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Evidence of Dissolved Organic Compounds in a Mexican High-Temperature Geothermal Field

Juan Ignacio SÁNCHEZ-AVILA, Brenda GARCÍA-SÁNCHEZ, Gabriela VARA-CASTRO and Thomas KRETZSCHMAR

CICESE. Carretera Ensenada-Tijuana 3918. Zona Playitas, CP. 22860. Ensenada, B.C. Mexico

tkretzsc@cicese.mx

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ABSTRACT

Dissolved organic compounds (DOC) of medium volatility in hydrothermal systems are attracting attention, due to the close relationship of the reactions involved in the formation of the compounds, with the origin of life on Earth. DOC have been recently reported by few authors as tools for comprehend the biogenic and abiogenic reactions within a continental hydrothermal system. In our case, we report herein for the first time, the presence and relative concentrations of (DOC) in samples from a high-temperature geothermal field in Mexico. The geothermal field of Los Humeros in Mexico is a super-hot steam-dominant geothermal system with temperatures superior than 300 °C. Within the Mexican-European collaboration Project Framework, called GEMex, were analyzed dissolved organic compounds from ten water/vapor condensate samples from active exploitation wells. Besides them, three samples from groundwater and three from cold springs were taken from the surrounding area. Sampling was performed on November-December 2018. For the characterization of the organic compounds, solid Phase Extraction (SPE) was used and analysis by Gas Chromatograph coupled to a Mass Spectrometry (GC-MS). In exploitation geothermal well condensates, a wide range of compounds (38) were identified, pertaining to eight homologue series (alkanes, alkenes, terpenes, aromatics, alcohols, aldehydes, ketones and Sulfur-containing hydrocarbons). In condensates, aromatics and sulfur-containing hydrocarbons were the predominant compounds. Differences in the composition of the DOC were noticed in the geothermal wells fluids with lower estimated temperature. The most typical compounds found in the six cold waters in appreciable concentrations were alkenes, followed by alkanes, alcohols and aromatic hydrocarbons. Monoaromatic hydrocarbons dominated the composition of aromatics in some wells and cold-springs. Our findings do not provide enough evidence to suggest circulation flow paths from the geothermal wells to cold-water sampling sites. Especially if the origin of monoaromatic hydrocarbons in cold springs and groundwater samples is unclear. However, is probable a hydrothermal influence of these compounds. The results of this study increase the scarce knowledge of dissolved organic fraction in hydrothermal systems. On the other hand, the information obtained herein will be useful to other similar studies dealing with the problem of the origin of primary forms of life under hydrothermal environments.

1. INTRODUCTION

The chemical reactions synthesizing organic species in hydrothermal systems are of biotic or abiotic origin. Abiotic processes involve the interaction between high pressures and temperatures, with the presence of minerals and chemical constituents from water-bearing rocks such as H_2S, CO_2 and HCl (Pasek et al., 2017; Simoneit et al., 2009; Welhan, 1988). Biotic synthesis of organic compounds has been related with thermophylic algae and bacteria (Konn et al., 2011; Poturay and Kompanichenko, 2019; Simoneit et al., 2009).

Volatile organic compounds (VOC) have been studied deeply in hydrothermal and volcanic systems. There is available information about the origin and behavior of VOC in those systems around the globe, such as Italy (Tassi et al., 2010, 2005), Russia (Bonini et al., 2013), Spain (Nisi et al., 2013), Argentina (Tassi et al., 2016), Chile (Aguilera et al., 2012; Tamburello et al., 2014; Tassi et al., 2005) and Mexico (Tassi et al., 2009), among others. The study of the organic fraction in hydrothermal fluids is an important activity for geochemical exploration. Since, being species naturally generated in the hydrothermal system, their inclusion in geochemical analyzes will help to prioritize areas with geothermal potential. Compounds of low-molecular weight analyzed from the volcanic/hydrothermal gas phase such as methane, thiophene, alkanes, aromatics and sulfur (S) and O-substituted compounds, have been recommended as geo-indicators in geothermal exploration and volcanic monitoring (Tassi et al., 2010, 2009).

