Organochlorine Pesticides and Polychlorinated Biphenyls in High Mountain Lakes, Mexico

Liliana García-Solorio
TecNM Instituto Tecnológico de Toluca
Claudia Muro (cmurou@toluca.tecnm.mx)
Tecnológico Nacional de México Instituto Tecnológico de Toluca https://orcid.org/0000-0002-4394-5851
Isaías De La Rosa
Instituto Tecnológico de Toluca: Instituto Tecnologico de Toluca
Omar Amador-Muñoz
Universidad Nacional Autonoma de Mexico Centro de Ciencias de la Atmosfera
Guadalupe Ponce-Vélez
Universidad Nacional Autónoma de México Instituto de Ciencias del Mar y Limnología

Research Article

Keywords: Alpine lakes, Nevado de Toluca, Pesticides OCPs, Biphenyls PCBs, Mass spectrometry, Atmospheric aerosol, Sediments, Plankton, Tubifex tubifex, Endosulfan

Posted Date: November 16th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-980777/v1

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on February 25th, 2022. See the published version at https://doi.org/10.1007/s11356-022-19177-z.

Abstract

Pollution levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were investigated in the El Sol and the La Luna alpine lakes. The lakes are located in central Mexico, in the crater of the Nevado de Toluca volcano. The El Sol and the La Luna lakes are extremely relevant in Mexico and in the world because they are recognized as pristine regions and environmental reservoirs.

Samples of atmospheric aerosol, sediment, plankton, and *Tubifex tubifex* were collected at three different sample locations for three years (2017, 2018, and 2019) at three different times of year, meaning that the weather conditions at the time of sampling were different. Pollutants were analysed by gas chromatography–mass spectrometry with negative chemical ionisation (GC-MS/NCI).

Endosulfan was the most frequent and abundant pollutant, showing the highest peaks of all. Atmospheric aerosol revealed Σ_2 = 45 pg/m^3, including α and β, while sediment lakes displayed α, β and endosulfan sulphate as Σ_3 = 1963 pg/g, whereas plankton and *Tubifex tubifex* showed Σ_2 = 576 pg/g and 540 pg/g for α and β respectively. Results of endosulfan ratios (α/β) and (α-β/endosulfan sulphate) suggest that both fresh and old discharges continue to arrive at the lakes

This study shows for the first time the pollution levels of OCP and PCB in high mountain lakes in Mexico. These results that must be considered by policy makers to mitigate their use in the various productive activities of the region.

Introduction

Organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) are environmental pollutants known for their high toxicity, perseverance, and bioaccumulation.

Due to their harmfulness, the production and use of these pollutants have been banned for several decades; however, despite such restrictions, OCPs and PCBs still exist in the atmosphere because they have low degradation rates and high persistence. In addition, some OCPs are still produced, commercialized, and principally applied in pest control and the agricultural activities; consequently, fresh discharges of OCPs have been detected in several places of the world (Choi et al. 2008; Kallenborn et al. 2013; Yadav et al. 2016; Fang et al. 2017; Lan et al. 2019; Kim et al. 2020).

Similarly, the presence of PCBs is a menace for biodiversity. The production of PCBs was banned in 1979, but given their chemical stability, they continue leaving their mark around the globe. Moreover, the disposal of PCBs and/or their storage is not effectively regulated (Tanabe 1998). According to Bursian et al. (2012), 370 thousand tons of PCBs are held in the atmosphere, and another 780 thousand tons are stored in old electrical equipment, which lacks proper storage control. Therefore, leaks of PCBs from damaged heat exchangers and transformers, as well as landfill sites are potential sources of PCB emissions, increasing the atmospheric levels of PCBs, leading to severe environmental effects in the planet. Also, indirect PCB formation and PCB emissions are caused by processes involving chloride and organic carbon, contributing to the pollution levels in the atmosphere. Such processes include industrial paper bleaching, polymer production, and the burning of various kinds of refuse and plastics in domestic fireplaces/stoves (Wolska et al. 2014).

Currently, OCP and PCB pollution levels have practically spread all over the world, including remote areas and polar regions. Long-Range Atmospheric Transport (LRAT) has permitted their movement to distant locations. Several reports showing OCP and PCB levels in the Arctic and Antarctic confirm this fact (Carlsson et al., 2018). This demonstrates that the glacial regions are authentic reservoirs and observatories of pollution caused by these contaminants (Guzella et al. 2011; Vecchiato et al. 2015; Zhang et al. 2015; Guzzella et al. 2016; Bigot et al. 2017; Cabrerizo et al. 2017; Carrizo et al. 2017; Wang et al. 2019). The presence of lindane (HCH), endosulfan, HCB, chlordane, DDTs, and diverse PCB congeners evidence the LRAT associated with the pollutants and their historically excessive usage (Chakraborty et al. 2016; Gao et al. 2018; Madaj et al. 2018; Cabrerizo et al. 2019; Hao et al. 2019. Wu et al. 2020; Kim et al. 2020).

Comparably, mountainous territories in the Americas, such as the Chilean Andes, Argentinian Patagonia and the Brazilian Highlands also reveal the global impact of these pollutants on these regions (Ornellas et al. 2016; Cipro et al. 2017; Miglioranza et al. 2021). The high mountains and cold temperatures are the main cause of their becoming trapped and deposited in far-off regions (Wania and Westgate 2008). Global warming has also contributed to the presence and accumulation of these pollutants because extreme temperatures, high wind speeds, precipitation, and solar radiation all increase the distances they can cover (Nadal et al. 2015; Potapowicz et al. 2019).

OCPs and PCBs have also been studied in arctic mountains and alpine lakes; however, their presence in such areas has been scarcely documented. Their presence is principally attributed to Altitude-Range Atmospheric Transport (ARAT) (Tremolada et al. 2009). In this case, the pollution is principally linked to the surrounding region because high-altitude lakes are generally linked to nearby areas with high levels of agricultural and industrial activities (Daly and Wania 2005).

Regarding high mountain lakes from other parts of the world, the Tibetan Plateau, Lake Como (Italy), and lakes in the Himalayas show alarming concentrations of OCPs and PCBs (Yang et al. 2013; Cheng et al. 2014; Bettinetti et al. 2016; Ren et al. 2016; Wang et al. 2016: Li et al. 2017; Sun et al. 2017; Nawab et al. 2020). However, other alpine lakes have yet to be explored, limiting the available information on this topic.

In the present work, we studied two alpine lakes, El Sol and La Luna, in order to observe OCP and PCB contamination in Mexico. The selected lakes are unique in the country, and they are in the crater of the Nevado de Toluca volcano.

Worldwide, the volcano region in the center of Mexico is considered to be a pristine region and a nature reserve for different species of flora and fauna. Due the altitude of this region, the lakes remain relatively unexplored.

The OCP and PCB pollution levels in the lakes were analyzed by collecting atmospheric aerosol samples, lake sediment, and organisms from the lake; namely, plankton and *Tubifex tubifex* (sludge worms).

This is the first monitoring study of OCPs and PCBs in the El Sol and the La Luna alpine lakes. This study forms part of the environmental program organized by Mexican NGOs. The data will provide important information regarding the levels of these chemical substances and the pollution risk in these alpine lakes in Mexico.

Materials And Methods

2.1 Materials

Acetone, n-hexane, ethyl ether, acetonitrile, dichloromethane, and isooctane (HPLC grade) were acquired from Honeywell-Burdick & Jackson Muskegon MI, USA. Florisil cartridges were obtained from Chromabond, USA. A mixture of twenty OCP standards was purchased from AccuStandard, New Haven, USA, and the purity was > 99%. Alpha-HCH, gamma-HCH, beta-HCH, heptachlor, delta-HCH, aldrin, heptachlor epoxide, chlordane I and II, endosulfan I and II, p-p’ DDE, dieldrin, endrin, p-p’ DDD, p-p’ DDT, endrin aldehyde, endosulfan sulfate, endrin ketone and methoxychlor. Six PCBs standard congeners (28, 52, 101, 118, 138 and 153) were purchased from AccuStandard, New Haven, USA, and the purity was > 99%. In all cases, the purest available products were purchased. Internal standard, 1-bromo-2-nitrobencene ($1Br_2NB$) was purchased from Chem Service Inc. (USA); >99% purity.

2.2 Description of the study area

The alpine lakes called El Sol and La Luna (The Sun and The Moon) are located in the crater (4200 m.a.s.l) of the Xinantécatl volcano, known as Nevado de Toluca (19° 06’30”, -99°45´30” west longitude 4230 m amsl) (Alcocer et al., 2008; Alcocer et al., 2020) (Figure 1).

The volcano covers an area of 927 km^2; the summit of the crater measures 1.5 km. Due to its environmental importance, 19.41 km^2 of the surrounding area are considered a Flora and Fauna Protection Area. In addition, El Sol and La Luna are scenically beautiful because the highest mountains of Nevado de Toluca surround the lakes, protecting their natural formation.

The volcano is situated in the central region of Mexico and volcano is located ~ 80 km West-South-West of Mexico City (the capital). The volcano area contains 10 municipalities; among which are Toluca, Zinacantepec, Villa Guerrero and Coatepec. All these municipalities are agriculturally very active.

Toluca is the state capital of the State of Mexico and is especially important because it is a densely-populated city with a population of nearly 1 million. It is a highly industrialized region with 535 000 industries, accounting for 12.6% of the national total. Automotive, food, chemical, and plastic sectors are among the main industries found in Toluca (INEGI 2021). The weather at the volcano is generally mild and rainy. The annual average temperature in the mountains is 3.8±2°C (SMN-CONAGUA 2017); however, temperatures reach -4±1°C at the summit. Figure 1 (supplementary information) shows a panoramic view of the Nevado de Toluca volcano and the El Sol and La Luna lakes.

Both lakes have a similar origin, age, and water regime (polycmitic and perennially astatic) (Alcocer et al. 2020). The total area of the surface of El Sol Lake is 23.7 ha, while that of the La Luna Lake is 3.1 ha. The maximum water depth is 10 m and 15 m, respectively (SMN-CONAGUA 2017). The temperature of the water in both lakes is generally<10° C; however, during winter it drops to <0°C, and in summer reaches 15°C. Although the lakes are separated by a dacitic dome, the water in each of the lakes presents different pH, transparency, suspended solids, and chlorophyll (Alcocer et al. 2020). Both lakes have little mineralization with low conductivity (18 mS/cm).

The phytoplankton and zooplankton biomass in La Luna is lower than in El Sol. Biomass is associated with pH; the lowest pH (5-6) is found in La Luna (Cuna et al. 2014). El Sol has aquatic life due to the artificial introduction of rainbow trout (*Oncorhynchus mykiss*). However, the proliferation of this fish failed in La Luna, which has been attributed to its low pH. This difference in pH is surprising because the lakes are connected and separated by a small rocky mound (formed by a lava vault) (Armienta et al. 2008).

The Nevado de Toluca and its crater lakes capture and infiltrate rainwater and snow, which feed the basins of the Lerma and Balsas rivers in Mexico. This process allows the recharge of these aquifers and the equilibrium of their environment. In addition, the water of the basin is exploited intensively to meet the water demands for water potable uses in Mexico.

2.3 Sampling sites and sample collection

Sample collection consisted of the capture of atmospheric aerosol, sediments, phytoplankton, and *Tubifex tubifex* from the El Sol and La Luna lakes. The samples were collected at three different times of year, each one with different weather conditions: dry and warm (April-July), rainy (August-November), and dry and cold (December-March). Samples were taken in 2017, 2018, and 2019. Sampling sites were selected according to height, location, position, and lakes dimensions.

Figure 2 presents the geographical position of the sampling sites for atmospheric aerosol, sediments, phytoplankton, and *Tubifex tubifex* from the El Sol and La Luna lakes. The geographical position of the sampling stations is depicted in Table S1 (supplemental material).

The sample-collecting procedure was as follows:

1. Atmospheric aerosol samples were collected by way of passive samplers (TE-PAS-200) containing polyurethane foam (PUF). Tisch Environmental high-volume air samplers were installed at three sites on the mountains around the summit of volcano. The sites were designated as follows: site1-Northern Mountain (1-NM), site 2-Eastern Mountain (2-EM), and site 3, mountain located between lakes (3-BM).

2. Sediment samples were collected at lake sites designated as 4-North side of the El Sol lake (4-NLS), 5-Center side of the El Sol lake (5-CLS) and 6-South side of the El Sol lake (6-SLS); while sites on the La Luna lake were indicated as 7-North side the La Luna lake (7-NLL), 8-Center side of the La Luna lake (8-CLL) and 9-South side of the La Luna lake (9-SLL).

The sediments were collected at a depth of 10-30 cm, using a Van Veen dredge. The sediment samples were sieved through a 100-mesh; after, the samples were kept in a freezer at 0°C for further use.

3. Samples of phytoplankton-zooplankton mixture and *Tubifex tubifex* were collected at the same sites as the samples of lake sediment. Samples of phytoplankton-zooplankton were collected using a Clark–Bumpus sampler (mesh: 200 μm), which vertically filtered the water column of 0-10 m corresponding to the layer where most phytoplankton and zooplankton are present in the lakes.

Tubifex tubifex samples were collected from sediments, separating the sediment with small shovels, digging up the surface layers of the sediment and on the shore of the lakes. Sediment and *Tubifex tubifex* samples were stored in 1L glass containers for transport and analysis.

