. One of those aquifers is located in the Yucatan Peninsula, Mexico, within and around a hydrological area called the Ring of Cenotes (‘Anillo de Cenotes’ in Spanish). This region is distributed over 27 municipalities on the Northern Yucatan Peninsula and contains about 100 water-filled sinkholes or ‘cenotes’. This ‘ring’ is approximately 5 km wide and has a radius of approximately 90 km with its centre in the port of Chicxulub, associated with the Chicxulub Impact Crater (Sharpton *et al*. 1992). The centre of the peninsula constitutes the main recharge area of the aquifer in the Northern region of the Yucatan Peninsula (Escolero *et al*. 2002; Perry *et al*. 2002). Underground water flows from South to North, traversing the Ring of Cenotes region, and radiates towards the coast of the Gulf of Mexico, in the coastal areas of Dzilam and the Celestun Estuary (Perry *et al*. 2002; González *et al*. 2002; Batllori *et al*. 2006).

Groundwater flows through dissolution fractures, channels and caverns, which eventually collapse, giving rise to the most common sinkholes known as ‘dolines’ (Munro-Stasiuk & Manahan 2010). The Ring of Cenotes is recognized as a Ramsar site, a priority area for the conservation of water resources. Ramsar is the Convention on Wetlands of International Importance for the conservation, called the *Ramsar Convention* (Ramsar Convention 2012).

The karstic soils in that region render groundwater highly vulnerable to contamination from the surface (Bakalowicz 2005), primarily by compounds known as persistent organic pollutants (POPs), widely used in agricultural and livestock activities. The presence of organochlorine pesticides (COPs) in the environment cause neurological health effects and other diseases like asthma, congenital malformations and cancer in humans (Van Maele-Fabry *et al*. 2006; Cohn *et al*. 2007; Cohn 2011; EEA 2012). OCPs have high stability because of a high resistance to chemical and biological degradations (Yang *et al*. 2013), and they are linked to endocrine disruption, that is, they interfere with the synthesis, transport, binding and activity of natural hormones (Mustafa 2010). Soil is the principal pool of environmental pesticides and plays an important role in their global distribution, particularly into groundwater (Zhang *et al*. 2013).

While OCPs have been banned in many developed countries like the United States and many European countries (Stockholm Convention 2009), they are still in use in developing countries. It is well documented that many problems in public health and the environment in Asia, Africa and Latin America are linked to the lack of control or training in the handling and application of pesticides (Jeyaratnam 1990; UNEP, United Nations Children's Fund and WHO 2002; Abdulhamid 2012). For example, studies have shown associations between agriculture and pesticides management with endometrial cancer in Jaipur, India (Vibha *et al*. 2008), and breast and uterus cancers mortality in Punjab, India (Thakur *et al*. 2008). A study in Veracruz, Mexico showed that concentrations of dichlorodiphenyltrichloroethane (DDT) and its metabolites were larger in women with breast cancer than those in a control group (Waliszewski *et al*. 2003).

In the state of Yucatan, social conditions of high marginalization (INEGI 2010) push rural communities to produce their food at any cost, and this includes the use of OCPs without regulation. To make things worse, 30% of the population in the rural zone drinks water from wells or sinkholes (Polanco *et al*. 2012). It is thought that all these factors explain why in the last 15 years, the state of Yucatan has suffered a high prevalence of deaths in women caused by cervix uterine cancers, as well as increases in birth defects, and foetal and infant mortality (INEGI 2009, 2010), among other general health problems. Epidemiological studies are necessary in order to objectively link diseases caused by environmental chronic exposure to OCPs or any endocrine disruptor (Parron *et al*. 2010; Cohn 2011; Atreya *et al*. 2011).

In the 1990s, a study was carried out in Yucatan, seeking to diagnose health conditions of farmers and how pesticides are managed. It was found that between 20% and 44% of workers showed acute poisoning symptoms linked to OCPs (Alvarado *et al*. 1992). More recent studies about pesticides for agriculture and livestock activities in Mexico are scarce, particularly in the region of Yucatan. For example, Polanco *et al*. (2011) found that women with cervix uterine cancer in 18 municipalities showed high levels of pesticides in the blood: 7.352 ppm of endosulfan I, 3.695 ppm of aldrin, 2.336 ppm of 4,4'dichlorodiphenyldichloroethane (DDD), 1.434 ppm of heptachlore in Tizimin, Yucatan, and levels in breast milk of 18.436 ppm of heptachlore epoxide in Kanasin, Yucatan, 1.024 and 2.10 ppm of dieldrin in Peto, Yucatan. On the other hand, a study in milk mother in Chelem, Yucatan reported levels of 4,4'dichlorodiphenyldichloroethylene (DDE) 3041.36 ± 5056.83 ng/g (Rodas-Ortíz *et al*. 2008). Before the present study, there was no indication of documented studies in the area seeking to accurately measure concentration levels of pesticides in groundwater as a means to identify regions at health risk by the use of OCPs.