On the other hand, the information of medium to high-molecular weight organic compounds in hydrothermal systems is scarce. In recent years the geothermal regions of the world are attracting attention due to the connection with a rapid development of concepts relating to a hydrothermal origin of life (Holm et al., 2006; Kompanichenko, 2017a; Konn et al., 2009). A few studies report the occurrence of dissolved organic compounds (DOC) with a biogenic and abiogenic origin such as carboxylic acids, alkanes, cycloalkanes, aromatic and polyaromatic hydrocarbons, organometals, among other compounds, in the fluids of marine (Konn et al., 2015, 2009) and continental hydrothermal manifestations (Kompanichenko, 2017b; Kompanichenko et al., 2016; Poturay and Kompanichenko, 2019). Because of their chemical structure, organic compounds tend to volatilize, facilitating their transport when exposed to high temperatures and pressures, as in geothermal systems. Therefore, when they are dissolved in the groundwater, they can migrate through faults and fractures, towards areas far from their hydrothermal origin (Amend et al., 1998). In this study, we intend to lay the ground for the usage of DOC as a tool in the exploration of hydrothermal-activity sites. For this reason, we carried out the identification of DOC in condensates of water–steam mixture from wells of a Mexican high-temperature geothermal field. Additionally, we included groundwater and cold spring water samples from sites nearby the geothermal field. The identification of DOC of medium volatility in condensates and water samples will be a useful starting point for the selection of natural organic tracers during the exploration and exploitation stages of hydrothermal resources. This study forms part of a Mexican-European collaboration Project Framework, called GEMex. It was created with the aim to have a better understanding of super-hot geothermal systems, such as Los Humeros in Mexico. We expect that the information obtained from DOC will be a helpful tool that increases the knowledge about the behavior, nature and dynamics of the reservoir.

2. METHODOLOGY

2.1 Sampling site

In the NE of the state of Puebla in Mexico, within the caldera of The Los Humeros, is located an active geothermal field (Fig. 1). The Los Humeros geothermal field belongs to the eastern portion of the Trans-Mexican Volcanic Belt (TMVB). It is operated by the national Mexican Electrical company (Comisión Federal de Electricidad, CFE). On December 2016, it was estimated a total running power capacity of ~70 MW, being the third most important geothermal field in Mexico after Cerro Prieto (570 MW) and Los Azufres (225 MW) (Romo-Jones et al., 2017). There was reported that at least seven deep (>2100 m) wells have estimated stabilized temperatures higher than >380 °C (Elders et al., 2014; Peiffer et al., 2018), and it is considered a supercritical system (Reinsch et al., 2017). Arellano et al. (2003) proposed a model where geothermal fluids are produced from two reservoirs at depth: a shallow (1000–1650 m a.s.l.) liquid-dominated reservoir with a temperature of 290–330 °C, and a deeper (0–900 m a.s.l.) steam-dominated and hotter one (300–400 °C). Both reservoirs would be separated by a low-permeability vitreous tuff unit. However, the impermeable unit is not observed in all wells and is considered to be discontinuous (Cedillo-Rodríguez, 2000). Recently developed studies propose a conceptual model involving a single reservoir with geothermal wells intercepting different feeding zones. The surface is limited by welded ignimbrite deposits that act as a low-permeability barrier. Accordingly, thermal superficial manifestations within the caldera are scarce, and mainly consist of steaming grounds and weak steam vents in localized areas, associated with advanced argillic alteration (Carrasco-Núñez et al., 2017; Gutiérrez-Negrín et al., 2010). Thermal abnormalities in groundwater were identified (Table 1), with more than 10 °C above the ambient temperature (≈15 °C). Although numerous studies on the geology, as well as on the fluid geochemistry have been carried out at the Los Humeros system, the dynamics of fluids is still uncertain (Pinti et al., 2017).

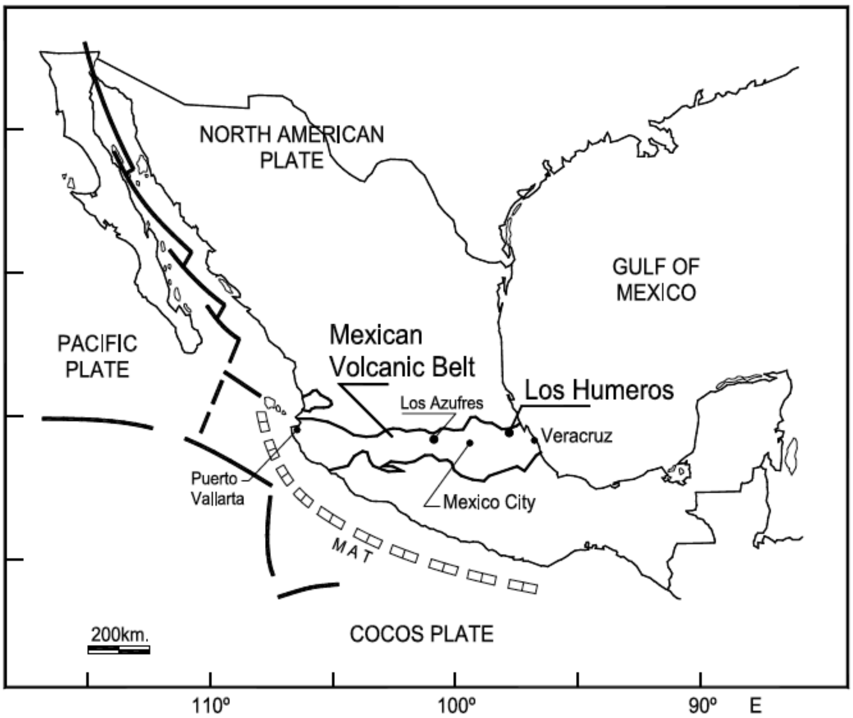

Figure 1: Location of the Los Humeros geothermal field (Figure taken from Arellano et al., 2003).