Samples of *Tubifex tubifex* worms were subsequently freeze-dried, lyophilized, and crushed, until a fine and homogeneous powder was obtained. The samples of both sediment and organisms were kept in a freezer at 0°C for further use.

2.4 Extraction of OCPs and PCBs from lakes samples

1. Atmospheric aerosol

Contaminants were extracted from PUF disks by a modified ultrasound-assisted extraction micro-scale cell with reflux (UAE-MSC) (Amador-Muñoz et al., 2014; Arias-Loaiza et al., 2018). Briefly, PUFs were located inside the MSC and 50 mL of dichloromethane was poured. Two consecutive ultrasound extractions (Branson 8800) at 60°C for 30 min were performed at 37 Hz. The organic extracts were filtered (Teflon filters 13 mm Ø, 0.25 µm pore), the solvent excess was evaporated in a rotatory evaporator, and the final volume adjusted to 1 mL with nitrogen gas (Infra, 99.998%).

2. Samples of sediment and organisms from the lakes

The extraction procedure was carried out according to the EPA 3550B method, using ultrasound-assisted extraction by a mixture of n-hexane and HPLC grade acetone (50:50 v/v). The sample was placed in a 10 mL test tube with 3 mL of the solvent mixture (50% v/v acetone/n-hexane). The samples were stirred in a vortex (Scilogex SCI-VS (MX-S), US Plug) for 1 min and sonicated for 30 min in a water bath at 60°C (Branson 1800 at 35 kHz and 30 watts).

The organic extracts were cooled at room temperature and centrifugated at 3000 rpm for 3 min. The supernatant of each extract was placed in a flat bottom vial which was previously washed and baked. The residual solid was washed three times with 3 mL of 50% v/v acetone/n-hexane, stirred and centrifuged. The supernatants were combined in the same vial, obtaining the extract of OCPs and PCBs from the samples. Subsequently, a multiple collector Manifold chamber (Supelco-Sigma Aldrich) with a florisil cartridge was used for cleaning the extracts. Previously the florisil cartridge was washed and activated with 4 mL of n-hexane at 1mL/min and vacuum of the chamber 12 kPa. Another 3 mL of n-hexane was added, until the solvent reached the surface of the column. The column was filled to avoid the florisil from drying out (García et al. 2020). 1 mL of organic extract was transferred into the florisil cartridge. Elution of the fractions was established according to the EPA method 3620B (1996), using 0.5 mL of n-hexane and 9 mL of acetone/n-Hexane (10 % v/v) with a constant flow of 1 mL/min. The eluates obtained were concentrated with inert nitrogen gas until the volume was reduced to 1 mL organic extract which was kept at 20°C until they were instrumentally analyzed.

2.5 Calibration curves for OCPs and PCBs

The calibration curves for OCPs and PCBs were prepared at seven concentration levels (1, 10, 20, 40, 60, 80 y 100 pg/µL). Linearity was evaluated with the Pearson correlation coefficient (r). The precision of calibration curves was calculated by way of the relative standard deviation (RSD %) of the slope. The limits of detection (LODs) and quantitation (LOQs) of the instrument for each analyte were calculated based on Equation (1) and Equation (2) respectively (Miller and Miller et al. 2018).

$$\text{LOD (pg/µL)} = 3sb/m \quad (1)$$

$$\text{LOQ (pg/µL)} = 10sb/m \quad (2)$$

Where m is the slope of the weighted regression line, and sb is the standard deviation of the weighted intercept. To calculate the LOD and LOQ of the method for the aerosol samples, instrumental LOD, LOQ and the recoveries of the analytical method were considered. LOD and LOQ for sediment and organism samples were calculated based on 3 and 10 times the standard deviation of the blank samples.

2.6 OCPs and PCBs recovery

1. Atmospheric aerosol

Recoveries of OCPs and PCBs were obtained by spiking clean PUF (blanks, N=3) and PUF disks with atmospheric aerosol (previously sampled in another campaign and solvent-washed) (N=9), with 50 µL of 20 OCPs and 6 PCBs at 100 pg/µL each. Analytes were extracted by UAE-MSC as explained in Section 2.4. Recoveries were calculated based on Equation 3.

2. Sediment samples

OCPs and PCBs recoveries were evaluated with the certified referenced material IAEA-417 (International Atomic Energy Agency). Extraction conditions were indicated in Section 2.4.

3. Organisms from lakes

OCPs and PCBs recoveries were obtained from lyophilized and pulverized phytoplankton and worms spiked with 50 pg/µL of the mixture of OCPs and PCBs analytes. Contaminants were extracted under conditions indicated for sediment samples.

Internal standard $1Br_2NB$ was added (50 pg/µL) to the final volume, and samples were analysed by gas chromatographic technique. Recoveries of OCPs and PCBs were calculated according to Equation 3 and expressed as percentages.

$$\text{Recovery \% of analyte} = \frac{A}{B}\ X100 \qquad (3)$$

Where, A is the amount of OCP and PCB obtained after the spiked sample extracted and analysed by GC-MS-NCI, while B is the standard used for spiking the samples and analysed by GC-MS-NCI.

2.7 Instrumental analysis of OCPs and PCBs

OCPs and PCBs were analysed by gas chromatography (7890A)–mass spectrometry (5973N) with single quadrupole in negative chemical ionisation (GC-MS/NCI) (Agilent Technologies, United States).

Samples were automatically injected by triplicate in spitless mode (2 µL) at 280°C. Helium (99.998%, infra) was used as a carrier gas at a constant flow of 1.2 mL/min. A capillary column DB35 (J&WScientific; 60 m, 0.25 mm, 0.25 µm) was used to separate the compounds. The oven program was: 40°C for 1 min, 50°C/min up to 110°C, 5°C/min to 303°C, 20°C/min to 335°C for 5.4 min (Arias-Loaiza et.al., 2018; García et al., 2020). The transfer line was at 280°C. The quadrupole and ion source temperatures were 150°C. Methane was used as the reactive gas for chemical ionisation. Selected ion monitoring (SIM) mode was used to increase sensitivity and acquire the data. The Agilent MSD ChemStation Classic Data Analysis software program was used for data processing.

2.8 Statistical analysis

An ANOVA test was used to compare averages of the OCP and PCB data, using TIBCO Statistica® Software Release 13.5. Additional data analyses were completed in Microsoft Excel 2013.

Results And Discussion

Table S2 (in supplementary information) shows the OCPs, and PCBs analysed by GC-MS/NCI, while Figure S2 illustrates the total ion chromatogram, showing good resolution in terms of the development of the qualitative and quantitative analyses.

3.1 Performance of analytical methods

Table S3 shows the calibration curves of OCPs and PCBs by GC-MS/NCI. Analytical parameters showed that the chromatographic method was effective for the determination of standard OCPs and PCBs in the 1-100 pg/µL range.

Linearity measured by the Pearson coefficient (r) was r>0.990, with a value of RSD <10%, meeting the acceptance criterion of <20% (Christian, 2019). The relative sensitivity for OCPs ranged from 0.4 to 3.7, while PCBs presented a range of 1.0-1.1, demonstrating high sensitivity, observed in the low instrumental LODs and LOQs. LODs and LOQs for OCPs ranged between 0.030-2.24 pg/µL and 0.11-7.41 pg/µL respectively, while LODs and LOQs for PCBs ranged between 0.51-0.77 pg/µL and 1.65-2.59 pg/µL respectively. Table 1 shows recoveries, LODs and LOQs for OCPs and PCBs in matrices of aerosol, sediment, and organisms.

LODs and LOQs in PUF were found between 30-2200 pg and 200-6900 pg, respectively. In terms of organisms, these values were between 500-3900 pg/g and 200-16400 pg/g, while for sediments these values were between 60-4400 pg/g and 200-14800 pg/g, respectively.

The recovery range for OCPs and PCBs were acceptable. Reference material (IAEA-417) shows values of OCPs 78-120% The aerosol afforded recoveries between 78 and 114%, while the recovery range for OCPs in the matrix corresponding to organisms was 73-114%, whereas the PCB range was 78-88%.

The recovery range of OCPs were like our previously reported results (80-120%). These results are higher than those reported by Arias-Loaiza et al. (2018) (55-85%) for aerosol samples. This is probably due to the matrix effect.

Table 1
LODs, LOQs and recoveries of OCPs and PCBs for each matrix

Target analyte	LODs			LOQs			Recovery %		
	Aerosol ng/PUF	Sediment ng/g	Organisms ng/g	Aerosol ng/PUF	Sediment ng/g	Organisms ng/g	Aerosol	Sediment	Organisms
α-HCH	1.9 (±0.70)	3.4 (±0.90)	3.9 (±0.80)	6.3 (±0.20)	1.1 (±0.05)	13.2 (±1.15)	81.8 (±2.7)	88.6 (±1.7)	78.6 (±3.5)
g-HCH	0.9 (±0.20)	1.7 (±0.20)	1.9 (±0.09)	3.1 (±0.10)	5.7 (±0.10)	6.4 (±1.01)	91.3 (±8.7)	100 (±0.7)	89.3 (±8.8)
β-HCH	1.2 (±0.20)	2.2 (±0.50)	2.1 (±0.10)	3.4 (±0.50)	7.5 (±0.15)	7.1 (±0.08)	104 (±8.3)	94.3 (±1.7)	100 (±9.7)
Heptachlor	0.03 (±0.01)	0.06 (±0.01)	0.6 (±0.01)	0.2 (±0.01)	0.2 (±0.02)	0.2 (±0.01)	93.9 (±2.8)	94.4 (±1.7)	94.0 (±4.7)
d-HCH	1.7 (±0.10)	3.4 (±1.20)	3.9 (±0.50)	5.6 (±0.75)	1.1 (±0.05)	13.2 (±1.12)	96.1 (±2.8)	93.3 (±1.7)	81.6 (±1.6)
Aldrin	1.7 (±0.30)	1.9 (±0.20)	3.8 (±0.45)	5.5 (±0.20)	9.9 (±0.10)	12.8 (±1.18)	103 (±9.1)	114 (±1.5)	87.9 (±7.8)
heptachlor epoxide	0.3 (±0.01)	0.5 (±0.05)	0.5 (±0.05)	0.9 (±010)	1.8 (±0.01)	3.1 (±0.05)	117 (±0.4)	120 (±0.2)	114 (±0.20)
chlordane I	0.7 (±0.10)	1.2 (±0.02)	1.1 (±0.04)	2.3 (±0.50)	4.2 (±0.10)	3.9 (±0.05)	98.3 (±1.2)	104 (±0.8)	114 (±0.20)
chlordane II	1.3 (±0.20)	2.4 (±0.70)	2.6 (±0.70)	4.2 (±0.30)	8.2 (±1.00)	8.7 (±0.09)	88.7 (±1.9)	89.6 (±1.9)	85.0 (±2.0)
α-endosulfan	0.3 (±0.01)	0.6 (± 0.01)	0.5 (±0.02)	1.3 (±0.05)	2.0 (±0.15)	1.9 (±0.01)	89.6 (±5.7)	89.6 (±1.7)	92.7 (±3.30)
4,4'-DDE	0.5 (±0.01)	0.9 (±0.02)	0.9 (±0.01)	1.5 (±0.02)	3.3 (±0.05)	3.3 (±0.05)	110 (±9.1)	103 (±1.1)	103 (±4.70)
Dieldrin	2.2 (±0.70	4.4 (±1.50)	5.0 (±0.52)	7.4 (±0.50	14.8 (±1.67)	16.4 (±0.05)	100 (± 1.7)	100 (±1.7)	89.9 (±3.0)
congener-28	0.5 (±0.05)	1.0 (±0.05)	1.1 (±0.01)	1.2 (±0.08)	1.0 (±0.01)	3.9 (±0.08)	104 (±0.8)	100 (±2.3)	86.8 (±1.3)
congener-52	0.7 (±0.01)	1.3 (±0.50)	1.7 (±0.04)	2.2 (±0.10)	4.6 (±1.01)	5.9 ±1.01)	114 (±1.0)	112 (±3.0)	87.8 (±0.9)
Endrin	1.2 (±0.51)	2.4 (±0.05)	2.8 (±0.06)	4.0 (±0.18)	8.1 (±0.19)	9.3 (±1.05)	109 (±5.6)	109 (±1.6)	94.7 (±1.0)
4,4'-DDD	0.7(±0.03)	1.5 (±0.05)	1.7 (±0.05)	2.5 (±0.13)	5.0 (±1.05)	5.79± 0.03	102 (±2.1)	102 (±1.6)	89.4 (±6.7)
congener-101	0.6 (±0.02)	1.3 (±0.20)	1.7 (±0.03)	2.1 (±0.15)	4.4 (±1.10)	5.7 (±1.09)	103 (±1.1)	102 (±2.9)	78.1 (±2.0)
β-endosulfan	0.6 (±2.70)	1.2 (±0.09)	1.2 (±0.01)	2.0 (±0.05)	4.0 (±0.05)	4.0 (±1.05)	103 (±1.8)	103 (±1.3)	102 (±1.20)
4,4'-DDT	0.7 (±0.10)	1.6 (±0.05)	1.4 (±0.17)	2.5 (±0.15)	4.7 (±0.05)	4.7 (±1.01)	90.2 (±4.7)	94.9 (±0.3)	94.9 (±4.20)
endrin aldehyde	2.0 (±1.10)	4.0 (±0.90)	3.6 (±0.70)	6.9 (±1.20)	13.6 (±1.50)	12.2 (±1.15)	81.8 (±2.2)	83.3 (±2.2)	93.0 (±1.10)
endosulfan sulfate	0.5 (±0.01)	0.9 (±0.05)	1.0 (±0.02)	1.6 (±0.02)	3.2 (±0.07)	3.5 (±0.05)	99.5 (±0.5)	99.5 (±0.7)	91.7 (±5.80)
congener-118	0.6 (±0.02)	0.7 (±0.01)	1.5 (±0.05)	1.8 (±0.05)	4.2 (±0.06)	4.6 (±0.03)	102 (±1.8)	89.4 (±0.3)	81.6 (±0.80)