In order to recognize high-risk geographical areas, it is necessary to use geographical information systems (GISs) to display the varying concentration levels in an area alongside the locations of human settlements (Chica-Olmo *et al*. 2005; Mishra *et al*. 2012). The present research was carried out for the purpose of producing the first assessment of pesticide contamination of groundwater in the area. Map of the distributions of OCPs in the study area will be provided as by-products of this assessment, aiming to highlight potential risks to the environment and public health associated to OCPs.

Description of study area

The geographical distribution of the study area overlaps the semicircular path of the Ring of Cenotes (Fig. 1), covering 11 municipalities of Yucatan, Mexico, and was taken from a study by Pérez-Ceballos *et al*. 2012 (Table 1). The climate is warm and humid, with an average temperature of 25–27°C. The pluvial precipitation averages 1100 mm, the majority falling in the wet or rainy season (June–October). Underground water in this area flows from SW to NE in the dry season (November–May) and from SE to NW in the rainy season (Bautista *et al*. 2011; Orellana 2011).

Experimental procedure

Chemicals

The solid phase extraction cartridges (6 mL syringe body) containing 500 mg of C18 stationary phase were obtained from J. T. Baker Co. Methanol, methyl-tert-butyl ether (MTBE), and hexane used for elution were high-performance liquid chromatography (HPLC) grade and were purchased to Sigma-Aldrich Co. (St. Louis, MO, USA). Deionized water (H_2O) was obtained in the laboratory by ultrafiltration. The analytical standards of 17 OCPs (aldrin, α-lindane, β-lindane, γ-Lindane, δ-lindane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulphate, endrin, endrin aldehyde, heptachlor, heptachlor exo-epoxide and methoxichlor) was obtained from Sigma-Aldrich Co. as Supelco EPA Appendix IX OCPs Mix. The grade analytical standard 4-chlorophenyl benzene sulphonate was used as internal standard and was purchased to Fluka Analytical (Buchs, Switzerland).

Sample pretreatment

The water samples were collected from 20 cenotes during the rainy season (June–October, 2010) and the dry season (November–May, 2011), 1 L per cenote per season, 250 mL of each cardinal point, north, south, east, west, and at a depth of 50 cm. The samples were kept until analysis at 4°C. Each sample was allowed to reach an ambient temperature before they were filtered in vacuum to remove all solid waste. A volume of 500 mL of each filtered sample was pulled through a previously conditioned SPE cartridge under vacuum. The impurities were rinsed with H_2O (10 mL), and the organochlorine compounds were extracted with MTBE (5 mL). The MTBE extract was dried under a stream of N_2, and the residue was dissolved in 1 mL of hexane.