2.2 Sampling techniques

Sampling of geothermal condensates, spring and ground waters was performed during November-December 2018. Figure 2 shows the location of the sampling sites. Ten condensates of vapor–water mixture were taken directly of the head of the geothermal field wells using a cooling coil of stainless steel (Fig. 3a). Due to the lack of superficial manifestations, we decided to include in the study, groundwater and cold spring water, from sites surrounding the geothermal field. The cold springs samples were taken directly while they are flowing naturally from the rocks (Fig. 3b). Groundwater was sampled from drinking water supply deep wells (180-220 m deep) (Fig. 3c). Pipelines were purged during 5 min before sampling. All water samples were taken in 250 mL amber glass flasks (previously cleaned sequentially with phosphates-free detergent, deionized water, acetone and finally baked during 4 h at 450 °C) and capped with PTFE liners. Samples were transported in coolers and stored at 4 °C until analysis. General physicochemical parameters of the samples are reported in Table 1.

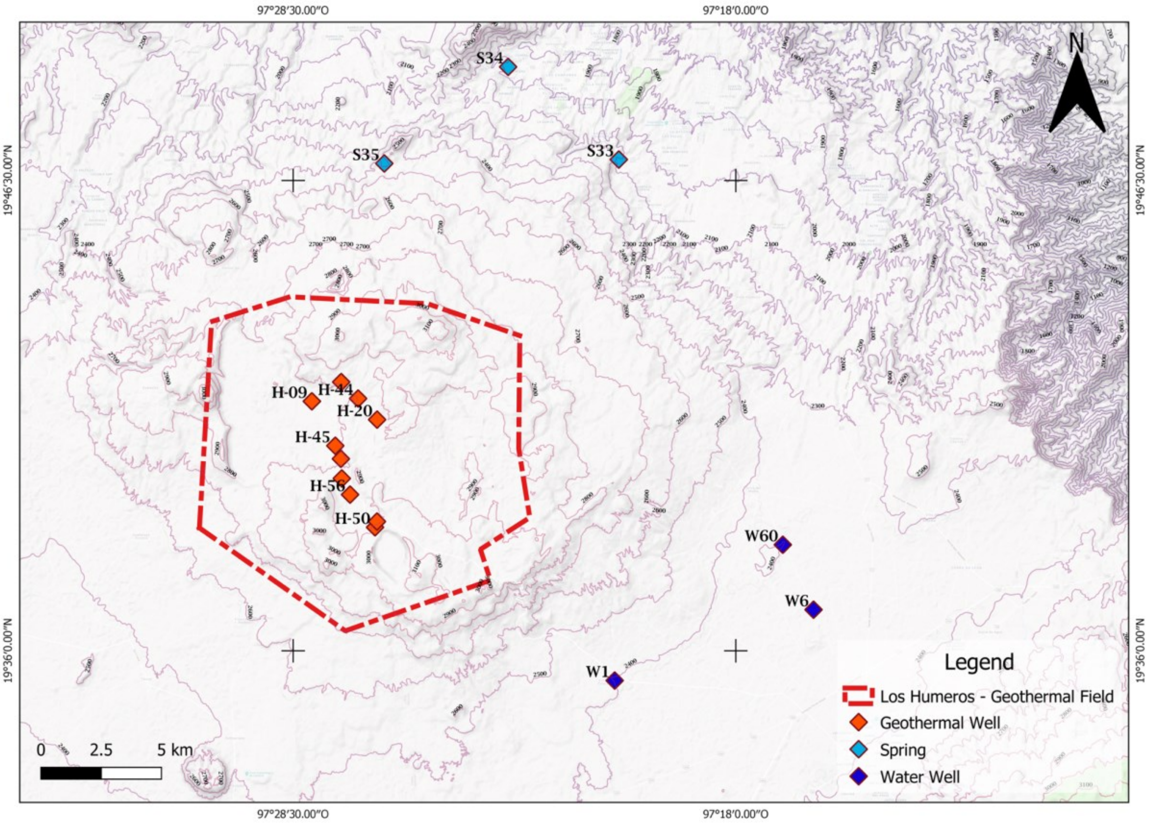

Figure 2. Location of the Los Humeros geothermal field, showing the geothermal wells analyzed and the sampling sites from cold spring and ground water (well).

Figure 3. Sampling of the different waters reported herein: (a) condensates from geothermal wells; (b) cold springs and (c) groundwater from pipes.

