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Persistent and semivolatile contaminants in sediments of Nutrias Lagoon (Uruguay): historical trends and potential ecological implications

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Abstract

Sediments provide long-term archives of environmental change and are critical for reconstructing historical contaminant dynamics in aquatic systems. This study analyzed polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), mercury (Hg), and previously reported polycyclic aromatic hydrocarbons (PAHs) in a dated sediment core from Nutrias Lagoon, a small, shallow, and low-impact coastal lagoon in southeastern Uruguay. The site's protected status and minimal local anthropogenic pressure make it an ideal reference system to evaluate diffuse and long-range pollution inputs.

Results show that PCB 52 was sporadically detected, particularly in layers corresponding to the late 20th and early 21st centuries, consistent with historical global production and atmospheric redistribution. PBDEs were not detected, suggesting negligible inputs to the region. Mercury concentrations remained relatively stable (65–85 μg kg^{-1}) throughout the core and consistently below international sediment quality guidelines, reinforcing the interpretation of atmospheric deposition as the dominant source. In contrast, PAHs were more consistently present, with light compounds enriched toward the surface and isolated exceedances of ecotoxicological thresholds, indicating potential localized risks for benthic organisms.

The temporal overlap between PAH maxima, PCB 52 detections, and the highest Hg values suggests periods of enhanced contaminant influx likely linked to regional or global emission events. Overall, the findings highlight that even protected, low-impact lagoons are susceptible to diffuse atmospheric contamination. Nutrias Lagoon thus provides a valuable paleoenvironmental baseline for assessing contaminant dynamics in South American coastal systems and underscores the need for continued monitoring under scenarios of global environmental change.

Introduction

Sediments act as integrative and conservative archives of environmental processes, storing physical, chemical, and biological signals over time (Arocena, 2016; Smol, 2008). In aquatic ecosystems, the vertical structure of sediment cores allows for the reconstruction of historical contamination patterns, offering valuable insights into the onset, intensity, and evolution of pollutant inputs (Smol, 2019). Paleolimnological approaches are particularly valuable in regions with limited long-term monitoring, as they allow the establishment of environmental baselines and retrospective assessments of anthropogenic influence under varying degrees of impact (Gros et al., 2023).

Persistent and semivolatile pollutants, such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and mercury (Hg), are of global concern due to their toxicity, environmental persistence, and capacity for long-range atmospheric transport (Campos et al., 2022; Cooke et al., 2020; Hung et al., 2013). Once deposited, these contaminants can accumulate in aquatic sediments and exert chronic effects on benthic organisms and higher trophic levels through processes of bioaccumulation and biomagnification (Oregel-Zamudio et al., 2021; United Nations Environment Programme, 2013). PCBs and PBDEs, widely used as dielectric fluids, flame retardants and additives in industrial and consumer products, are known to disrupt endocrine, reproductive, and neurological functions in aquatic fauna (Green et al., 2025; La Guardia et al., 2024; Okuthe et al., 2025). Similarly, mercury and its methylated derivatives are highly toxic compounds that can

impair growth, reproduction, and behavior in aquatic organisms, with potential implications for ecosystem functioning and human health via trophic transfer (Anual et al., 2018; UN Environment, 2019).

Despite regulatory bans and restrictions, these substances continue to be detected in sediments worldwide, including in remote or protected environments (Azcune et al., 2022; UN Environment, 2019). In such contexts, the absence of direct emission sources highlights the relevance of atmospheric deposition as a major pathway of entry. Therefore, understanding the temporal dynamics of these contaminants in low-impact systems is crucial to characterize background levels, identify diffuse pollution signals, and assess potential ecological risks in the absence of confounding local inputs (Bolaños-Alvarez et al., 2024; Cooke et al., 2020; Muir & de Wit, 2010; Nipen et al., 2022). This approach is particularly valuable for evaluating historical atmospheric contamination in small, hydrologically constrained systems, where sedimentary records can preserve integrative signals of long-range pollutant inputs.