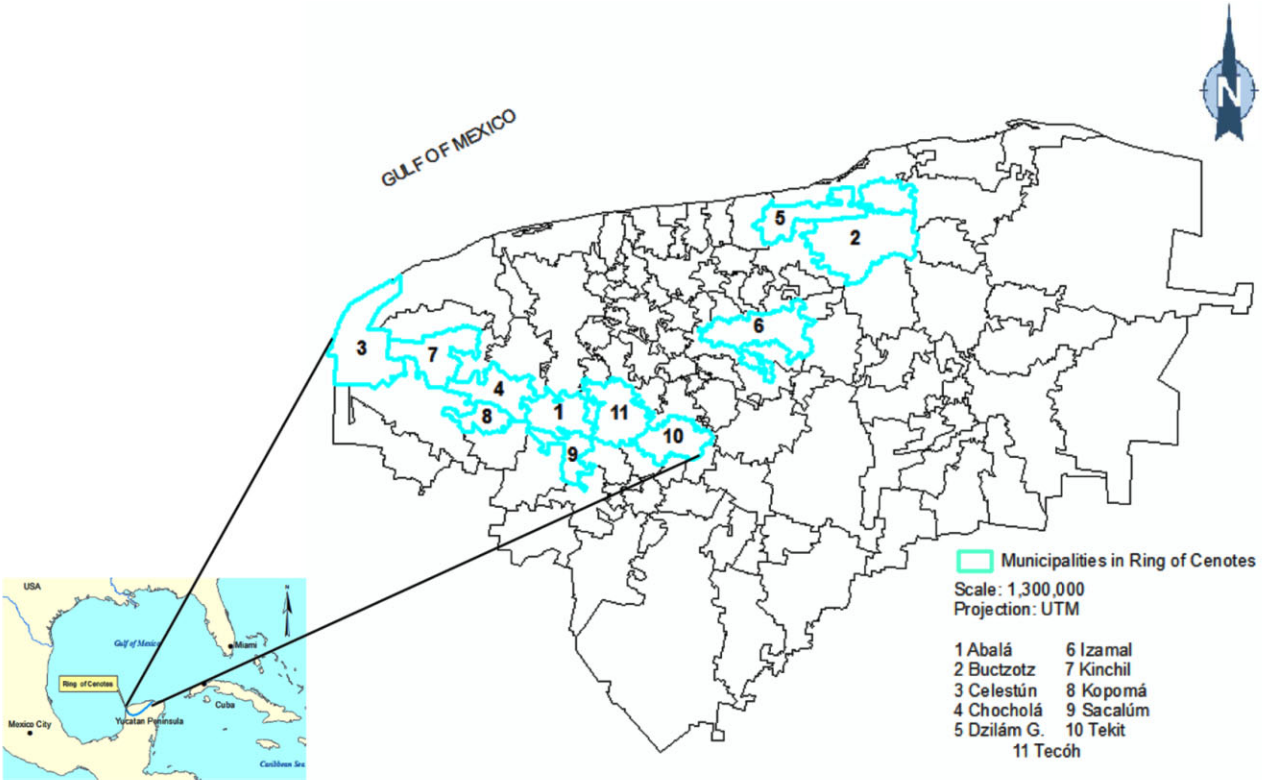

Fig. 1. Ring of Cenotes, Yucatan, Mexico.

Analysis methods

An aliquot of 1 μL of the hexane solution containing organochlorine compounds was injected in splitless mode in a Thermo Scientific gas chromatograph (Pittsburgh, PA, USA) equipped with a 63Ni electron capture detector and an Alltech fused silica capillary column (Deerfield, IL, USA) (30 m × 0.32 mm × 1.0 μm) coated with cross-linked 5% phenyl-95% methyl polysiloxane. Ultrahigh purity helium was used as carrier gas, and high purity nitrogen was the auxiliary gas; the flow rates were 1.1 and 40 mL/min, respectively. Oven temperature was set at 100°C for 2 min, increasing at a rate of 4°C/min to 260°C for 2 min. Injector and detector temperatures were 260 and 290°C, respectively. The detection limits of OCPs are listed in Table 2.

GIS

Following a similar methodology described by Chica-Olmo *et al.* (2005), a GIS was implemented to show the spatial distribution of pesticides in the Ring of Cenotes of Yucatan, Mexico. The platforms used were Idrisi Andes 15.0, Surfer and ArcGis 9.3. A geographical database was created, containing (1) sinkhole coordinates and (2) concentrations of pesticides found in the 11 municipalities for the rainy and the dry seasons.

Table 1 Cenotes georeference

Cenote	Municipality	X	Y
Sabtun	Celestun	−90.23559	20.85026
Xelactun	Kinchil	−90.08106	20.88964
Chunchucmil	Celestun	−90.19667	20.81305
Chen Ha	Kopoma	−89.87589	20.68948
Yax Ha	Chochola	−89.77415	20.67264
Kankirixche	Abala	−89.63298	20.63723
Sabak Ha	Sacalum	−89.58824	20.58049
Nayah	Tecoh	−89.40467	20.64651
X'pakay	Tekit	−89.36504	20.53915
Uitzán	Tekit	−89.34214	20.58069
Noria	Tecoh	−89.34429	20.63776
Tanimax	Tecoh	−89.37227	20.64891
Telchaquillo	Tecoh	−89.26018	20.60223
X'Kol- Ac	Izamal	−88.86629	20.90977
Chen Vazquez	Buctzotz	−88.65785	21.14838
Buenaventura	Buctzotz	−88.65962	21.18907
Itzincab	Buctzotz	−88.67929	21.22751
Dzonot Sabila	Dzilam G.	−88.74779	21.31051
Xlabon	Dzilam G.	−88.78817	21.30679
Dzonot Trejo	Dzilam G.	−88.66786	21.31206

Pérez-Ceballos *et al*. 2012.