Table 1. Physicochemical parameters of the samples analyzed.

Station		pH	Conductivity (µS/cm)	ORP (mV)	Temperature (°C)	Pressure (psi)	Sampling site
Geothermal wells	H-49	8.60	1290	-40	nd	360	Los Humeros geothermal field
	H-56	5.72	390	130.8	nd	460	Los Humeros geothermal field
	H-09	5.83	559.5	128.6	nd	340	Los Humeros geothermal field
	H-44	5.71	293.000	133.6	nd	430	Los Humeros geothermal field
	H-31	5.57	236.8	122.3	nd	260	Los Humeros geothermal field
	H-20	5.63	373.1	120.4	nd	420	Los Humeros geothermal field
	H-07	8.35	2376	-37	nd	222	Los Humeros geothermal field
	H-45	5.20	162.3	143	nd	320	Los Humeros geothermal field
	H-50	5.56	256.9	124.5	nd	420	Los Humeros geothermal field
	H-39	5.64	438	118.9	nd	500	Los Humeros geothermal field

Cold springs	S33	7.53	141.3	13.7	16.3	-	Bosque
	S34	8.17	339.1	-22.5	14.7	-	Chignautla
	S35	8.08	139.5	-16.6	13.5	-	Chagchar
Ground water	W1	7.34	917.7	42.3	24.9	-	Frijol Colorado
	W6	7.75	465.4	20.5	15.6	-	La Victoria
	W60	7.74	768	1.5	22.6	-	Rancho San Francisco

ORP: Oxidation Reduction Potential
nd: Not determined

2.3 Extraction and analysis of dissolved organic compounds

Samples were analyzed within 5 days of being sampled. Extractions and analysis were done in the facilities of the Mexican Center for Innovation of Geothermal Research (CeMIE-Geo/CICESE) at Ensenada, Mexico. DOC was extracted by solid phase extraction (SPE) using 6 mL C-18 (500 mg bed) SPE cartridges acquired from Supelco (Bellefonte, USA). SPE cartridges were conditioned sequentially with hexane, dichloromethane, methanol and ultrapure-water. A total of 250 mL water samples were passed through SPE cartridges and after this, were dried using a vacuum pump. DOC were eluted with 9 mL of dichloromethane. Solvent was evaporated until almost dryness under gentle nitrogen flow and finally reconstituted with 250 µL of dichloromethane.

Qualitative analysis of DOC was carried out using an Agilent (Santa Clara, CA) 7890B/7000C gas chromatograph-mass spectrometer (GC-MS) equipped with an autosampler. The separation was performed in an Agilent DB5MS-UI (5% of phenyl and 95% of dimethyl polysiloxane, 30 m x 0.25 mm DI, 0.25 µm) quartz capillary column. The rate of carrier gas (helium) flow was 1 mL/min. Injector and transfer line temperatures were 290 °C, respectively. Oven was programmed initially at 73 °C during 2 min; then, an increment of 10 °C/min up to 100 °C; finally, an increment of 5 °C/min, up to 290 °C holding during 10 min. Mass spectrometer operated in electronic impact mode at 70 eV. Data acquisition was performed in the full scan mode from 50 to 350 m/z, with a sampling rate of 2 s. Peaks were identified using mass spectra and retention indices (RI) and a library database (NIST-Mass Spectral, vers. 2.2.). The relative concentrations of compounds in a sample were evaluated from peak areas.

3. PRELIMINARY RESULTS AND DISCUSSION

3.1 Blanks and peaks discarded

The total ion current (TIC) chromatograms of the condensates and water samples evidenced the presence of more than 90 different organic compounds (Fig. 4). In some of the cases, the organic compounds occurred in very low concentration and the low intensity of the peak signal could not be separated from noise. Because of this, the score of the identification of some peaks versus the NIST library was very low. Total ion chromatograms contained phthalates ester homologues. These compounds are considered ubiquitous environmental contaminants. On the other hand, phthalates are used as plasticizers in the laboratory material such as the SPE cartridges, septa, among others. Same criteria were applied to siloxanes that could leachate from GC column and septa. Because of this, we excluded these compounds from the summarizing table 2 that list the relative concentrations of a homologous series of organic compounds.