Target analyte	LODs			LOQs			Recovery %		
	Aerosol ng/PUF	Sediment ng/g	Organisms ng/g	Aerosol ng/PUF	Sediment ng/g	Organisms ng/g	Aerosol	Sediment	Organisms
congener-138	0.5 (±0.01)	1.1 (±0.01)	1.5 (±0.05)	1.6 (± 0.02)	3.6 (±0.08)	3.9 (±0.01)	99.5 (±0.5)	91.7 (±0.7)	82.7 (±1.80)
endrin ketone	1.2 (±0.02)	2.2 (±0.03)	2.3 (±0.03)	3.9 (± 0.10)	7.4 (±1.10)	7.9 (±0.05)	73.5 (±0.8)	78.3 (±2.3)	72.9 (±1.10)
Methoxychlor	1.1 (±0.05)	2.2 (±0.04)	2.4 (±0.05)	3.8 (±0.15)	7.5 (±1.08)	8.1 (±0.03)	78.4 (±1.2)	78.9 (±1.9)	73.5 (±0.70)
congener-153	0.6 (±0.07)	1.5 (±0.03)	1.6 (±0.04)	2.2 (±0.12)	4.9 (±0.05)	5.2 (±1.05)	103 (±2.0)	87.9 (±0.9)	83.3 (±1.80)

3.2 OCPs and PCBs in the El Sol and La Luna lakes.

3.2.1 Atmospheric aerosol

OCP and PCB concentrations in the atmospheric aerosol (Figure 3) were calculated as pg/m^3, counting 150 m^3 of filtered air through PUF (Harner et al., 2005). The data presented are the average of three climate periods for the three sampling sites, 1-NM, 2-EM and 3-BM. No differences among them were observed (ANOVA, $p>0.05$). Results showed the presence of heptachlor, chlordane, endosulfans, and DDTs. Chlordane and endosulfans were observed at the three sampling sites (relative frequency = 3/3), whereas heptachlor and DDTs were detected at site 1-NM and 3-BM (relative frequency 2/3). The lower concentration of OCPs was identified at site 2-EM for chlordane I and α-endosulfan (3 pg/m^3), whereas site 3-BM showed the highest value of OCPs (19 pg/m^3 of 4,4'-DDD).

The detected PCBs were congeners 28, 52, 118, 138, and 153. The highest concentration was observed in congener 153 (50 pg/m^3), followed by congeners 118 and 138 (16 pg/m^3).

The total concentrations of OCPs and PCBs were $\sum_2$ chlordane = 30 pg/m^3; $\sum_2$ endosulfan = 32 pg/m^3, $\sum_3$ DDTs= 64 pg/m^3 and $\sum_5$ congeners= 124 pg/m^3.

The presence of endosulfan, chlordane, DDTs, and PCB congener 153 in atmospheric aerosol from lakes is chiefly attributed to ARAT and LRAT. The high affinity to clay and organic matter could also explain their carriage as adhesive $PM_{2.5}$ and powder, reaching the airspace surrounding the El Sol and La Luna lakes (Daly and Wania 2005; Beristain-Montiel et al. 2020).

The sampling sites affected the capture of pollutants. Sites 1-NM and 3-BM indicated the highest capture of OCPs, whereas site 2-EM, exhibited the maximum capture of PCBs ($p<0.05$). Sites 1-NM and 2-EM correspond to the east and north of the lakes respectively. However, site 3-BM is located between both lakes; which is geographically characterized by a sinking between mountains; therefore, the contaminants were probably captured by passive samplers located in this gap. The presence of OCPs and PCBs at sites 1-3 from could be attributed to the mixing of local and adjacent emissions because the Nevado de Toluca volcano is surrounded by different provinces such as Villa Victoria, Almoloya de Juárez, Zinacantepec, Toluca, Coatepec and Villa Guerrero. These municipalities are very active both agriculturally and industrially. Specifically, the presence of α- and β-endosulfan at the three sites showed a relative frequency of 3/3 and 2/3 respectively, confirming their extensive use in agriculture which affects lakes' environment (Kim et al. 2020).

The absence of endosulfan sulfate in atmospheric aerosol was associated with the recent arrival of relatively fresh discharges because it is the main degradation product of α- and β-endosulfan; however, a low biodegradation of these isomers by the environmental conditions found in lakes could indicate older releases and re-emissions (Pawlak et al. 2021). Nevertheless, the lack of endosulfan sulfate might also be explained by vapour pressure because it has lower values (~4-fold) than α- and β-isomers; thus, due to altitudinal transport they presented higher incidences in the atmosphere of the lakes. In turn, the origin of endosulfan emissions could be predominantly local, because Coatepec and Villa Guerrero are provinces close to the Nevado de Toluca, and they are known for their flower, carrot, and potato cultivation and commercialization.

Several studies (2005-2012) described the presence of endosulfan as fresh emissions in Asia, India, Africa, and America (Weber et al. 2010; Arinaitwe et al. 2016; Kirchner et al. 2016; Yadav et al. 2016). Particularly, Mount Everest showed 27.6 pg/m^3 (Li et al. 2006); whereas the concentration from Dalian, Northeast China was 0.1- 52.6 pg/m^3 (Li et al. 2012); however, National Park of Serra dos Orgaos (Rio de Janeiro, State) and National Park of Sao Joaquin (Santa Catarina State) displayed ranges from 50 to 5,600 pg/m^3 (Meire et al. 2012). This is the strongest presence of endosulfan in Brazil.

Currently, Arctic sites (Alert, Pallas and Villum) show declining emissions of endosulfan, including a null concentration of β isomer (Wong et al. 2012; Balmer et al. 2019). Decreasing emissions of endosulfan were attributed to international regulations (Stockholm Convention, UNEP, UNEP/FAO, UNECE and others); however, after 2018, other programs and actions to reduce endosulfan discharges have not been documented (Balmer et al. 2019).

Furthermore, control of production and use of endosulfan has taken longer in other countries. According to the National Agency for the Regulation of International Pesticide Commerce (CICOPLAFEST, Spanish initials), endosulfan has been widely used in Mexico for several decades. Since 10 July 2012, the use of products containing endosulfan has been controlled by the European Union Regulation (CICOPLAFEST, 2021). In addition, it is unknown whether the importation of endosulfan from Asia is still ongoing; therefore, high levels of endosulfan as fresh emissions are expected in North and Central America.

Conversely, the finding of the isomers, DDE, DDD, heptachlor chloride and chlordane, were associated with less recent releases of pesticides. However, the strong agricultural activity in provinces nearby the lakes, shows that the principal participation of OCPs and PCBs could be of regional origin because they are still used in public health programs. Chlordane is predominantly used to remove termites by injection into the subsoil, and heptachlor is used for the control of various pests in central and South America (Alegria et al. 2006; Wu et al. 2014; Wang et al. 2016; Shunthirasingham et al. 2016).

The presence of PCBs in atmospheric aerosol was also associated with their ARAT and LARAT characteristics, and their high resistance to degradation processes. In turn, PCB levels were associated with less recent discharges; re-emissions from pollutant accumulation (Armitage et al. 2011; Stemmler and Lammel 2012), and fresh releases by waste incineration (Wolska et al. 2014), because in the lower zone of the Nevado de Toluca volcano, the antiquated practice of slash-and-burn for the agricultural preparation is common practice. In addition, waste is often disposed of my burning. Herein it is also notable that site 2 showed an outstanding level of congener 153, confirming its abundance in the environment (Hung et al. 2016).

PCB levels from the El Sol and La Luna lakes were comparable to the reported range in the Arctic (< 5–30 pg/m^3). Particularly, the PCB-153 shows the highest levels at Zeppelin station (2004-2009); however, after 2009, the levels of PCBs have notably reduced, as was indicated in Hung et al. (2016) and Carlsson et al. (2018).

3.3.2 Sediment

Figure 4 shows concentrations of OCPs and PCBs in lake sediment, for three climate periods (dry warm, rainy, and dry cold). Data are average concentrations of pollutants from 3 sampling sites. The data do not present significative differences (p<0.05) between sites. The averages (± standard deviation) were expressed as pg/g of sediments.

The most frequent pollutants were chlordane, endosulfan, and congeners 118, 138 and 153, revealing a high concentration of the pollutants detected in aerosol samples.

Total concentrations of OCPs and PCBs in the El Sol lake were $\sum_3$ endosulfan = 2067 pg/g; $\sum_2$ chlordane = 457 pg/g; $\sum_3$ PCBs = 70 pg/g; $\sum_1$ DDT = 82 pg/g; whereas total concentrations in sediment from La Luna Lake were $\sum_3$ endosulfan = 1633 pg/g; $\sum_2$ chlordane = 646 pg/g; $\sum_3$ PCBs = 71 pg/g.

Endosulfan ranged from 180 to 280 pg/g, 200-300 pg/g of β-endosulfan, and 50-100 pg/g of endosulfan sulfate. Chlordane I ranged from 150-170 pg/g and chlordane II from 45-55 pg/g, whereas levels of PCBs were found in congeners 153 and 118 as 17-20 pg/g.

In turn, α-endosulfan was the only OCPs which showed variability (p>0.05) between years 2017-2019. The highest concentration was observed in 2019.

The El Sol and La Luna lakes showed significative differences in total concentrations of endosulfan and chlordane (p<0.05); however total concentration of PCBs did not present significant differences (p<0.05).

The presence of endosulfan, chlordane, DDTs, and PCB congeners 118, 138 and 153 (medium level of chlorinated compounds) in the volcano lakes was attributed to their altitudinal and medium transport. Subsequently their occurrence in lake sediments was mainly due to thaw and rain by quick sorption and accumulation. Specifically, endosulfan in the lakes suggest long-established global and recent use, while the presence of the other pollutants was attributed to their perseverance in the environment by older usage.

Isomers such as endosulfan sulfate and chlordane II could show the age of the detected OCPs, indicating that recent emissions were the primary source and chief contributor. Re-emissions, on the other hand, were secondary sources. Previous experiments showed that α-endosulfan is more quickly desorbed from sediments than the ß-isomer, and it is associated with endosulfan sulfate (Peterson and Batley 1993).

The age of endosulfans from the lakes was also linked to their half-life. The α- and β-isomers have been in water and sediment for 2-6 months, whereas endosulfan sulfate has a longer environmental half-life (Weber et al. 2010). However, Fenner et al. (2003) demonstrated that the association of endosulfans would result in considerably longer environmental half-lives, which is dependent of environmental conditions.

Ratios between α or β-endosulfan/endosulfan sulfate were found as 1.39-1.51, demonstrating continuous endosulfan arrival to the El Sol and La Luna lakes.

The highest ratio of α or β-endosulfan/endosulfan sulfate was observed in the humid period (ambient temperature 10-12°C), corroborating the temperature effect on the endosulfan sulfate formation.

In addition, the ratio α/β of 1.25 suggests higher volatility of α-endosulfan (Kim et al. 2020) and low altitudinal transport of β-endosulfan.

On the other hand, the ratio of chlordane I/II showed a range of 2.06-4.08, indicating emissions from time ago, due to the degradation of chlordane I and formation of chlordane II.

PCBs in lake sediment revealed the lowest levels. Congener 153 showed 17 pg/g, followed by congener 118 (11 pg/g), and congener 138 (9 pg/g), which could be related to their degradation by past emissions. A similar result was detailed in Vecchiato et al. (2015), indicating low concentrations of PCBs (10 and 634 pg/g) in Antarctic sediments.

Other important data regarding OCPs in sediments are also notable. Unlike air from lakes, heptachlor was not detected in sediment samples; however, a low concentration of DDE was found in the El Sol lake during the cold period. These results were also associated with degradation by old discharges.

According to the quality guidelines provided by the Ministry of the Environment of Ontario, Canada (NOAA, 1990), the levels of 4,4'-DDE found in sediment from the El Sol lake (82 pg/g), do not represent an impact on the lake ecosystem, referring to the potential risk of biomagnification and toxicity of the trophic chain in benthos. These guidelines indicate that the 4,4'-DDE levels which cause this risk are those classified as a Low Effects Level (LEL), which is around 5000 pg/g/The Severe Effects Level (SEL) is around $19x10^4$ pg/g. Therefore, the concentration of 4,4'-DDE in the El Sol lake is very far from the LEL and SEL indicated in this guide.

The detection of OCPs and PCBs in sediments of the El Sol and La Luna lakes could be associated with temperature, wind direction, and wind speed. Alcocer et al. (2021) found that the wind speeds in the crater are weakened due to the dome and the high walls of the crater. The wind speed range is < 0.5 m/s, except in winter; in this period, it is 1–2 m/s, which shows that winds are predominantly calm in this area. In addition, the heat exchange between the near-surface layer with deeper waters occurs only due to vortex diffusion, and not by wind mixing as expected. Consequently, the mix of pollutants could remain intact for many years.