Table 2 Detection frequencies, concentration range, mean concentration and detection limit

	Rainy season (n = 20)			Dry season (n = 20)			
Pesticide	Detection frequency (%)	Concentration range (ppm)	Mean concentration (ppm)	Detection frequency (%)	Concentration range (ppm)	Mean concentration (ppm)	Detection limit (μg/L)
α-endosulfan	45	ND – 0.144	0.016	40	ND – 0.457	0.033	0.096
β-endosulfan	40	ND – 0.29	0.027	35	ND – 0.135	0.014	0.070
Dieldrin	80	ND – 0.52	0.059	20	ND – 0.045	0.003	0.061
4,4’DDE	80	ND – 0.846	0.081	70	ND – 1.255	0.112	0.226
4,4’DDD	75	ND – 0.113	0.017	75	ND – 0.417	0.109	0.232
Endrin	50	ND – 2.567	0.248	50	ND – 3.265	0.359	0.065
Endrin aldehyde	95	ND – 0.941	0.120	80	ND – 0.245	0.068	0.115
Endosulfan sulphate	75	ND – 0.134	0.024	55	ND – 0.253	0.036	0.073
4,4’DDT	60	ND – 0.112	0.016	70	ND – 0.235	0.032	0.309
Heptachlore	70	ND – 0.918	0.421	100	ND – 13.617	2.804	0.090
α-lindane	ND	ND	ND	95	ND – 6.538	0.639	0.093
β-lindane	ND	ND	ND	75	ND – 0.924	0.100	0.071
γ-lindane	10	ND – 0.794	0.044	80	ND – 5.233	1.511	0.078
δ-lindane	ND	ND	ND	95	ND – 10.864	0.462	0.087

Permitted concentration value in ppm: heptachlore, 0.00008; aldrin, 0.00003; dieldrin, 0.00003; endrin, 0.00002; DDT, 0.001; endosulfan, 0.00002; lindane, 0.0004 (Mexican Norm: NOM-127-SSA1 1994).

DDT, dichlorodiphenyltrichloroethane; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; ND, no detected.

Statistical analysis

Nonparametric comparisons of medians for paired samples based on Wilcoxon’s signed-ranks were used to test for differences in concentrations between the rainy and dry seasons (Helsel & Hirsch 2002). This analysis took into account pesticides detected in 50% or more of the sampled cenotes in each season only, and the permitted concentration value (PCV) for each pesticide, as indicated by the Mexican Norm: NOM-127-SSA1-1994, was reported as a reference. Calculations needed for these comparisons were performed in R (R Core Team 2013), and $\alpha = 0.05$ was used as the significance level for each comparison.

Results and discussion

Concentrations of OCPs

A total of 324 positive detections were made, and a total of 14 OCPs and their metabolites were identified in varying concentrations during both the rainy and the dry seasons. Table 2 shows detection frequencies, concentration range, mean and the detection limit during the rainy and the dry seasons.

The presence and elevated levels of prohibited pesticides are widespread features of the water samples taken from the cenotes. Whenever an OCP was detected in this study, the corresponding concentration surpassed the PCV established by the Official Mexican Norm; it is noticed that concentration levels were higher in the dry season than in the rainy season.

Metabolites of lindane were more frequent during the dry season, and with the exception of one cenote in the municipality of Celestun, these metabolites were found in all the municipalities.

Comparisons of concentrations between the rainy and dry seasons based on Wilcoxon ranked sum tests are shown in Fig. 2. Heptachlor and 4,4 ’DDD were the only pesticides whose median concentrations differed significantly between periods. Outliers of concentrations in each box plot are labelled by the cenote’s name, and the PCVs are also shown. Nevertheless, the box plots show that very large concentrations were consistently attained by cenotes located in the municipalities of Dzilam, Tecoh and Celestun, mainly in the dry period.

The highest concentrations of 13.61 and 12.54 ppm of heptachlor found in Dzilam in the dry period are not unusual in this and other regions of the world with marked differences between the rainy and dry seasons. High concentrations have been found in similar studies, such as one carried out in the estuaries of southern Honduras, where 23 ppm of lindane and 45.8 ppm of aldrin because of the use of toxic pesticides in agriculture were found (Pratt & Quijandría 1997). In another study in water from the Poas river in Costa Rica, within a coffee growing area, 4.5, 5.4, 6 and 8.3 ppm of endosulfan sulphate were found during the months of May and June (Vargas 2004).