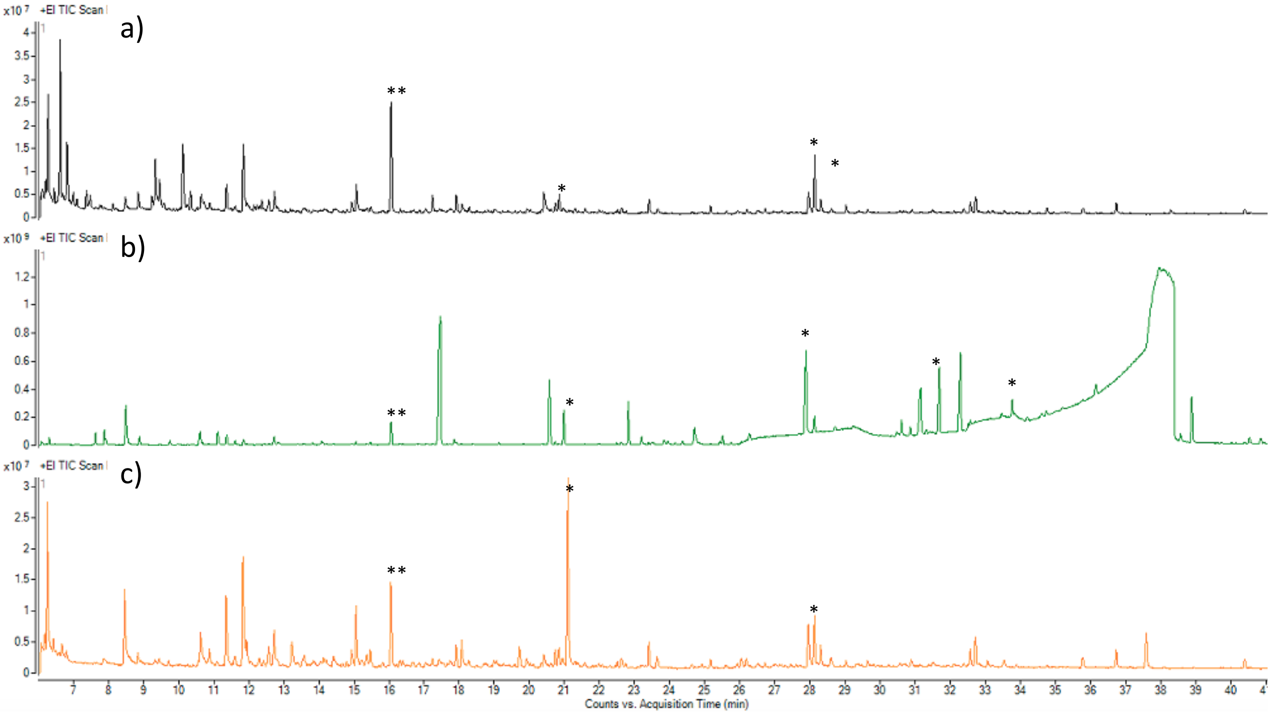

Figure 4: TIC chromatograms of (a) cold spring water, (b) condensate from geothermal well and (c) groundwater samples. Phthalates (*) and siloxanes (**) are showed.

In this report, we only summarized compounds identified with a 85% of NIST-library and RI match, being necessary time and detailed attention in the rest 30 different compounds detected in TIC chromatograms.