This study examines the historical profiles of PCBs, PBDEs, and Hg in sediment cores collected from Nutrias Lagoon, a shallow coastal water body located in southeastern Uruguay. The lagoon is embedded within a protected landscape and exhibits limited anthropogenic pressure, making it a suitable reference system for regional paleoenvironmental assessments (Azcune et al., 2024). The concentrations and temporal trends of the studied contaminants are interpreted in light of known ecological thresholds and potential biological effects (Buchman, 2008; Long & MacDonald, 1998), an approach that allows evaluation of when contaminant levels may have reached ecologically relevant limits under conditions of chronic, low-intensity exposure. Within this framework, ecological thresholds provide a useful conceptual tool to link historical contaminant accumulation with potential biological responses, even in systems considered relatively pristine. Selected data on polycyclic aromatic hydrocarbons (PAHs), previously reported for the same sediment core (Azcune et al., 2024), are included to contextualize cumulative pressures and contaminant interactions.

In doing so, this work aims to contribute to the understanding of contaminant dynamics in coastal lentic systems of South America, offering insights into historical pollution patterns, sources, and ecological relevance. By focusing on contaminants largely influenced by atmospheric transport, the study highlights the role of diffuse and non-local sources in shaping sedimentary contaminant records. The findings are expected to inform future research and management strategies focused on the conservation of aquatic ecosystems under increasing pressure from global environmental change.

Materials and Methods

Study area and sediment core collection

Nutrias Lagoon is a small, shallow coastal lagoon located in the southeastern region of Uruguay (34°40'50.8" S, 54°17'42.0" W), within the Paisaje Protegido Laguna de Rocha, part of Uruguay's National System of Protected Areas (SNAP) (Ministerio de Vivienda Ordenamiento Territorial y Medio Ambiente, 2010). It has an area of 33.8 ha, a maximum depth of approximately 1.5 m, and a drainage basin of 44.7 ha predominantly covered by natural grasslands and scattered forest patches (Kruk et al., 2009). The absence of urban settlements or industrial activities within its basin, combined with low-intensity livestock grazing as the main land use, results in minimal local anthropogenic pressure (Azcune et al., 2024; de Álava et al., 2013). These characteristics make

the system particularly suitable for evaluating background levels of contamination and assessing the contribution of diffuse or long-range atmospheric sources.

A 65 cm-long sediment core (NUT1) was collected in February 2018 from the deepest zone of the lagoon using a manual push corer (internal diameter: 15 cm). The core was immediately sealed, kept refrigerated at 4°C, and transported to the laboratory. Subsampling was carried out under refrigerated conditions: the upper 30 cm were sectioned every 1 cm, and the deeper sections every 2 cm. Further stratigraphic, granulometric and biogeochemical characterization of the core is detailed in Azcune et al. (2024).

The chronological framework applied in this study is based on validated age-depth models developed using ^{210}Pb and ^{137}Cs profiles. Both Constant Flux (CF) (Appleby & Oldfield, 1978; Sanchez-Cabeza et al., 2012) and Bayesian (Aquino-López et al., 2018, 2020) models were previously constructed and cross-validated through stratigraphic markers, as described in Azcune et al. (2024). This framework was used here to assign calendar ages to the contaminant profiles.

Sample preparation and chemical analyses

For the determination of PCBs and PBDEs, 10 g of raw sample were extracted using a modified QuEChERS extraction, assisted with sonication (Anastassiades et al., 2003, 2007; Azcune et al., 2024; Pareja et al., 2022). Samples were sonicated for 20 min with 10 mL of acetone: hexane (50:50), both HPLC grade (Fischer Chemicals and Carlo Erba, respectively), in a 50 mL centrifuge tube. Afterwards, 4g of MgSO4 and 1g of NaCl (both ACS grade, Carlo Erba) were added. The tube was hand-shaken for 1 min and then centrifuged for 10 min at 4000 rpm. 1 mL of the organic layer was filtered by a 0.22 µm PTFE filter and placed in a vial for chromatographic analysis.