Another study in Nicaragua showed high concentrations of DDT and its metabolites in the dry period (Hellar & Kishimba 2004). The highest concentrations in the dry period may relate to the physicochemical characteristics of water insolubility of OCPs (Hamilton & Crossley 2004). Evaporation is

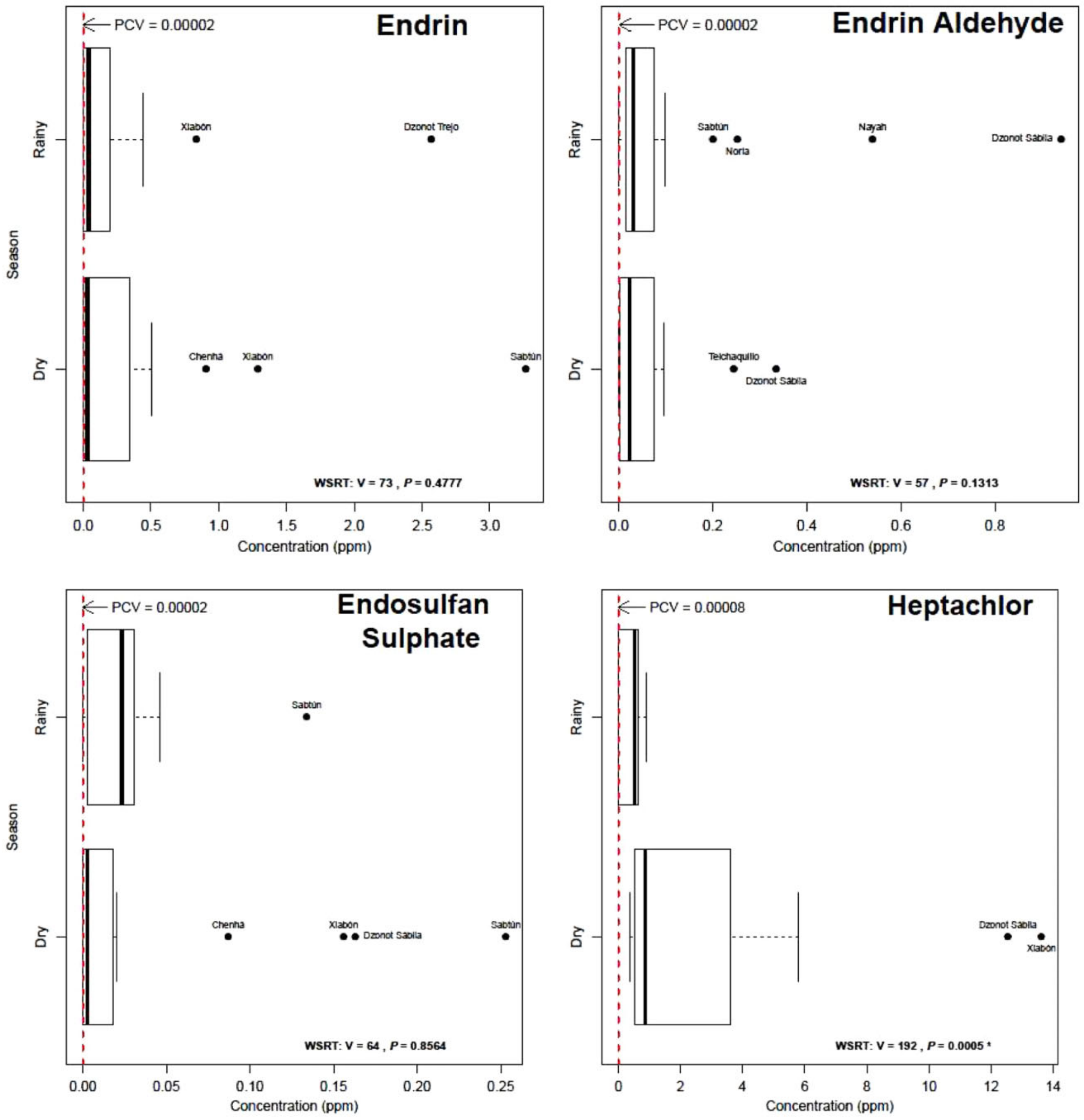

Fig. 2. Comparison based on Wilcoxon tests of pesticide concentrations during two seasons (rainy and dry) for endrin, endrin aldehyde, endosulfan sulphate, heptachlor, 4,4'DDE, 4,4'DDD and DDT. PCV, permitted concentration value; DDT, dichlorodiphenyltrichloroethane; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; WSRT, Wilcoxon signed-rank test.

accentuated in the dry season, causing an increase in the amount of total dissolved solids of pesticides in the cenote water (Van der Kamp 1995). Hydrological studies in China showed that in the rainy season, the hydraulic flow has a dilution effect on pollutants, but the undercurrent water column gets reduced during dry season, increasing the concentration of pollutants, such as DDT and its metabolites in that region (Ta *et al*. 2006). This was again confirmed in a river in Thailand, in which concentrations of aldrin and dieldrin were 3–10 times higher in dry season that in the rainy season (Onodera and Tabucanon 1986). Spatiotemporal analyses of the variation of other solutes in cenotes in Yucatan, such as nitrates, also indicated a predominance of highest concentrations in the dry season (Baker 1987; Pacheco *et al*. 2004).