3.1 Dissolved organic compounds in steam-water condensates

This is the first report of dissolved organic compounds from fluids from a high-temperature hydrothermal system in Mexico. The 10 samples from condensates were taken from operative wells. The wells are under pressure, ranging from 222 to 500 with pH varied within a wide range of pH from 5.2-8.6. Gutiérrez-Negrín et al. (2010) reported that wells mainly produce steam with high enthalpy (more than 2000 kJ/kg) and the water is chemically homogeneous of type sodium-chloride to bicarbonate-sulfate with high content of boron, ammonia and arsenic. In the condensates, we positively identified 38 different organic compounds from 8 different homologues groups (Table 2). Herein we reported only the compounds identified with a conservative identification match of 85% vs. NIST library and RI. The most ubiquitous compounds were styrene and naphthalene, found in 9 wells; followed by biphenyl, dibenzothiophene hexathiepane and tridecanol, in 6 wells (Table 2). TIC chromatograms of geothermal condensates evidenced high concentrations of elemental octaatomic sulfur (S_8), as can be appreciated at Figure 4b (minute 35-39) and several sulfur-containing hydrocarbons. The exception was condensate from well H-7, where there is an absence of S_8 and only traces of sulfur-containing hydrocarbons (Table 2); this well had very different composition than the rest of the condensates (Fig. 5), being the most abundant monocyclic aromatics (54.9%), followed by alcohols (22.9%), aldehydes (8.2%), alkanes (6.9%), alkenes (4.5%) and terpenes (2.6%). Condensates from well H-50 were the most diverse (Fig. 5), with 20 compounds identified; bicyclic aromatics were the most abundant homologues (35.1%), followed by polycyclic aromatics (30.5%), sulfur-bearing (15.8%), monocyclic aromatics (12.9%), alcohols (4.3%) and finally aldehydes (1.4%). Wells H-20, H-31, H-45 and H-56 had similar composition (Fig. 5), being sulfur-bearing hydrocarbons the most abundant (47.3, 50.1, 37.1 and 68%, respectively), followed by monocyclic aromatics (27.2, 25.2, 26.0, 12.8% respectively), alcohols (12.2, 12.5, 7.9 and 0.0%, respectively), aldehydes (10.0, 6.7, 5.3 and 6.5%, respectively) and bicyclic aromatics (3.3, 2.3, 15 and 9.9%, respectively); in this group, well H-31 was the only one with alkanes (1.4%) and H-45 and H-56 presented polycyclic aromatics (8.7 and 2.8%, respectively). On wells H-9, H39 and H-44, the majoritarian homologue series (Fig. 5) were the S-bearing compounds (31.9, 62 and 37.6%, respectively) but with differences on proportion of bicyclic aromatics (9.1, 16.1 and 37.5%, respectively), polycyclic aromatics (26.5, 21.8 and 0%, respectively), monocyclic aromatics (25.0, 0 and 8.4%, respectively), alkanes (only H-9, 3.5%) and ketones (only H-44, 16.5%). Finally, condensates from well H-49 were also different of the rest (Fig. 5), because the most abundant homologues were alkanes (39.3%), followed by monocyclic aromatics (18.8%), aldehydes (16.3%), alcohols (9.9%), polycyclic aromatics (9.7%) and finally S-bearing hydrocarbons (5.9%). Our results agreed with DOC analyzed in condensate of water–steam mixture taken from the deep wells (1600–2000 m) from hydrothermal systems of Kamchatka Peninsula (Kompanichenko, 2017b; Kompanichenko et al., 2016). The most diverse homologous series in these condensates were aromatic hydrocarbons (naphthalene, 1,2- methylnaphthalene biphenyl, phenanthrene, fluorene, squalene, 1,3-diethylbenzene, trichlorobenzene, etc.) and alkanes (decane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, etc.). The highest temperature (175 °C) sample contains only polycyclic aromatic hydrocarbons (naphthalene, biphenyl, phenanthrene, fluorene, and 1-methylnaphthalene). Biphenyl and phenanthrene are absent in the wells with the lower temperature of fluid (108–124 °C). However, these samples contain other aromatic hydrocarbons (benzenes, xylenes), as well as compounds of other homologous series. It is noticeable that condensates from Los Humeros geothermal field, could be grouped according the distribution of homologues. Wells H-7 and H-49 had very different distribution of homologues than the rest of the wells. These differences could be attributed to the temperatures of the fluids. Even we do not dispose the real temperatures on the head of the wells neither the estimated temperatures of each well, we noticed during sampling that wells H-7 and H-49 exhibited a water dominant phase. More detailed studies are needed to strength this affirmation. It is necessary to compare our findings with the real or estimated temperatures and the inorganic composition of the fluids. However, the few studies that consider the analysis of dissolved organic compounds in continental geothermal fields, report differences in the distribution of homologues due to temperatures in wells.

Table 2. Dissolved organic compounds identified in the condensates of geothermal wells.

Compounds	Formula	H-7	H-9	H-20	H-31	H-39	H-44	H-45	H-50	H-49	H-56
n-alkanes											
Decane	$C_{10}H_{22}$	X	X		X					X	
Dodecane	$C_{12}H_{26}$	X								X	
Tridecane	$C_{13}H_{28}$	X									
Hexadecane	$C_{16}H_{34}$									X	
Octadecane	$C_{18}H_{38}$									X	
Alkenes											
1-Nonadecene	$C_{19}H_{38}$	X									
Terpenes											
3-Carene	$C_{10}H_{16}$	X			X						
Aromatics											
Monocyclic											
Ethylbenzene	C_8H_{10}	X							X		
Styrene	C_8H_8	X	X	X	X			X	X	X	X
Benzene, 1,3-dimethyl-	C_8H_{10}	X		X	X			X	X		
Benzene, 1,2,4-trimethyl-	C_9H_{12}	X									
Biphenyl	$C_{12}H_{10}$		X		X		X	X	X		X
1,1'-Biphenyl, 4-methyl-	$C_{13}H_{12}$								X		
Bicyclic											
Naphthalene	$C_{10}H_8$		X	X	X	X	X	X	X		X
Naphthalene, 2-methyl-	$C_{11}H_{10}$						X	X	X		X
Naphthalene, 1-methyl-	$C_{11}H_{10}$						X	X	X		
Naphthalene, 2-ethyl-	$C_{12}H_{12}$								X		