Samples were analyzed using a Shimadzu TQ8040 GC-MS/MS system equipped with a Restek RXI-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Injections of 1 µL were performed in splitless mode at an injector temperature of 250°C. Helium was employed as the carrier gas at a constant flow rate of 1 mL min^{-1}. The GC-MS/MS operated in Multiple Reaction Monitoring (MRM) mode for quantification, with a source temperature of 230°C and quadrupole temperature of 150°C.

Quantification was based on a five-point external calibration curve. Analytical standards were obtained from AccuStandard as certified mixed solutions (PCBs: AE-00059-R1-10ML; PBDEs: BDE-CSM), and triphenyl phosphate (TPP), used as a surrogate standard, was purchased from HPC Standards. The limits of quantification (LOQs) for PCBs, determined as the lowest level meeting acceptable recovery criteria, were 10 µg kg^{-1} for all congeners except PCB 153, which had a LOQ of 1 µg kg^{-1}. For PBDEs, LOQs were 1 µg kg^{-1} for all analytes except PBDE 183, with a LOQ of 10 µg kg^{-1}.

All determinations adhered to the QA/QC requirements in the SANTE guidelines (European Commission, 2021). For GC-MS/MS analysis, two transitions per analyte were monitored, with a retention time tolerance of ± 0.2 min and compliance with ion ratio criteria between quantifier and qualifier transitions. Method performance was evaluated based on recovery rates between 70% and 120% and relative standard deviations (RSD) ≤ 20%. Calibration linearity was verified according to the SANTE guideline, requiring residuals within ± 20%.

Mercury concentrations were measured in dry, homogenized sediment using a direct mercury analyzer (DMA-80, Milestone Inc.), based on thermal decomposition, gold amalgamation, and atomic absorption detection. Analytical quality was assured using procedural blanks and IAEA-456 certified reference material. Analytical precision was within ± 1,84% with an average recovery of 103%.

Data processing and ecological thresholds

Temporal concentration profiles of PCBs, PBDEs and Hg were interpreted in the context of the sediment chronologies. Where applicable, measured concentrations were compared against published ecotoxicological thresholds, including the Threshold Effect Level (TEL) and Probable Effect Level (PEL) guidelines, as references for potential biological effects in benthic organisms (Birch, 2011; Buchman, 2008; Long & MacDonald, 1998).

In addition, previously published data on PAHs from the same sediment core (Azcune et al., 2024) were considered to complement the interpretation of cumulative contaminant exposure and possible synergies in toxicity profiles.

Results

Polychlorinated biphenyls (PCBs) and Polybrominated diphenyl ethers (PBDEs)

Recoveries for PCBs and PBDEs, performed in triplicate and presented with their respective standard deviations, are shown in Table 1. The limit of quantification (LOQ) was determined as the lowest level of effective recovery for each compound. The surrogate standard triphenyl phosphate (TPP), used for QA/QC purposes, showed acceptable recoveries throughout the run, except for the 48–50 cm sample, which yielded 0% recovery; consequently, data from this sample were discarded.

Table 1
Recoveries of PCBs and PBDEs and their relative standard deviation

	1 μg kg^{-1}		10 μg kg^{-1}		100 μg kg^{-1}	
	%Rec	%RSD Rec	%Rec	%RSD Rec	%Rec	%RSD Rec
PCB 28	101%	39%	99%	1%	112%	1%
PCB 52	91%	31%	95%	3%	112%	1%
PCB 101	95%	27%	91%	5%	107%	2%
PCB 118	128%	7%	84%	3%	101%	3%
PCB 138	95%	23%	79%	8%	99%	3%
PCB 153	93%	15%	90%	8%	101%	2%
PCB 180	135%	4%	76%	9%	98%	2%
PBDE 28	120%	2%	92%	0%	102%	3%
PBDE 47	118%	4%	77%	5%	98%	3%
PBDE 99	119%	5%	72%	5%	94%	4%
PBDE 100	114%	12%	74%	3%	100%	2%
PBDE 153	118%	10%	79%	8%	93%	2%
PBDE 154	80%	12%	71%	5%	89%	7%
PBDE 183	40%	138%	70%	5%	102%	5%