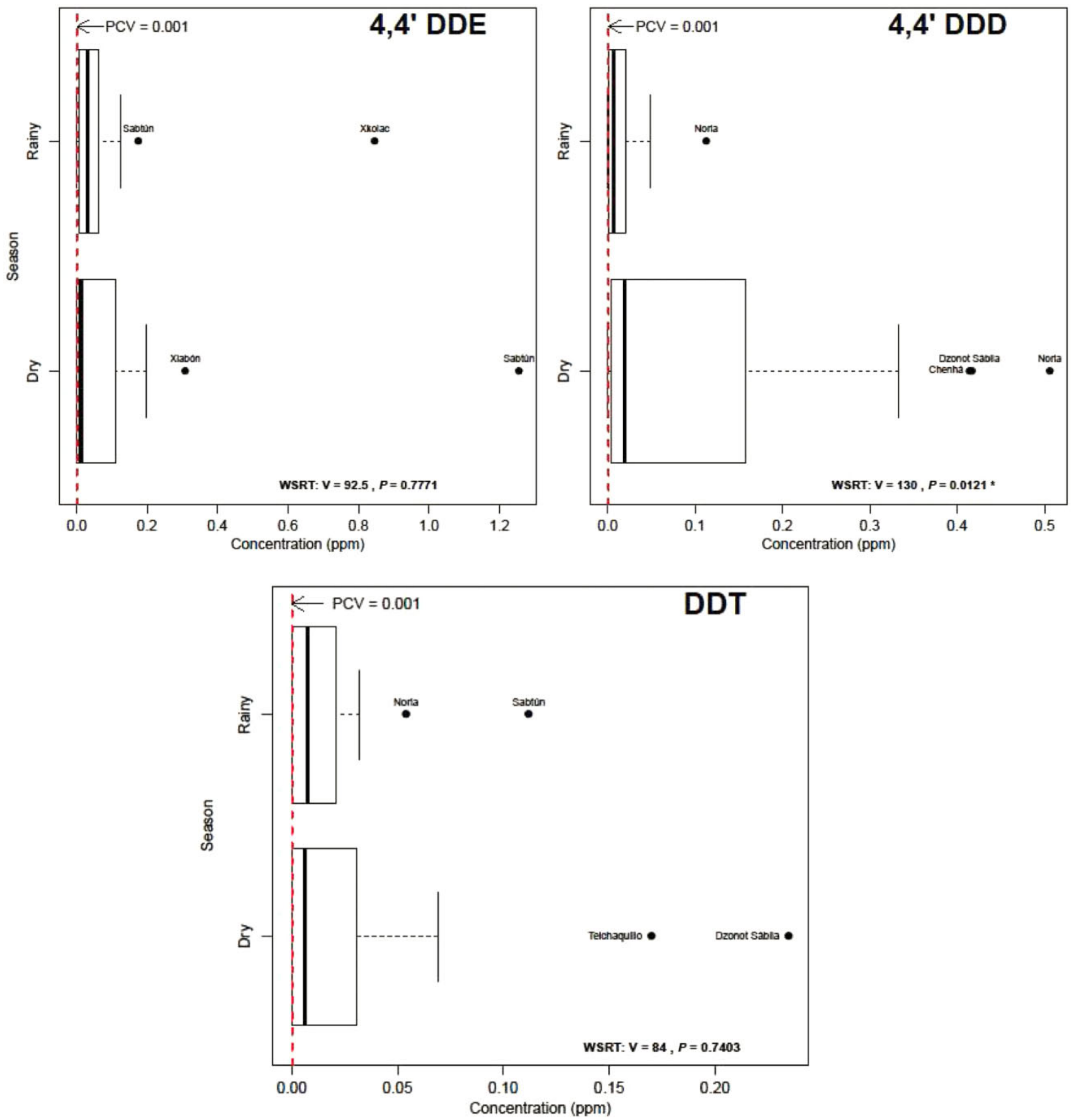

Fig. 2. Continued.

Geographical analysis for pesticides

The spatial analysis allows us to see the water quality variability in both seasons in the study area (Joost and Lammert 2009) and shows the spatial distribution of pesticides above of the PCV in the study area. The spatial pattern of pesticide concentrations shows high degradation of water quality in the municipalities of Dzilam, Celestun and Tecoh in the northeast, northwest and in the centre of the Ring of Cenotes, respectively, with high concentrations of heptachlor and lindane. Dzilam, the discharge zone of the Ring, is located in the livestock region of the Yucatan peninsula, covering ca. 440 000 ha of grasslands that have replaced indigenous tropical forest since the 1940s (INEGI 2013); it is noteworthy that in the last 24 years, Yucatan has lost 30% of its vegetation, and the zone with the highest impact is the livestock region with induced pasture in the northeastern part of the State (Durán 2010). This deforestation has promoted soil erosion, easing filtration of agrochemicals to groundwater (Rashid 2011); moreover, in this geographical area, there is the highest concentration of cenotes (440) in Yucatán, which worsens the vulnerability for the contamination of these cenotes and aquifer because of intensive farming and agricultural activities (Perry *et al*. 2002).