Compounds	Formula	H-7	H-9	H-20	H-31	H-39	H-44	H-45	H-50	H-49	H-56
Polycyclic											
Fluorene	$C_{13}H_{10}$							X	X		
Phenanthrene	$C_{14}H_{10}$		X			X		X	X		
Fluoranthene	$C_{16}H_{10}$					X			X		
Pyrene	$C_{16}H_{10}$		X							X	X
Perylene	$C_{20}H_{12}$									X	
3H-Benz[e]indene, 2-methyl-	$C_{14}H_{12}$								X		
1H-Phenalene	$C_{13}H_{10}$					X					
9H-Fluorene, 9-methyl-	$C_{14}H_{12}$								X		
Alcohols											
Ethanol, 2-butoxy-	$C_6H_{14}O_2$	X		X	X			X	X		
1-Tridecanol	$C_{13}H_{28}O$	X		X	X			X	X	X	
alkylated-Cyclohexanol	$C_{10}H_{18}O$				X				X		
Aldehydes											
Nonanal	$C_9H_{18}O$		X		X					X	X
Pentadecanal	$C_{15}H_{30}O$	X									
Benzaldehyde	C_7H_6O	X		X	X			X	X		
Ketones											
Acetophenone	C_8H_8O						X				
Sulfur-containing hydrocarbons											
Dibenzothiophene	$C_{12}H_8S$		X	X	X		X	X			X
Hexathiepane	CH_2S_6			X	X	X	X	X	X		
Naphtho[2,1-b]thiophene	$C_{12}H_8S$					X			X	X	X

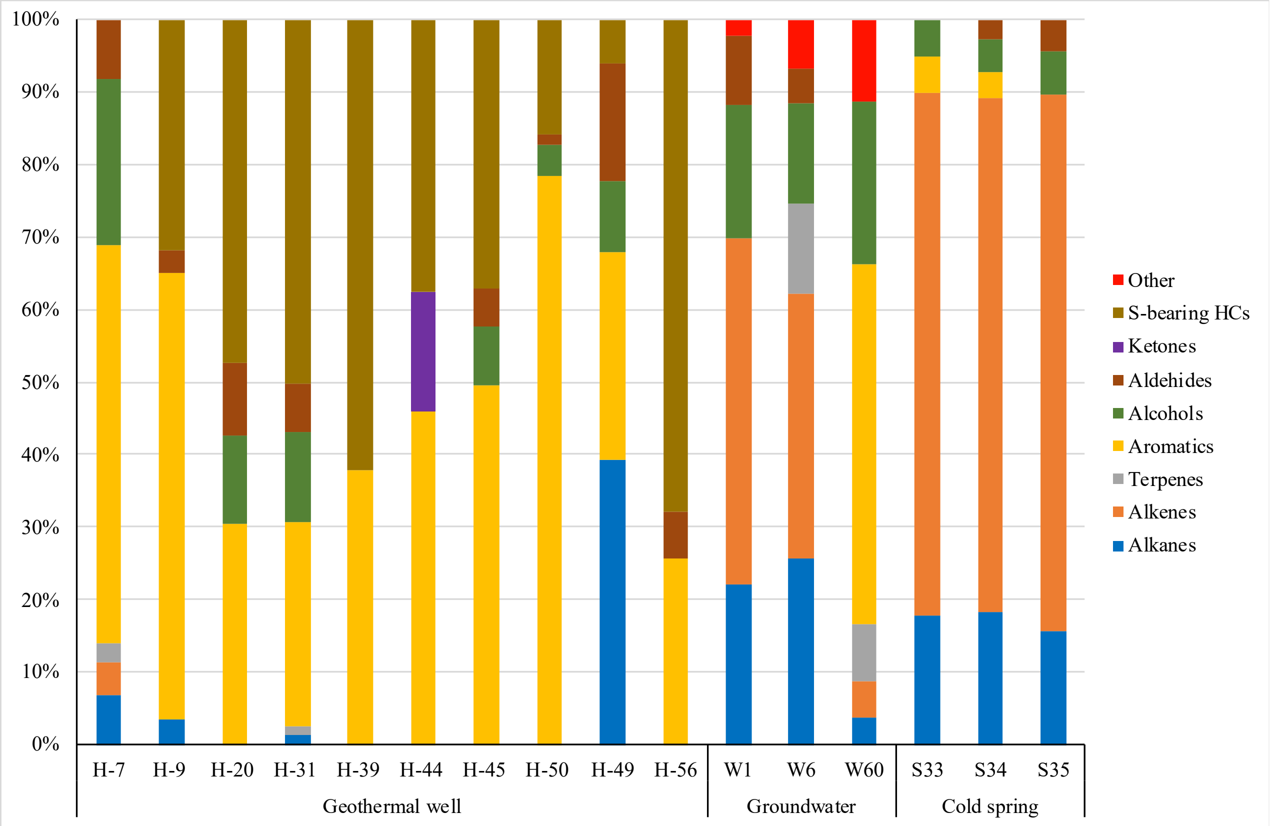

Figure 5: Distribution of homologues series of dissolved organic compounds in geothermal well condensates, groundwaters and cold spring waters from the Los Humeros geothermal field.