3.3.3 Aquatic organisms

Endosulfan and chlordane were the OCPs found in plankton and *Tubifex tubifex* (Figure 5) at three different times of year with different climatic conditions and three at sampling sites. However, PCBs were not observed in the organisms.

The presence of OCPs in plankton and *Tubifex tubifex* were coincident with the occurrence of endosulfan and chlordane in the air and sediment, whereas the OCP concentration was different between the El Sol and La Luna lakes. The difference was attributed to aquatic life and lake size, because the El Sol lake is bigger than the La Luna lake, and the pH of this lake limits the natural life.

Plankton from the El Sol lake showed 550 pg/g of $\sum_2$ endosulfan, including α and β endosulfan, while plankton from the La Luna lake displayed 150 pg/g of α-endosulfan. In turn, *Tubifex tubifex* from the El Sol lake exhibited 400 pg/g of $\sum_2$ endosulfan, including α and β endosulfan, whereas *Tubifex tubifex* from the La Luna lake showed 100 pg/g of β-endosulfan. Levels of chlordane I were similar for both plankton and *Tubifex tubifex*, showing 150 pg/g.

The ratio between α/β endosulfan isomers was lower in plankton (1.02) than in *Tubifex tubifex* (1.7). These results, plus the absence of endosulfan sulphate and the presence of chlordane isomers in the organisms, could indicate the recent and continued occurrence of endosulfan and chlordane; however, a longer life of these pollutants in the sediments could also be the reason for this result, because these lakes are recognized as having weak or no levels of biomagnification of pollutants, due to a low mixture of water and sediment, as well as a small amount of aquatic life, which limits their continued biodegradation (Sun et al. 2017). In addition, Ren et al. (2017) used a dynamic model to describe the biomagnification of OCPs and PCBs in the fish *Gymnocypris namensis* from the Nam Co Lake on the central Tibetan Plateau, indicating strong bioaccumulation in fish aged by DDEs, DDDs, PCB-138, -153 and -180. However, long residence times with half-lives up to two decades were recognized because of higher chlorinated PCBs.

3.3.4 Global analysis of OCPs and PCBs

Table 2 and Figure 6 summarize the average concentrations of total OCPs and PCBs in the El Sol and La Luna lakes. Data are relative to three sampling sites for each matrix. The metric includes the whole sampling period (2017-2019).

The total concentration of pollutant levels in atmospheric aerosol, sediments, plankton and *Tubifex tubifex* from lakes show significative differences in the levels of pollution (p<5%). In turn, the dominant presence of endosulfan and chlordane in the lakes was notable. The highest levels of endosulfan and chlordane were observed in lake sediments, followed by plankton, *Tubifex tubifex*, and atmospheric aerosol, while DDTs and PCBs (118, 138 and 153) were only found in sediments and atmospheric aerosol.

As mentioned above, the occurrence of these pollutants in the El Sol and La Luna lakes is documented by their ARAT, while the main contributions were associated with local sources.

The absence of isomers and low isomeric ratios of endosulfan explain its presence as a mix of fresh and not so recent discharges. Subsequently, the presence of chlordane, DDTs, and PCBs was recognized as a result of emissions from considerable time ago. However, it is known that only 10% of chlordane can be found ten years or more after application, and it is inferred that it usually comes from nearby places because its low vapor pressure allows its volatilization to be minimal. Therefore, its arrival at the lakes could be recent, and its presence is due to terrigenous runoff; chlordane usually remains adsorbed on clay particles or soil organic matter in the upper layers and slowly volatilizes into the atmosphere.

On the whole, levels of OCPs and PCBs in the El Sol and La Luna lakes confirmed the information previously described regarding remote areas. Endosulfan, chlordane, DDTs and PCBs are the most detected pollutants. Furthermore, their levels were comparable with preceding reports on this topic.

Particularly, the presence of endosulfan in the El Sol and La Luna lakes recognized that endosulfan is now the most notable pesticide in the world, and its levels depend on sampling locations and sampling time. According to Kim et al. (2020), endosulfan presents a rising trend, as evidenced by recent air monitoring in South Korea, which demonstrated an increment of $\sum_3$ endosulfan levels (274 pg/m^3).

Table 2
Average concentration of OCPs and PCBs in atmospheric aerosol, sediments, plankton and *Tubifex tubifex* from Lakes El Sol and La Luna.

Pollutant type	Pollutant	Aerosol (pg/m^3)	Sediment (pg/g)	Plankton (pg/g)	*Tubifex tubifex* (pg/g)
OCPs	heptachlor epoxide	26 (±3)	<LOD	<LOD	<LOD
	chlordane I	33 (±3)	328 (±7)	144 (±5)	147 (±3)
	chlordane II	<LOD	133 (±5)	<LOD	<LOD
	α-endosulfan	31 (±3)	763 (±8)	206 (±7)	240 (±5)
	β-endosulfan	14 (±3)	1200 (±10)	370 (±8)	300 (±5)
	endosulfan sulfate	<LOD	1100 (±7)	<LOD	<LOD
	4,4'-DDE	27 (±2)	82 (±3)	<LOD	<LOD
	4,4'-DDD	29 (±2)	<LOD	<LOD	<LOD
	4,4'-DDT	10 (±2)	<LOD	<LOD	<LOD
PCBs	Congener-28	8 (±1)	<LOD	<LOD	<LOD
	Congener-52	8 (±2)	<LOD	<LOD	<LOD
	Congener-118	40 (±2)	30 (±1)	<LOD	<LOD
	Congener-138	20 (±1)	10 (±2)	<LOD	<LOD
	Congener-153	51 (±3)	90 (±5)	<LOD	<LOD

In turn, concentrations of PCBs and other pesticides such as DDTs, chlordane, and HCB confirmed low levels in the El Sol and La Luna lakes. This information is like what has been reported elsewhere. Low levels of PCBs, DDT, and HCB indicate that the control of production and emissions regulation of these pollutants had has a result in the world.

Declining trends of α-HCH, γ-HCH, chlordane, and DDT, including α-endosulfan from analysis of Arctic air at eight sites over 25 years of monitoring (AMAP program) were previously discussed by Wong et al. (2021). However, the authors of the present work observed a slight increase in PCBs, which was attributable to warming in the region and continued primary emissions at source.

In short, there are controversial results regarding the global distribution and concentration of OCPs and PCBs. Specifically, pollution in the air has been associated with their deposition cycles, more than recent emissions; in addition, their detection has incremented in the last year because of the climatic conditions. Wang et al. (2016) explained that the increased temperatures and changing coverage of snow and glaciers have affected the behaviour and distribution of OCPs and PCBs in the Tibetan Plateau (East Asian monsoon, Indian Monsoon).

Other significant results regarding air samples show debatable data. Samples from the south of Mexico indicated the highest concentrations of endosulfan and DDTs. Results ranged from 239 to 2360 pg/m^3; while, chlordane, dieldrin, heptachlor, and PCBs presented the lowest concentrations. Endosulfan and chlordane DDT, were mostly recognized as fresh emissions (Alegria et al. 2004; Wong et al. 2010). The result was associated with the monitoring site (fields in Chiapas, south Mexico) and the sampling period, showing an intense use of these pesticides.

Furthermore, studies on particulate matter from samples collected in the Metropolitan Zone of the Mexico Valley (MZMV), during 2013 and 2014, showed endosulfan presence and transport (4-5 pg/m^3) (Beristain-Montiel et al. 2020), indicating aged endosulfan from regional contribution.

On the other hand, Arctic air (1990-2000) from different monitoring sites displayed 3-6 pg/m^3 of endosulfan. Mountain air in Mexico, Columbia, and the eastern fringes (Prince Island) of Canada presented the highest pollutant concentration (Shen et al. 2005), indicating the predominant use of endosulfan in these territories during this time.

Furthermore, endosulfan in the range of >1000 pg/m^3 was detected in the Artic air in Canada/US, which was linked to the peak discharges from Europe and Asia (Harner et al. 2004).

According to Carrera et al. (2002), endosulfan was also detected at remote lakes in the Pyrenees, Alps, and Caledonian mountains, exposing fluxes ranging between 190 and 340 ng/m^2/month, with a significant contribution of β-endosulfan, due to the highest evaporation of α-endosulfan.

More OCPs were also detected at different mountains sites. Shunthirasingham et al. (2016) also reported endosulfan, DDTs, dieldrin, and g-HCH having monitored the air at the Canadian Great Lakes Basin (GLB) (1992-2012). However, diminishing trends of these pollutants were observed after 2004. Particularly g-HCH and DDTs showed a notable decrease in air samples. The reduction of pollution levels was associated with regulatory efforts to control pesticide emissions (U.S. in 2007 and Canada in 2010). Nevertheless, the concentration of atmospheric endosulfan was observed as stable at all monitoring sites, demonstrating its usage in America, Asia, and Europe.

A gradual decline of endosulfan was also observed in the air at Little Fox Lake Canada's Western Sub-Arctic (2003-2013), displaying ranges < 61 pg/m^3, whereas DDTs were undetected. In this case, Northern Canada, Asia-Pacific, and East Asia were recognised as potential sources in warm seasons, while the Pacific Rim was indicated as a potential source in cold seasons (Yu et al.,2015).

Jacobi et al. (2015) analysed air samples from three sites of the Alps from 2005 to 2010, detecting higher deposition rates in summer than in winter. The average annual deposition of ∑DDT, ∑DDD, ∑DDE, and ∑chlordane was 579, 210, 144 and 98 pg/m^2 respectively. The levels of OCPs at each site were also affected by air masses; however, a decline in OCPs levels was not observed.

Conversely, the Arctic Monitoring and Assessment Programme (AMAP) reported a notable decline in the concentration of PCBs, DDTs, and chlordane. The reduction levels were attributed to the diminished use of these pollutants in the United States over the last 20-25 years (Hung et al. 2016). The decrease in endosulfan in the air at the Greak Lakes Basin was also observed from 2015 (Hites 2019).

Nonetheless, the recent information on endosulfan levels show different behaviour. Balmer et al. (2019) indicated that endosulfan presents low levels in the air, but freshwater fish from the Canadian Arctic showed recent increases, which are associated with an increase in deposition, with food webs, or climatic factors.

Wang et al. (2019) discussed numerous studies of OCPs and PCBs in air from sites located in the Arctic and on the Tibetan Plateau. From 1995 to 2005 the pollutants exhibited concentration ranges of 5-500 pg/m^3 of endosulfan, 0.1-100 pg/m^3 of PCBs, and 1-800 pg/m^3 of DDTs. The principal contribution to air pollution was attributed to air transport from India and Asia. In turn, levels of OCPs in mountain regions from south Brazil (2015) displayed 170-260 pg/m^3 of Σ_3 endosulfan, indicating fresh discharges with contributions from various sources (Ornellas et al. 2016).

Concerning OCPs and PCBs in sediment the Lakes El Sol and La Luna lakes, their levels were comparable to high mountain sediments from Arctic and Antarctic Lakes.

Specifically, endosulfan presence was found in several research projects. According to a review presented by Weber et al. (2010), endosulfan has been detected in high mountain lakes, revealing a marked increase from the 1980s onwards. The northern hemisphere reached the maximum levels dated to 2003 (Usenko et al. 2007); however, the decline of endosulfan has not been reported, confirming continued use since that date. Nevertheless, more reports on lake sediment are necessary to document this observation.

In terms of reports regarding endosulfan, Stern et al. (2005) detected 40 pg/g of α isomer and a flux range of 6.2 ng/m^2/year on core sediment from Lake DV09 in the Canadian Arctic Archipelago, indicating a high occurrence of this pollutant and fresh discharges.

Recently, Kim et al. (2020) showed data variability in terms of endosulfan in the river sediments from South Korea; average levels of Σ_3 endosulfan were 100 pg/g. In this case, endosulfan sulfate was dominant at most of the sediment sampling stations; therefore, old emissions were proclaimed.

The prevalence of DDTs and PCBs in sediment lakes was found in Gusella et al. (2011). In this case, the sediments from several high-altitude sites in Sagarmatha National Park (Nepal) (included in the Himalayan ridge) showed 1 ng/g as total ∑PCBs, containing medium-level chlorinated congeners as the most dominant contaminants. After, Barakat et al. (2013) reported high contamination in sediment from 34 locations in Lake Qarun, Egypt, indicating ranges from 1.01 to 16.48 ng/g of OCPs, and 1.48 to 13.72 ng/g of PCBs, respectively. The most abundant compounds were HCH, heptachlor, aldrin, endrin, DDE, and endosulfan I and II, whereas PCB congeners was dominated by light chlorinated biphenyls. The isomeric ratios specified new inputs of lindane, endrin, heptachlor and technical endosulfan, while the ratios of DDTs isomers indicated earlier usage of this pollutant: DDT.

Wu et al. (2014) analysed sediment from Qinghai Lake (northeast Qinghai–Tibet plateau). The range displayed was 860 pg/g for DDTs and 260 to 1730 pg/g for other OCPs. As a result of the percentage of DDT isomers, age discharges were linked to significant degradation of this pollutant.