Furthermore, to the East and Northeast of the Ring of Cenotes in Yucatán, there is a vast geographical area of geological strata fracturing, as shown in the Carta Geológica de Fallas of the INEGI, scale 1 : 1 500 000. These geological faults and fractures are formed by the dissolving action of the carbonic gas within the rocks of karstic hydric systems (SARH 1988; INEGI 1990), and they facilitate the transport of pollutants such as pesticides and heavy metals into the underground aquifer (Bauer Gottwein *et al*. 2011).

In the municipality of Tecoh, concentrations of 6.5 ppm of α-lindane, 10.86 of δ-lindane were found during the dry season, in an area where there are 128 cenotes and 724 agricultural production units, distributed in an area of about 4000 hectares, and is part of the recharge zone of the Ring (which receives the pollutants from the intensive agriculture areas in the southern part of the State), and it is a zone of the aquifer in its course towards the northern coast of the Yucatan Peninsula. Celestun, the northwest discharge zone of the Ring, with 4.42 ppm of heptachlore and 2.56 ppm of γ-lindane, also receives pollutants from the municipalities that are close to the southern part of the Ring because of agricultural and livestock activities. Among these three areas, Dzilam, Celestun and Tecoh draws our attention (Fig. 3).

Some studies show another factor of pesticide contamination, as the non-point source of groundwater from the south of state and the Yucatan Peninsula dragging all the water solutes in the aquifer towards the north, traversing the Ring of Cenotes on their way to the Gulf of Mexico (Leonard 1990; Albanis *et al*. 1998). This sort of dynamics of the aquifer along with the agricultural and livestock activities in the study area may explain the presence of particular spots where concentrations were the highest.

In general, there is a relaxed attitude in the regulation of pesticide retailing, and a complete absence of training on pesticide handling by farmers. It has been found also that people in the rural communities have a low-risk perception by the use of OCPs with respect to their adverse effects in the environment and human health. A chronic exposure study of forbidden toxic pesticides at low doses during long periods (1990–1999) in Gaza, Palestine, shows a positive correlation between the use of these substances and cancer in both women and men; this is only an example of the impact of such practice that can have on various illnesses, including prostate, brain, liver, uterine and breast cancers, among others (Safi Jamal 2002). Both agricultural farm workers labouring in their parcels of land, as well as their wives and children in their backyard farm animals and cultives, use pesticides in the field and even inside their homes, where they store their crops. This increases their risk for various diseases. Further, pesticides as lindane are also used for the control of ectoparasites in animal production (Alavanja *et al*. 2004; Hamilton & Crossley 2004; Aktar *et al*. 2009).

The only treatment consumed for drinking water in rural communities is chlorination for the biological control of pathogens, but not for pesticides. However, a monitoring of water chemical pollutants to improve data acquisition is not performed (Carr & Neary 2008). High concentrations of pesticides founded in water are a potential hazard to human health (Murray *et al*. 2010), and they are a high difference in the PCV pesticides values and the concentrations measured in the groundwater sources. In addition, 30% of rural populations even nowadays drink water directly from wells and cenotes (Polanco *et al*. 2012).

All these factors together in Yucatan, Mexico, with the results found in the present study pinpoints latent hazard to the human health, and the aquatic and terrestrial biodiversity present in the area, linked to the presence of OCPs. Therefore, it is urgent to launch programs for the environment protection and health risk prevention in the whole area (Joost and Lammert 2009; Plant *et al*. 2012).

Conclusions

(1) The present study shows that the Ring of Cenotes is polluted by OCPs at concentrations above the PCV according to the Mexican official standards. These dangerous concentrations represent a risk on human health and environment, given that handling and retailing of pesticides for agricultural and livestock activities are performed without strict regulation or control.

(2) The spatial analysis of distribution of OCPs allows to visualize that the highest concentrations are located near the coastal zone of discharge and in the centre in the water recharge zone of the Ring of Cenotes.

(3) Effective regulation in the use of pesticides is necessary, in such a way that monitoring programs and verification of the chemical quality of groundwater be established for the state of Yucatán, Mexico.