Organic compounds in geothermal fluids are mainly produced by degradation of organic matter (Tassi et al., 2012, 2009). Accordingly to Poturay and Kompanichenko (2019), organic compounds in condensates of high temperatures wells are considered lifeless (sterile), and hence, organic compounds in them could not be synthesized by a hydrothermal biota. The highest temperature at which hyper-thermophilic communities of microorganisms can exist is, according to different workers, between 113 and 122°C (Rampelotto, 2013). In the condensates, carboxylic acids were not detected. The presence of carboxylic acids in thermal waters is generally related to thermophilic microorganism activity (Kaur et al., 2011). It implies that the compounds were generated by abiogenic processes, including re-synthesis of biogenic organic remnant extracted from the host rocks. Since as that the estimated reservoir temperatures varies from 220-420 °C (Gutiérrez-Negrín and Izquierdo-Montalvo, 2010), it is expected that origin of dissolved organic compounds in the reservoir have an abiogenic process.

3.1 Dissolved organic compounds in cold springs and groundwater

The organic composition of cold spring water and groundwater from the surroundings of Los Humeros caldera is described for the first time herein. The most typical compounds found in the 6 cold waters in appreciable concentrations are alkenes (ranging from 5.1 to 72.1%), followed by alkanes (from 4.2 to 38.9%), alcohols (from 3.6 to 25.7%) and aromatic hydrocarbons (from 3.6 to 49.7%) (Fig. 5). Traces of other identified compounds were aldehydes, ketones, terpenes, and steroids. Similarities in the relative concentrations of DOC were found between the 3 cold springs (S33, S34 and S35) and groundwater W1 and W6. The origin of the organic compounds detected would be related to a non-specific origin due to the natural composition of the waters (Frazier et al., 2003). For example, the high concentration of alkanes and alkenes probably derive from aliphatic biopolymers such as cutin and suberin from vascular plants, or algaenan in algae (Jiang et al., 2017).

Aromatic hydrocarbons were detected in cold springs (S33, S34, S35) and a groundwater (H60). The composition is dominated by monoaromatic compounds such as styrene, ethylbenzene, dimethyl and tetramethyl benzenes which are not considered diagnostic of any source and are probably related to microbial proteinaceous material (Frazier et al., 2003; Jiang et al., 2017). In continental thermal waters from the Kamchatka Peninsula, high concentrations of monoaromatic hydrocarbons were found, ranging from 19 to 28% of the relative concentration of DOC (Kompanichenko, 2017b; Kompanichenko et al., 2016). This agree with our findings in sample W60, where monoaromatics corresponds to the 57.2% of the DOC, with styrene (35.9%), 1,3-dimethylbenzene (9.1%), 1,2,4-trimethylbenzene (2.4%) and ethylbenzene (2.4%) as principal compounds in the homologue series. Even styrene could be related to anthropogenic pollution by plastic residues, some similarities were found in the geothermal condensates H-7, H-45 and H-50, which are not impacted by pollution. In the 3 cold springs, styrene was also detected, ranging from 3.1 to 5.6% of the relative concentration. Laboratory experiments emulating hydrothermal conditions, at high temperature and pressure (300°C and 100MPa), suggest that aromatic hydrocarbons (in that particular case, toluene) were products in every experiment and they stayed unreactive under the experimental conditions (Shipp et al., 2013). We suggest that there exists an hydrothermal contribution of monoaromatic hydrocarbons in the samples, presumable transported from the geothermal reservoir due to their high solubility of these compounds in the fluids (Konn et al., 2009).

4. CONCLUSION

The primary goal of this work was to obtain evidence for the first time, of dissolved organic hydrocarbons of medium volatility at the Los Humeros geothermal field. A wide range of compounds (38) were identified in exploitation geothermal well condensates, pertaining to 8 homologue series. The high concentrations of monoaromatic hydrocarbons found in condensates, agreed with literature reported experimental studies developed at high pressures and temperatures and with condensates of the other geothermal fields. Differences in the composition of the DOC were noticed in the fluids with lower estimated temperature. According to the temperatures previously reported for the reservoir, it is expected an abiogenic origin of the DOC. Therefore, further investigation is needed to clarify the origin of the organic molecules detected.

Our findings do not provide enough evidence to suggest circulation flow paths from the geothermal wells to cold-water sampling sites. Especially if the origin of monoaromatic hydrocarbons in cold springs and groundwater samples is unclear. However, is probable a hydrothermal influence of these compounds. In this stage, we cannot recommend a specific organic compound or a homologue series as natural tracers of hydrothermal activity. Nevertheless, we will continue our studies paying special attention in monoaromatic hydrocarbons.

The information obtained herein will be useful to other similar studies dealing with the problem of the origin of primary forms of life under hydrothermal environments.

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