Bettinetti et al. (2016) revealed DDE ranging 27-75 ng/g, and maximum PCB concentrations which reached 80 ng/g in the sediment sampled from the Como Bay Lake (Northern Italy) (2006-2009). A decline in the concentration of PCBs was observed during the studied period; however, DDE levels were maintained.

In turn, a comparative study of soils in polar regions from the Antarctic and the Tibetan Plateau discovered maximum levels of pollutants during 2005-2007; the register indicates 7.7 ng/g of ∑DDTs and 1.02 ng/g of ∑PCBs. The effectiveness of the Stockholm Convention in reducing emissions was made evident by a significant decrease in ΣPCBs (Wang et al., 2016).

Historic deposition of pollutants in two sediment cores from the Yamzho Yumco Lake from the Tibetan Plateau also evidenced the concentration peaks of OCPs in the 1970s and 1990s (Sun et al., 2018). Moreover, the isomeric ratios at different times showed that environmental self-purification caused a stronger presence of the OCPs in the lakes. However, recent study by Li et al. (2017) demonstrated the prevalence of OCPs and PCBs in sediment from 52 lakes from China, detecting 120-45.24 ng/g of ∑OCPs and 6.33-17 ng/g of ∑PCBs, with a predominance of isomers, indicating mixes of emissions of different ages and high levels of contamination.

Regarding bioaccumulation, at present, there are several reports focused on OCP and PCB accumulation in fish from the Antarctic and Arctic lakes and rivers. However, few studies have analysed the plankton and worm as aquatic organisms of bioaccumulation of these pollutants; specially, *Tubifex tubifex* worms were not studied, even though these organisms are strong indicators of pollutants in sediment.

What is more, the levels of plankton, OCPs, and PCBs detected in the El Sol and La Luna lakes were low in comparison to those reported by Bettinetti et al. (2016), who detected 131 ng/g of $\sum_3$ DDTs and 981 ng/g of $\sum_7$ PCBs in zooplankton from the Como Bay alpine lake (Northern Italy) (2009). However, Como Bay is comprised of four lakes and their dimensions are not analogous to the El Sol and La Luna lakes. Cabrerizo et al. (2019) discussed zooplankton contamination from Arctic rivers and lakes; finding ranges from 26 to 35 ng/g of Σ_{70} PCBs, 1.9–6.9 ng/g of HCB, 1.3–1.7 ng/g of Σ_3 HCHs, and 1.5–4.1 ng/g of Σ_3 DDTs; however, the difference was attributed to river samples.

Diverse reports on fish bioaccumulation have demonstrated different contamination levels of OCPs and PCBs. The highest concentration was found in fish from the Cau Hai lagoon, demonstrating ranges from 26-43 ng/g of PCBs, and 182-277 ng/g of DDTs (Tran et al. 2019). However, contamination of the lagoon from a long time ago and a large decrease in ΣDDT residues in the following years was suggested as the cause. Nawab et al. (2020) showed low levels of PCBs (240 pg/g), DDE (1400 pg/g), and DDT (600 pg/g) detected in Brown Trout and Rainbow Trout in alpine lakes in the Himalayas, Pakistan. In this case, the levels were comparable to data regarding plankton and *Tubifex tubifex* from the El Sol and La Luna lakes.

Conclusions

Environmental samples (atmospheric aerosol, sediments, plankton, and *Tubifex tubifex*) from the high mountain El Sol and La Luna lakes showed pollution status by way of OCPs and PCBs in Mexico.

Investigation during 2018-2020 in three different climate periods (dry warm, rainy, and dry cold) revealed that analysis periods did not show a significative difference between levels of OCPs and PCBs in atmospheric aerosol samples (p<0.05); however, sediment showed differences according to the analysis period. Herein, it is notable that DDTs and PCB-153 were observed in the cold period, whereas chlordane II level was in decline.

Atmospheric aerosol samples from lakes presented the principal occurrence of pollutants (7 OCPs and 5 PCBs); however, the lowest levels of OCPs were detected in these samples. Particularly, PCBs showed the peak levels (maximum 50 pg/g). Lake sediments showed the highest concentration of OCPs, followed by plankton and *Tubifex tubifex.* However, PCBs levels were scarcely detected in sediment; in addition, plankton and *Tubifex tubifex* did not show an accumulation of these pollutants, indicating that the principal contribution of lake contamination is by rain and snow.

Endosulfan was the most detected pollutant, showing the highest levels in sediments (3500 pg/g); plankton (1000 pg/g) and *Tubifex tubifex* (800 pg/g).

The absence of isomers of OCPs indicated that the principal contribution of pollution by OCPs and PCBs is due to fresh and local discharges.

The levels of pollution were within the range of other high mountain lakes, including Antarctic and Arctic lakes.

The results of this study confirmed that endosulfan can cover great distances by way of altitudinal transport, which allows this pollutant to be the most common pesticide in the world today. On the other hand, declining levels of PCBs, chlordane, and DDTs were also observed.

This investigation corresponds to the first result of monitoring OCPs and PCBs in Mexico, through the Comisión Nacional de Áreas Naturales Protegidas (CONANP) (National Board for Protected Natural Areas) program organised by the Secretaría del Medio Ambiente y Recursos Naturales (Secretariat for the Environment and Natural Resources), Mexico.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analysed during this study are included in this published article and its supplementary information files.

Competing interests

The authors declare that they have no competing interests

Funding

This study was supported by the Tecnológico Nacional de México (TECNM 41222010 and 41571463) and Comisión Nacional de Áreas Naturales y Protegidas (CONANP, CAS2011067).

Authors' contributions

Conceptualization, C.M., I de la R-G. and O.A.M.; Methodology, C.M. and I. de la R-G.; Formal analysis, C.M., O.A-M. and G.P-V.; Investigation, L.G-S and G.P-V.; Resources, C.M. and L.G-S.; Writing—original draft preparation, C.M. and L.G-S.; writing—review and editing, C.M. and O.A-M.; funding acquisition, C.M. and L.G-S.

Acknowledgements

The authors thank the National Commission of Natural and Protected Areas (CONANP) for the permission and ease of sampling in the El Sol and La Luna lakes of Nevado de Toluca volcano.

References

1. Alcocer J, Ruiz-Fernández AC, Oseguera LA, Caballero M, Sanchez-Cabeza JA, Pérez-Bernald LH, Hernández-Rivera DM, Armienta MA, Vilaclara G, De la Cruz-Reyna S, Ramos S, Ceniceros N, Cruz O, Aguayo A, Arcega-Cabrera F (2008) Water chemistry of lakes related to active and inactive mexican volcanoes. J Volcanol Geotherm Res 178:249-258. https://doi.org/10.1016/j.jvolgeores.2008.06.019
2. Alcocer J, Ruiz-Fernández AC, Oseguera LA, Caballero M, Sanchez-Cabeza JA, Pérez-Bernald LH, Hernández-Rivera DM (2020) Sediment carbon storage increases in tropical, oligotrophic, high mountain lakes. Anthropocene 32:100272. https://doi.org/10.1016/j.ancene.2020.100272
3. Alegria H, Bidleman TF, Figueroa MS (2006) Organochlorine pesticides in the ambient air of Chiapas, Mexico. Environ Pollut 140: 483e491. https://doi.org/10.1016/j.envpol.2005.08.007
4. Barba-López MDR, Filonov A, Alcocer J, Ladah L, Tereshchenko I (2021) Complex interactions between meteorological parameters and the thermal regime of two tropical, high altitude crater lakes (Nevado de Toluca, Mexico). Sci Total Environ 1:145310. DOI:10.1016/j.scitotenv.2021.145310
5. Alegria H, Bidleman TF, Figueroa MS (2006) Organochlorine pesticides in the ambient air of Chiapas, Mexico. Environ Pollut 140: 483e491. DOI:10.1016/j.envpol.2005.08.007
6. Amador Muñoz O, Santos-Medina GL, Jazcilevich-Diamant A, Valle-Hernández BL (2014). Celda de extracción a microescala, asistida por ultrasonido, con y sin reflujo, acoplada a un sistema de filtración. Patent No. 325624. Instituto Mexicano de la Propiedad Intelectual. Owner: Universidad Nacional Autónoma de México.
7. Arias-Loaiza, GE, Beristain-Montiel E, Gómez-Arroyo S, & Amador-Muñoz O. (2018). A thermo-cavitation method to determine organochlorine pesticides in gas and particle phases collected in polyurethane foam used in passive air samplers. Water Air Soil Pollut 229:1-10. https://doi.org/10.1007/s11270-018-3941-8
8. Arinaitwe K, Kiremire BT, Muir DC, Fellin P, Li H, Teixeira C, Mubiru DN (2016). Legacy and currently used pesticides in the atmospheric environment of Lake Victoria, East Africa. Sci Total Environ 543: 9-18. 10.1016/j.scitotenv.2015.10.146
9. Armienta MA, Vilaclara G, de la Cruz-Reina S, Ramos S, Ceniceros N, Cruz O, Aguayo A, Arcega-Cabrera F (2008). Water chemistry of lakes related to active and inactive Mexican volcanoes. J Volcanol Geotherm Res 178: 249-258. https://doi.org/10.1016/j.jvolgeores.2008.06.019
10. Armitage JM, Quinn CL, Wania F (2011) Global climate change and contaminants-an overview of opportunities and priorities for modelling the potential implications for long-term human exposure to organic compounds in the Arctic. J Environ Monit 13:1532-1546. DOI:10.1039/c1em10131e
11. Barakat AO. Khairy M, Aukaily I (2013) Persistent organochlorine pesticide and PCB residues in surface sediments of Lake Qarun, a protected area of Egypt. Chemosphere 90:2467-76. https://doi.org/10.1016/j.chemosphere.2012.11.012
12. Barba-López MDR, Filonov A, Alcocer J, Ladah L, Tereshchenko I (2021) Complex interactions between meteorological parameters and the thermal regime of two tropical, high altitude crater lakes (Nevado de Toluca, Mexico). Sci Total Environ 1:145310. https://doi.org/10.1016/j.scitotenv.2021.145310
13. Beristain-Montiel E, Villalobos-Pietrini R, Nuñez-Vilchis A, Arias-Loaiza GE, Hernández-Paniagua IY, Amador-Muñoz O (2020) Polybrominated diphenyl ethers and organochloride pesticides in the organic matter of air suspended particles in Mexico valley: A diagnostic to evaluate public policies. Environ Pollut 267: 115637. https://doi.org/10.1016/j.envpol.2020.115637
14. Bettinetti R, Quadroni S, Boggio E, Galassi S (2016) Recent DDT and PCB contamination in the sediment and biota of the Como Bay (Lake Como, Italy). Sci Total Environ 15:404-10. https://doi.org/10.1016/j.scitotenv.2015.10.099
15. Bigot M, Hawker DW, Cropp R, Muir DG, Jensen B, Bossi R, Bengtson SM (2017) Spring Melt and the Redistribution of Organochlorine Pesticides in the Sea-Ice Environment: A Comparative Study between Arctic and Antarctic Regions. Environ Sci Technol 51: 8944-8952. https://doi.org/10.1021/acs.est.7b02481
16. Bursian S, Newsted J, Zwiernik M (2012) Polychlorinated biphenyls, polybrominated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans. In: Gupta RC (ed) Veterinary Toxicology. Oxford: Academic Press, pp. 779-796. ISBN: 978-0-12-385926-6. Elsevier Inc.
17. Cabrerizo A, Larramendi R, Albar JP, Dachs J (2017) Persistent organic pollutants in the atmosphere of the Antarctic Plateau. Atmos Environ 149: 104-108. https://doi.org/10.1016/j.atmosenv.2016.11.015
18. Cabrerizo A, Muir DCG, Teixeira C, Lamoureux SF, Lafreniere MJ (2019) Snow Deposition and Melting as Drivers of Polychlorinated Biphenyls and Organochlorine Pesticides in Arctic Rivers, Lakes, and Ocean. Environ Sci Technol 53:14377-14386. DOI:

10.1021/acs.est.9b05150

19. Chakraborty P, Khuman SN, Selvaraj S, Sampath S, Devi NL, Bang JJ, Katsoyiannis A (2016) Polychlorinated biphenyls and organochlorine pesticides in River Brahmaputra from the outer Himalayan Range and River Hooghly emptying into the Bay of Bengal: Occurrence, sources and ecotoxicological risk assessment. Environ Pollut 219: 998-1006. https://doi.org/10.1016/j.envpol.2016.06.067
20. Carlsson P, Breivik K, Brorström-Lundén E, Cousins I, Christensen J, Grimalt JO, Halsall C, Kallenborn R, Abass K, Lammel G, Munthe J, MacLeod M, Odland JØ, Pawlak J, Rautio A, Reiersen LO, Schlabach M, Stemmler I, Wilson S, Wöhrnschimmel H (2018) Polychlorinated biphenyls (PCBs) as sentinels for the elucidation of Arctic environmental change processes: a comprehensive review combined with ArcRisk project results. Environ Sci Pollut Res Int. 25:22499-22528. DOI: 10.1007/s11356-018-2625-7
21. Carrera G, Fernandez P, Grimalt JO, Ventura M, Camarero L, Catalan J, Nickus U, Thies H, Psenner R (2002). Atmospheric deposition of organochlorine compounds to remote high mountain lakes of Europe. Environ Sci Technol 36:2581-8. DOI: 10.1021/es0102585
22. Carrizo D, Sobek A, Salvado JA, Gustafsson O (2017) Spatial Distributions of DDTs in the Water Masses of the Arctic Ocean. Environ Sci Technol 51: 7913-7919. DOI: 10.1021/acs.est.7b01369
23. Cheng HR, Lin T, Zhang G, Liu GQ, Zhang WL, Qi SH, Jones KC, Zhang XW (2014) DDTs and HCHs in sediment cores from the Tibetan Plateau. Chemosphere 94:183-189. https://doi.org/10.1016/j.chemosphere.2013.10.012
24. Choi SD, Baek SY, Chang YS, Wania F, Ikonomou MG, Yoon YJ, Park BK, Hong S (2008) Passive Air Sampling of Polychlorinated Biphenyls and Organochlorine Pesticides at the Korean Arctic and Antarctic Research Stations: Implications for Long-Range Transport and Local Pollution. Environ Sci Technol 42: 7125-7131. https://doi.org/10.1021/es801004p
25. Comisión intersecretarial para el control del proceso y uso de plaguicidas y sustancias tóxicas (CICOPLAFEST). Permiso de importación de plaguicidas y sustancias tóxicas sujetos a control por SEMARNAT. https://www.gob.mx/tramites/ficha/permiso-de-importacion-de-plaguicidas-y-sustancias-toxicas-sujetos-a-control-por-semarnat/COFEPRIS732
26. Cipro CVZ, Taniguchi S, Montone RC (2017) Organic pollutants in snow and seasonal melting water from King George Island, Antarctica. Water Air Soil Pollut 228-149. DOI: 10.1007/s11270-017-3325-5
27. Cuna E, Zawisza E, Caballero M, Ruiz-Fernández AC, Lozano-García S, Alcocer J (2014) Environmental impacts of Little Ice Age cooling in central Mexico recorded in the sediments of a tropical alpine lake. J paleolimnol 51:1-14. DOI: 10.1007/s10933-013-9748-0
28. Daly GL, Wania F (2005) Organic contaminants in mountains. Environ Sci Technol 39:385-398. DOI: 10.1021/es048859u
29. U. S. Environmental protection Agency (EPA). Method 3620-B. Florisil cleanup. Method 3620C: Florisil Cleanup, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (epa.gov)
30. Fang Y, Nie Z, Die Q, Tian Y, Liu F, He J, Huang Q (2017) Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: Concentration, transmission, and risk evaluation. Chemospher. 178:340-349. https://doi.org/10.1016/j.chemosphere.2017.02.151
31. Fenner K, Scheringer M, Hungerbuhler K (2003) Joint persistence of transformation products in chemicals assessment: case studies and uncertainty analysis. Risk Anal 23:35-53. DOI: 10.1111/1539-6924.00288
32. Gao X, Huang C, Rao K, Xu Y, Huang Q, Wang F, Ma M, Wang Z (2018) Occurrences, sources, and transport of hydrophobic organic contaminants in the waters of Fildes Peninsula, Antarctica. Environ Pollut 241: 950-958. https://doi.org/10.1016/j.envpol.2018.06.025
33. García L, Muro C, De La Rosa I, Amador-Muñoz O, Ponce MG, Borja-Salim M (2020) Comparison of gas chromatography techniques for the analysis of organochlorine pesticides in sediments. Soil Sediment Contam. 29: 257-271. https://doi.org/10.1080/15320383.2019.1703099
34. Guzzella L, Poma G, De Paolis A, Roscioli C, Viviano G (2011) Organic persistent toxic substances in soils, waters and sediments along an altitudinal gradient at Mt. Sagarmatha, Himalayas, Nepal. Environ Pollut 159:2552-2564. https://doi.org/10.1016/j.envpol.2011.06.015
35. Guzzella L, Salerno, F, Freppaz M, Roscioli C, Pisanello F, Poma G (2016) POP and PAH contamination in the southern slopes of Mt. Everest (Himalaya, Nepal): long-range atmospheric transport, glacier shrinkage, or local impact of tourism? Sci Total Environ 544:382–390. https://doi.org/10.1016/j.scitotenv.2015.11.118
36. Hao Y, Li Y, Han X, Wang T, Yang R, Wang P, Xiao K, Li W, Lu H, Fu J, Wang Y, Shi J, Zhang Q, Jiang G (2019) Air monitoring of polychlorinated biphenyls, polybrominated diphenyl ethers and organochlorine pesticides in West Antarctica during 2011–2017:

Concentrations, temporal trends and potential sources. Environ Pollut 249:381-389. https://doi.org/10.1016/j.envpol.2019.03.039

37. Harner T, Shoeib M, Kozma M, Gobas FAPC, Li S-M (2005). Hexachlorocyclohexanes and endosulfans in urban, rural and high altitude air samples in the Fraser Valley, British Columbia: evidence for trans-Pacific transport. Environ Sci Technol 39: 724-731. DOI: 10.1021/es048700h
38. Hites RA (2019). Statistical approach for assessing the Stockholm Convention's effectiveness: great lakes atmospheric data. Environ Sci Technol 53: 8585-8590. DOI: 10.1021/acs.est.9b02190
39. Hung H, Katsoyiannis AA, Brorström-Lundén E, Olafsdottir K, Aas W, Breivik K, Bohlin-Nizzetto P, Sigurdsson A, Hakola H, Bossi R, Skov H, Sverko E, Barresi E, Fellin P, Wilson S (2016) Temporal trends of persistent organic pollutants (POPs) in Arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). Environ Pollut 217:52-61. https://doi.org/10.1016/j.envpol.2016.01.079
40. Instituto Nacional de Estadística y Geografía (INEGI). (2021). Población y Empresas en México. https://www.inegi.org.mx/temas/estructura/
41. Jakobi G, Kirchner M, Henkelmann B, Körner W, Offenthaler I, Moche W, Weiss P, Schaub M, Schramm K-W (2015) Atmospheric bulk deposition measurements of organochlorine pesticides at three alpine summits. Atmos Environ 101:158-165. https://doi.org/10.1016/j.atmosenv.2014.10.060
42. Kallenborn R, Breivik K, Eckhardt S, Lunder CR, Manø S, Schlabach M, Stohl A (2013) Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos Chem Phys 13: 6983-6992. https://doi.org/10.5194/acp-13-6983-2013
43. Kim L, Jeon J-W, Son J-Y, Kim Ch-S, Ye J, Kim H-J, Lee Ch-H, Hwang S-M, Choi S-D (2020). Nationwide levels and distribution of endosulfan in air, soil, water, and sediment in South Korea. Environ Pollut 265B:115035. https://doi.org/10.1016/j.envpol.2020.115035
44. Lan J, Jia J, Liu A, Yu Z, Zhao Z (2019). Pollution levels of banned and non-banned pesticides in surface sediments from the East China Sea. Mar Pollut Bull 139: 332-338. https://doi.org/10.1016/j.marpolbul.2019.01.006
45. Li J, Zhu T, Wang F, Qiu XH, Lin WL (2006) Observation of Organochlorine Pesticides in the Air of the Mt. Everest Region. Ecotoxicol Environ Saf 63:33-41. https://doi.org/10.1016/j.ecoenv.2005.04.001
46. Li Q, Wang X, Song J, Sui H, Huang L, Li L (2012) Seasonal and Diurnal Variation in Concentrations of Gaseous and Particulate Phase Endosulfan. Atmos Environ 61: 620-626. https://doi.org/10.1016/j.atmosenv.2012.07.068
47. Li Ch, Huo S, Yu Z, Xi B, Yeager K M, He Z, Ma Ch, Zhang J, Wu F (2017) National investigation of semi-volatile organic compounds (PAHs, OCPs, and PCBs) in lake sediments of China: Occurrence, spatial variation and risk assessment. Sci Total Environ 579:325-336. https://doi.org/10.1016/j.scitotenv.2016.11.097
48. Madaj R, Sobiecka E, Kalinowska H (2018) Lindane, kepone and pentachlorobenzene: chloropesticides banned by Stockholm convention. Int J Environ Sci Technol 15:471-480. https://doi.org/10.1007/s13762-017-1417-9
49. Meire RO, Lee SC, Yao Y, Targino AC, Torres JPM, Harner T (2012) Seasonal and Altitudinal Variations of Legacy and Current-use of Pesticides in the Brazilian Tropical Tropical and Subtropical Mountains. Atmos Environ 59:108-116. https://doi.org/10.1016/j.atmosenv.2012.05.018
50. Miglioranza KSB, Ondarza PM, Costa PG, De Azevedo A, Gonzalez M, Shimabukuro VM, Grondona SI, Mitton FM, Barra RO, Wania F, Fillmann G (2021) Spatial and temporal distribution of Persistent Organic Pollutants and current use pesticides in the atmosphere of Argentinean Patagonia, Chemosphere.266:129015. https://doi.org/10.1016/j.chemosphere.2020.129015
51. Nadal M, Marquès M, Mari M, Domingo JL (2015) Climate change and environmental concentrations of POPs: A review. Environ Res 143: 177-185. DOI: 10.1016/j.envres.2015.10.012
52. Nawab J, Wang J, Khan S, Tang Y, Rahman Z, Ali A, Dotel J, Li G (2020) New insights into the bioaccumulation of persistent organic pollutants in remote alpine lakes located in Himalayas, Pakistan. Environ Pollut 7:114952. DOI: 10.1016/j.envpol.2020.114952
53. Ornellas R, Khairy M, Créso A, Amaral PM, Machado JP, Malm O, Lohmann R (2016) Use of passive samplers to detect organochlorine pesticides in air and water at wetland mountain region sites (S-SE Brazil). Chemosphere 144:2175-2182. https://doi.org/10.1016/j.chemosphere.2015.10.133
54. Pawlak F, Koziol K, Polkowska Z (2021) Chemical hazard in glacial melt? The glacial system as a secondary source of POPs (in the Northern Hemisphere). A systematic review. Sci Total Environ 778:145244. https://doi.org/10.1016/j.scitotenv.2021.145244

55. Potapowicz J, Szumińska D, Szopińska M, Polkowska Ż (2019) The influence of global climate change on the environmental fate of anthropogenic pollution released from the permafrost Part I. Case study of Antarctica. Sci Total Environ 651:1534-1548. https://doi.org/10.1016/j.scitotenv.2018.09.168
56. Ren J, Wang X, Wang C, Gong P, Gongab, Wang X, Yao T (2017) Biomagnification of persistent organic pollutants along a high-altitude aquatic food chain in the Tibetan Plateau: Processes and mechanisms. Environ Pollut220:636-643. https://doi.org/10.1016/j.envpol.2016.10.019
57. Ryan EG (2008) Beyond the circle of poison: Significant shifts in the global pesticide complex, 1976–2008. Global Environ Chang 18:786-799. https://doi.org/10.1016/j.gloenvcha.2008.07.003
58. Shen L, Wania F, Ying DL, Teixeira C, Muir DCG, Bidleman TF (2005) Atmospheric distribution and long-range transport behaviour of organochlorine pesticides in North America. Environ Sci Technol 39:409-420. DOI:10.1021/es049489c
59. Shunthirasingham C, Gawor A, Hung H, Brice KA, Su K, Alexandrou N, Dryfhout-Clark H, Backus S, Sverko E, Shin C, Park R, Noronha R (2016) Atmospheric concentrations and loadings of organochlorine pesticides and polychlorinated biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and temporal analysis (1992-2012). Environ Pollut 217:124-33. https://doi.org/10.1016/j.envpol.2016.01.039
60. SMN-CONAGUA, 2017. Servicio Meteorológico Nacional, Comisión Nacional del Agua. Pronóstico Meteorológico General (conagua.gob.mx)
61. Stern GA, Macdonald CR, Armstrong D, Dunn B, Fuchs C, Harwood L, Muir DGC, Rosenberg B (2005) Spatial trends and factors affecting variation of organochlorine contaminants levels in Canadian Arctic beluga (*Delphinapterus leucas*). Sci Total Environ 352: 344-368. https://doi.org/10.1016/j.scitotenv.2004.10.033
62. Stemmler I, Lammel G (2012) Long-term trends of continental-scale PCB patterns studied using a global atmosphere-ocean general circulation model. Environ Sci Pollut Res Int. 19:1971-1980. DOI:10.1007/s11356-012-0943-8
63. Sun SY, Yuan GL, Tang J, Wang GH (2018) High-resolution sedimentary records of some organochlorine pesticides in Yamzho Yumco Lake of the Tibetan Plateau: Concentration and composition. Sci Total Environ 615: 469-475. https://doi.org/10.1016/j.scitotenv.2017.09.282
64. Tanabe S (1988) PCB problems in the future: foresight from current knowledge. Environ Pollut 50: 5-28. https://doi.org/10.1016/0269-7491(88)90183-2
65. Tran TAM, Malarvannan G, Hoang T L, Covaci A, Elskens M (2019) Occurrence of organochlorine pesticides and polychlorinated biphenyls in sediment and fish in Cau Hai lagoon of Central Vietnam: human health risk assessment. Mar Pollut Bull141:521-528. https://doi.org/10.1016/j.marpolbul.2019.03.006
66. Tremolada P, Parolini M, Binelli A, Ballabio C, Comolli R, Provini A (2009) Preferential retention of POPs on the northern aspect of mountains. Environ Pollut 57:3298-307. https://doi.org/10.1016/j.envpol.2009.05.041
67. United Nations Environment Programme/ (UNEP/FAO). (2007). Inclusion of the chemical endosulfan in Annex III of the Rotterdam Convention. United Nations Environment Programme and Food and Agriculture Organisation UNEP/FAO/RC/COP.4/9. http://www.pic.int/COPS/COP4/i9)/English/K0763331%20COP-4-9.pdf
68. United Nations Environment Programme (UNEP). (2011). Decision SC-5/3: Listing of Technical Endosulfan and its Related Isomers. https://www.informea.org/en/decision/listing-technical-endosulfan-and-its-related-isomers
69. United Nations Economic Commission for Europe (UNECE) (2010) Options for Adding New Substances to the Protocol on Persistent Organic Pollutants, Report by the Co-chair of the Task Force on Persistent Organic Pollutants. Meeting Document, ECE/EB.AIR/WG.5/2010/8. 2010. United Nations (unece.org)
70. Usenko S, Landers DH, Appleby PG, Simonich SL (2007) Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park. Environ Sci Technol41:7235-7241. DOI: 10.1021/es0710003
71. Vecchiato M, Zambon S, Argiriadis E, Barbante C, Gambaro A, Piazza R (2015) Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Antarctic ice-free areas: influence of local sources on lakes and soils. Microchem J 120:26-33. https://doi.org/10.1016/j.microc.2014.12.008
72. Wania F, Westgate JN (2008) On the mechanism of mountain cold-trapping of organic chemicals. Environ Sci Technol. 42(24):9092-9098. DOI:10.1021/es8013198
73. Wang X, Gong P, Wang Ch, Rena J, Wang JY (2016) A review of current knowledge and future prospects regarding persistent organic pollutants over the Tibetan Plateau. Sci Total Environ 573: 139-154. https://doi.org/10.1016/j.scitotenv.2016.08.107