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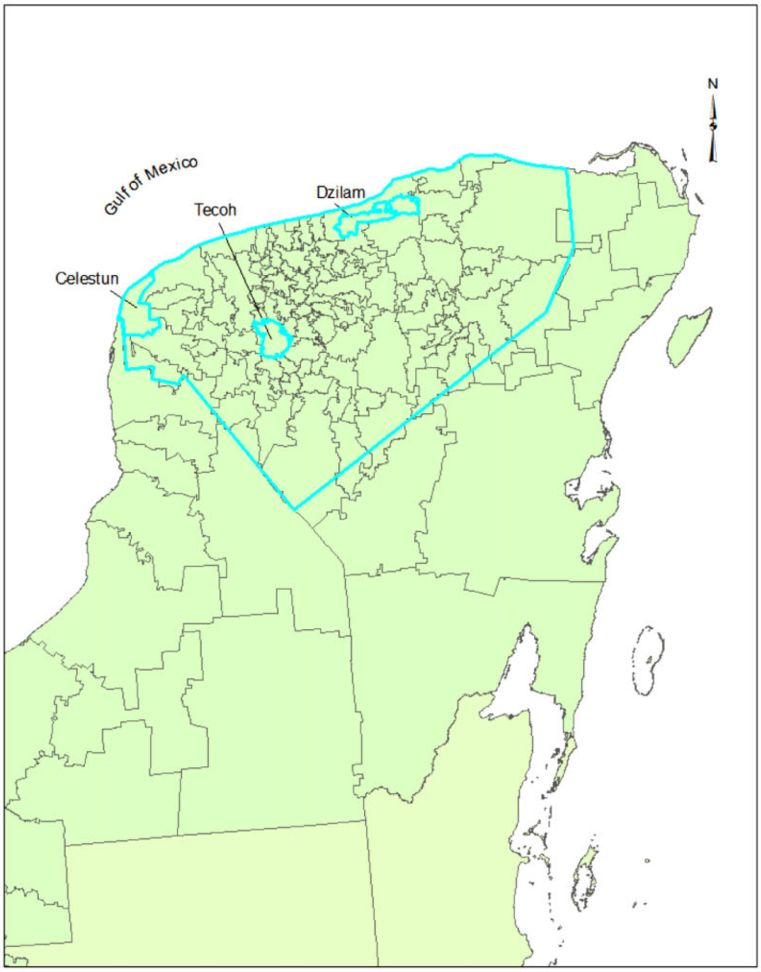

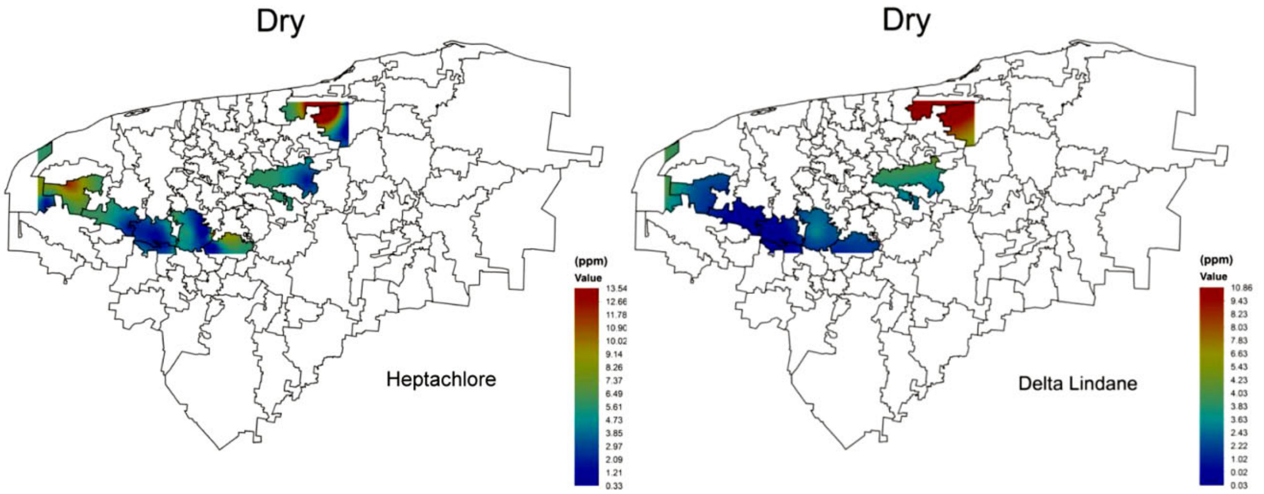

Fig. 3. Heptachlore and lindane highest pollution in Yucatan, México.

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