74. Wang X, Wang Ch, Zhu T, Gong P, Fu J, Cong Z (2019) Persistent organic pollutants in the polar regions and the Tibetan Plateau: A review of current knowledge and future prospects. Environ Pollut 248: 191-208. https://doi.org/10.1016/j.envpol.2019.01.093
75. Weber J, Halsall CJ, Muir D, Teixeira C, Small J, Solomon K, Bidleman T (2010) Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Sci Total Environ 408: 2966-2984. https://doi.org/10.1016/j.scitotenv.2009.10.077
76. Wolska L, Mechlinska A, Rogowska J, Namiesnies J (2014) Polychlorinated biphenyls (PCBs) in bottom sediments: Identification of sources. Chemosphere 11:151-156. https://doi.org/10.1016/j.chemosphere.2014.03.025
77. Wong F, Alegria HA, Bidleman TF (2010) Organochlorine pesticides in soils of Mexico and the potential for soil–air exchange. Environ Pollut 158: 749-755. https://doi.org/10.1016/j.envpol.2009.10.013
78. Wong F, Hung H, Dryfhout-Clark H, Aas W, Bohlin-Nizzetto P, Breivik K, Mastromonaco MN, Lundén EB, Ólafsdóttir K, Sigurðsson Á, Vorkamp K, Bossi R, Skov H, Hakola H, Barresi E, Sverko ED, Fellin P, Li H, Vlasenko A, Zapevalov M (2021) Time trends of persistent organic pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEAC) in Arctic air from 25 years of monitoring. Sci Total Environ 775:145109. https://doi.org/10.1016/j.scitotenv.2021.145109
79. Wu Ch, Xiong X, Huang X, Xing X, Liu J (2014) Occurrence and distribution of organochlorine pesticides and polycyclic aromatic hydrocarbons in surface sediments from Qinghai Lake, northeast Qinghai–Tibet plateau, China. J Great Lakes Res 40:675-683. https://doi.org/10.1016/j.jglr.2014.05.003
80. Wu X, Chen A, Yuan Z, Kang H, Xie Z (2020) Atmospheric organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the Antarctic marginal seas: Distribution, sources and transportation. Chemosphere 258: 127359. https://doi.org/10.1016/j.chemosphere.2020.127359
81. Yadav ICh, Devi NL, Li J, Zhang G, Shakya PR (2016) Occurrence, profile and spatial distribution of organochlorines pesticides in soil of Nepal: Implication for source apportionment and health risk assessment. Sci Total Environ.15:1598-1606. https://doi.org/10.1016/j.scitotenv.2016.09.133
82. Yang RQ, Zhang SJ, Li A, Jiang G.B, Jing CY (2013) Altitudinal and spatial signature of persistent organic pollutants in soil, lichen, conifer needles, and bark of the southeast Tibetan Plateau: Implications for sources and environmental cycling. Environ Sci Technol 47:12736-12743. https://doi.org/10.1021/es403562x
83. Yu Y, Hung H, Alexandrou N, Roach P, Nordin K (2015) Multiyear measurements of flame retardants and organochlorine pesticides in air in Canada's western sub- Arctic. Environ Sci Technol 49:8623-8630. DOI: 10.1021/acs.est.5b01996
84. Zhang Q, Chen Z, Li Y, Wang P, Zhu C, Gao G, Xiao K, Sun H, Zheng S, Liang Y, Jiang G (2015) Occurrence of organochlorine pesticides in the environmental matrices from King George Island, west Antarctica. Environ Pollut 206:142-149. https://doi.org/10.1016/j.envpol.2015.06.025

Figures

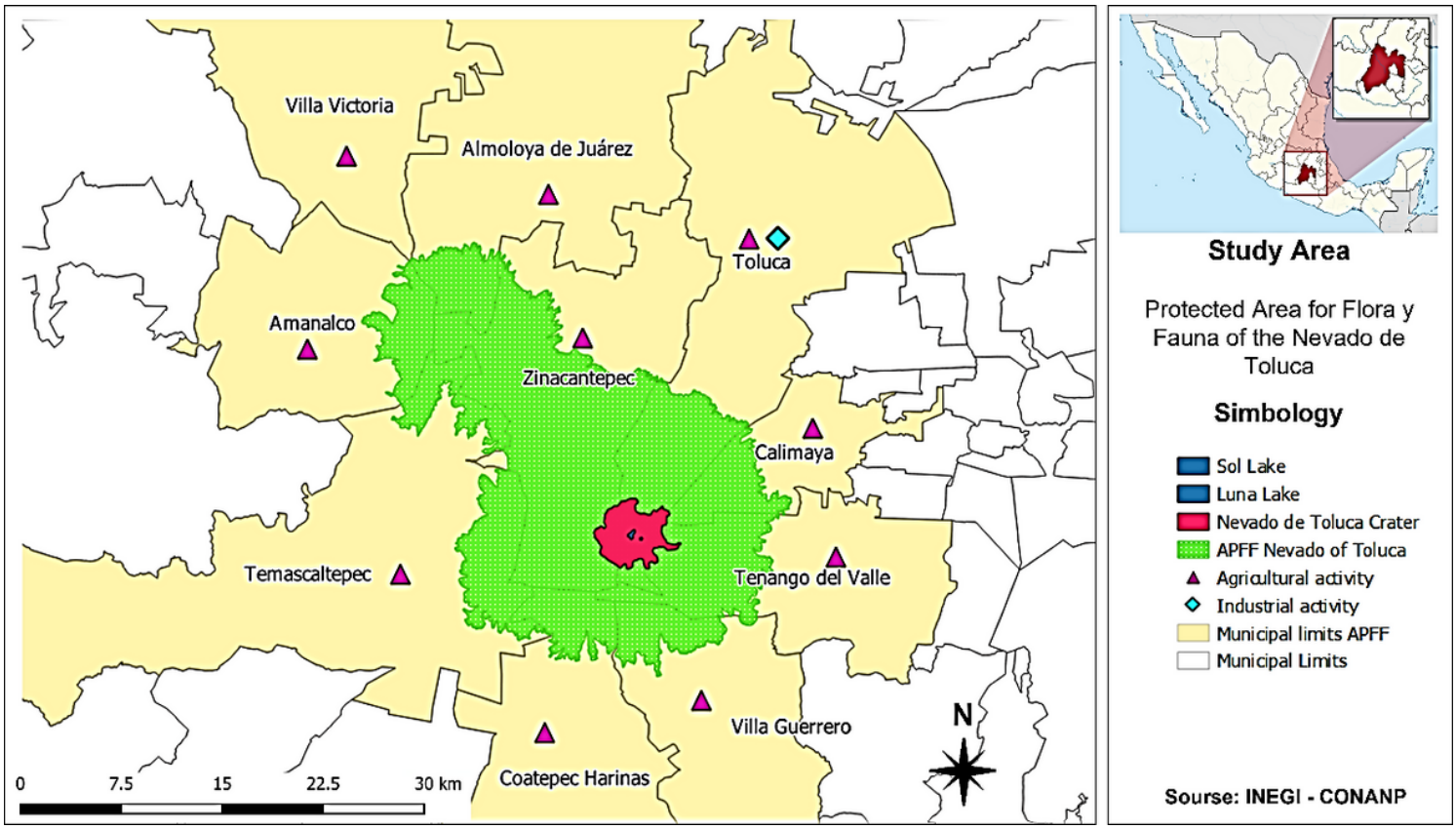

Figure 1

Map of Nevado de Toluca volcano, Lakes El Sol and La Luna, and surrounding region.

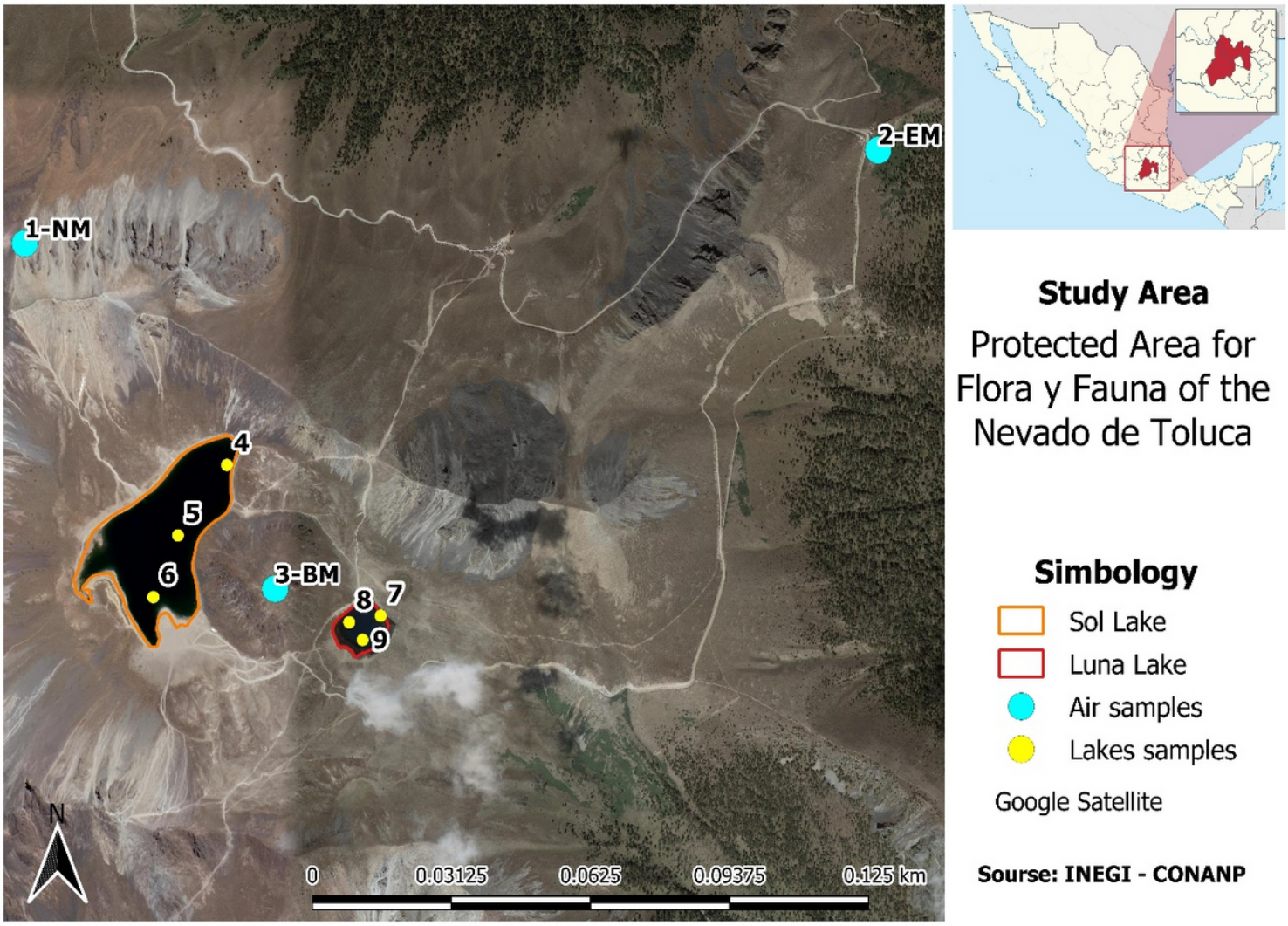

Figure 2

Geographical position of the sampling sites for atmospheric aerosol, sediments, phytoplankton, and Tubifex tubifex from the El Sol and La Luna lakes.

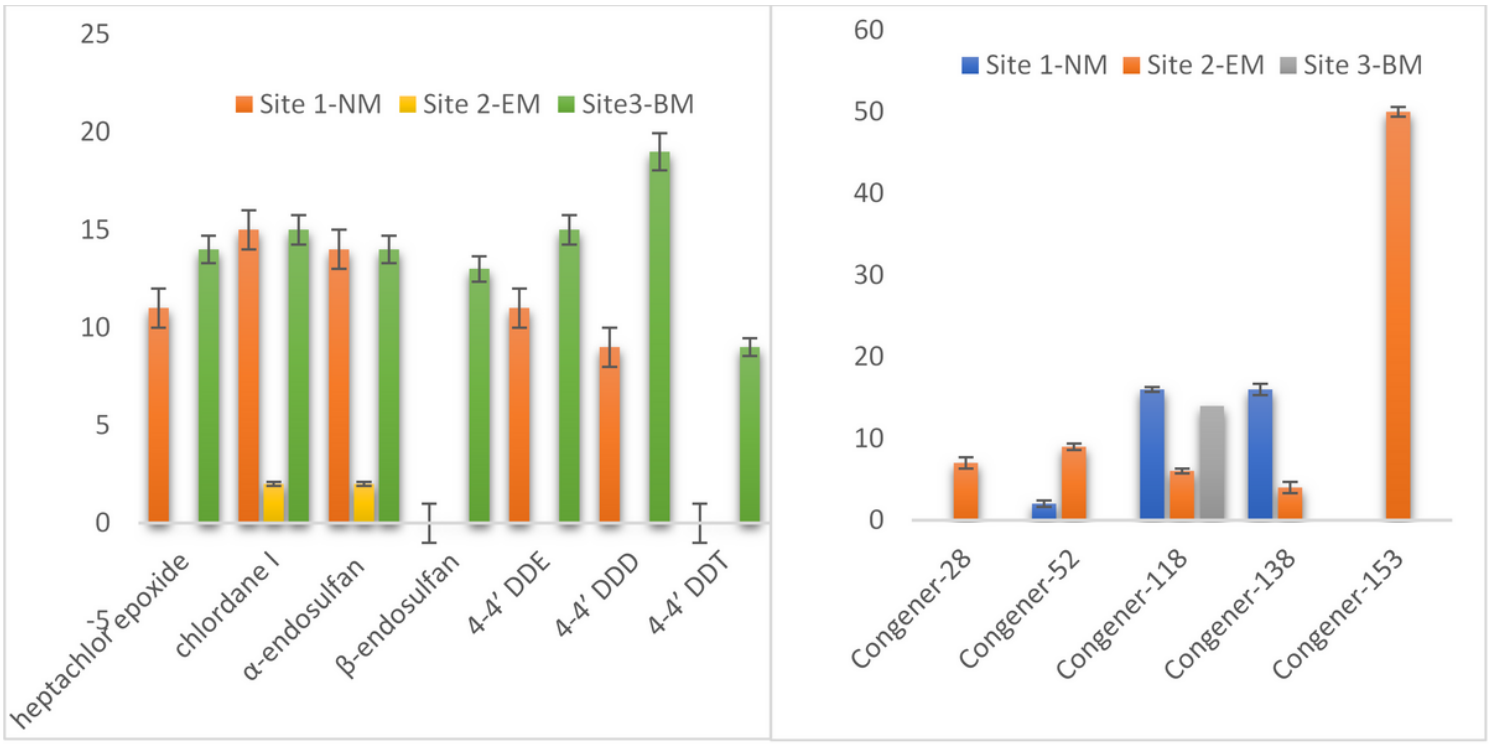

Figure 3

OCPs (left) and PCBs (right) average concentration (±standard deviation) in atmospheric aerosol (pg/m3) found in three sites located in the crater. N = 9. The metric includes the whole sampling period (2017-2019).

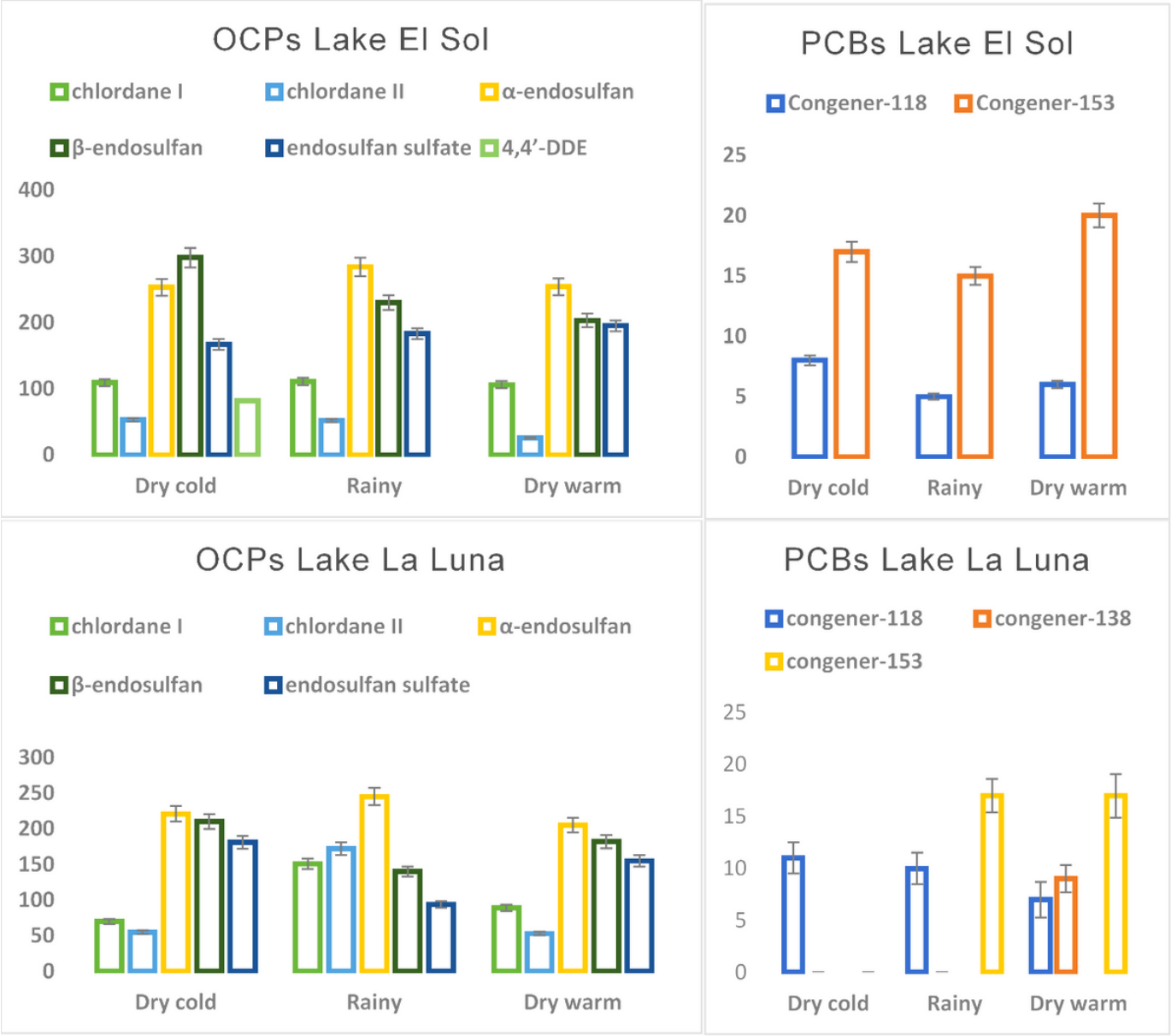

Figure 4

Average concentration (± standard deviation) of OCPs and PCBs (pg/g) in sediment from the El Sol and La Luna Lakes by season including 2017-2019. N = 9.

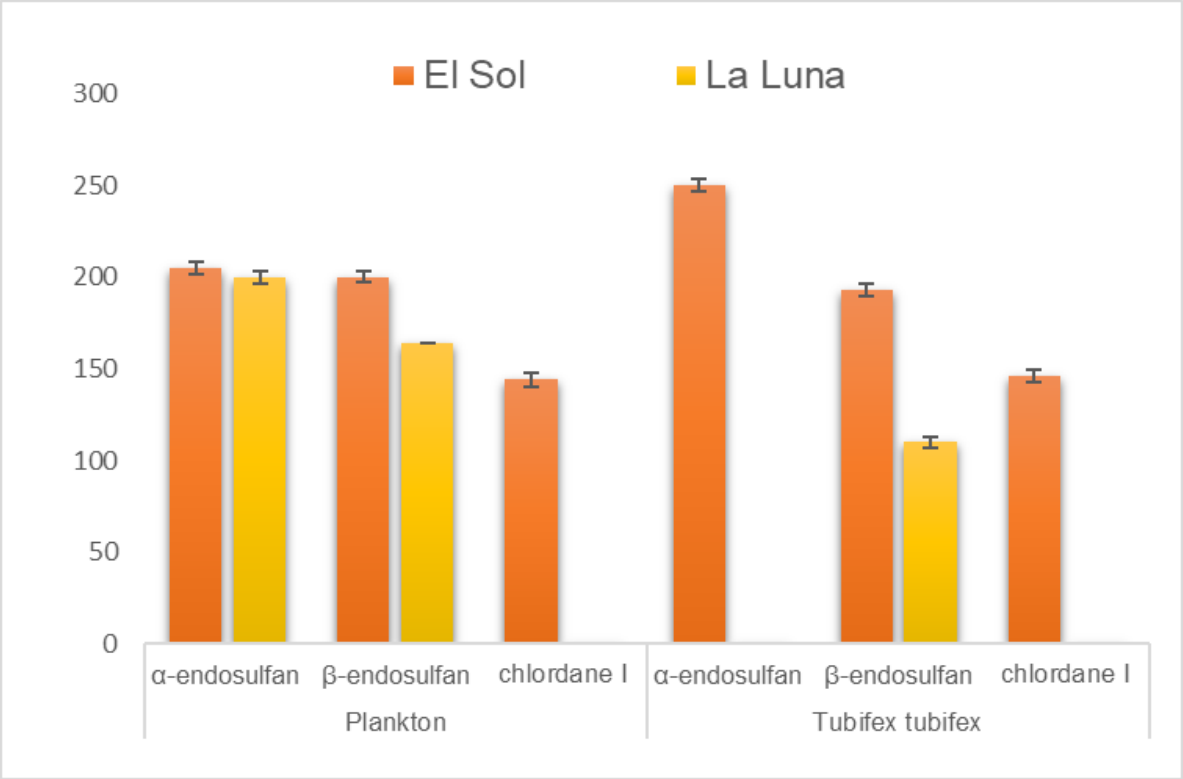

Figure 5

Average concentration (±standard deviation) of OCPs in plankton and Tubifex tubifex (pg/g) from three sites of the El Sol and La Luna lakes. N=9. The metric includes the whole sampling period (2017-2019).

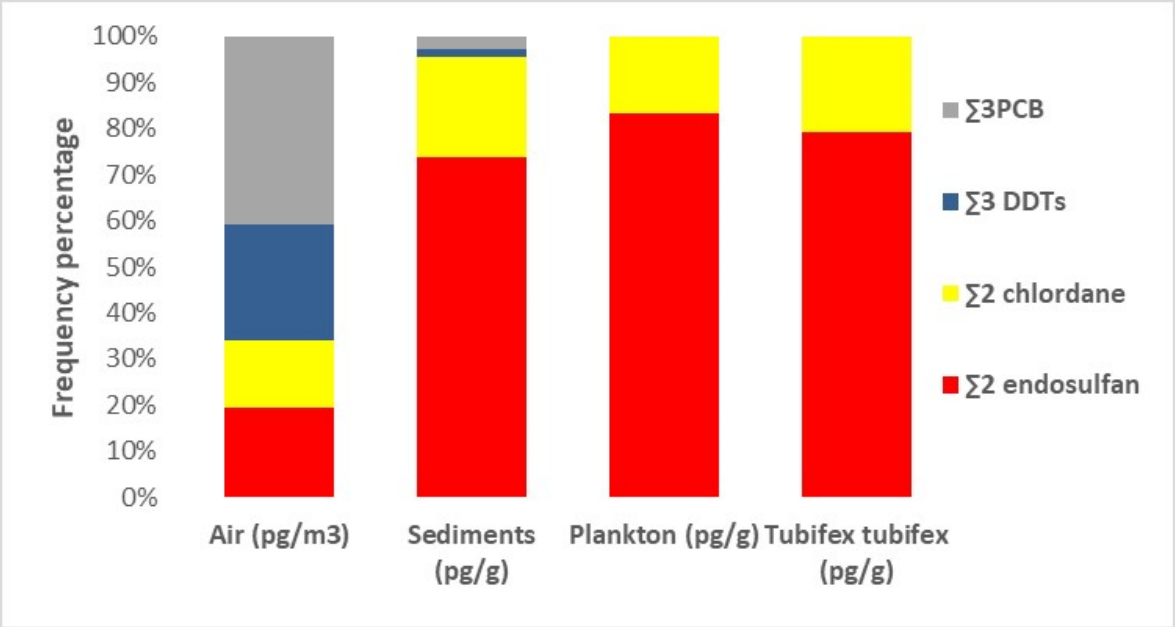

Figure 6

Frequency percentage of the most detected pollutants in atmospheric aerosol, sediments, plankton, and Tubifex tubifex from the El Sol and La Luna lakes.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Supplementarymaterial.docx