All analyzed PCBs were below the LOQ across the entire sediment core. However, detectable concentrations of the PCB 52 congener, although still below the LOQ, were found in the 2–3, 3–4, 4–5, 6–7, 7–8, 11–12, 25–26, 29–30, and 40–42 cm intervals. The number of values above the limit of detection (LOD) for PCB 52, grouped by time period, is shown in Fig. 1, based on ages estimated using the CF method with their corresponding expanded uncertainties. The matrix effect for all PCB analytes was positive, being moderate for PCBs 101 and 138, and strong for the remaining congeners.

No detectable concentrations of PBDEs were observed in any of the sediment samples. The surrogate standard TPP showed acceptable recoveries across the entire core. The matrix effect for PBDE analytes was also positive, being weak for PBDE 154 and moderate for the others.

Mercury (Hg)

Mercury concentrations in the sediment core showed relatively stable values throughout the profile (Fig. 2), with most measurements ranging between 65 and 85 μg kg^{-1}. The upper 10 cm displayed moderate variability, with concentrations fluctuating around 75–80 μg kg^{-1}. Between 10 and 35 cm depth, concentrations remained fairly consistent, although small oscillations were observed without any clear increasing or decreasing trend. A more noticeable decline occurred from 35 to 50 cm, where concentrations dropped from approximately 80 μg kg^{-1} to near 65 μg kg^{-1}. Below 50 cm, concentrations continued to fluctuate but tended to remain at the lower

end of the observed range. Overall, the profile indicates limited long-term variability, with only a gradual decrease in mercury concentrations toward the deeper sections of the core.

Contextualization with PAH data

As reported in Azcune et al. (2024), the same sediment core exhibited detectable concentrations of nine polycyclic aromatic hydrocarbons (PAHs), with six compounds consistently exceeding the LOQ. A general increase in light molecular weight PAHs (e.g. fluorene, phenanthrene, naphthalene) was observed toward the surface, while heavier compounds (e.g. dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene) were present in deeper layers.

Although PAHs are not the focus of this manuscript, their presence is relevant for interpreting potential cumulative effects. Notably, PAH concentrations in surface layers overlapped temporally with the detection of PCB 52 and moderately elevated Hg levels, suggesting a period of increased contaminant influx during the late 20th and early 21st centuries.

Contaminants and comparison with ecological thresholds

In order to evaluate the ecological relevance of the detected contaminants, the measured concentrations were compared against sediment quality guidelines from NOAA (Buchman, 2008) and the Canadian Council of Ministers of the Environment (CCME, 1999) (Table 2). Total PAH concentrations (ΣPAHs) reached up to ~ 600 μg kg^{-1}, remaining well below the Threshold Effect Concentration (TEC) of 1610 μg kg^{-1} established by NOAA. However, when considering individual compounds, naphthalene exceeded the Threshold Effect Level (TEL = 34.1 μg kg^{-1}) in surface layers, and indeno[1,2,3-cd]pyrene slightly surpassed the Lowest Effect Level (LEL = 200 μg kg^{-1}) in deeper sections. Dibenzo[a,h]anthracene concentrations remained below the Probable Effect Level (PEL = 135 μg kg^{-1}, CCME). For PCBs, only sporadic detections of PCB 52 were recorded, all below the limit of quantification and well under the NOAA TEL (34.1 μg kg^{-1}). PBDEs were not detected. Mercury concentrations ranged between 65 and 85 μg kg^{-1}, remaining below TEL (130 μg kg^{-1}). Overall, the results indicate limited exceedance of guideline values, with potential ecological concerns restricted to specific PAH compounds in certain intervals.

Table 2
Summary of contaminants detected in sediments of Nutrias Lagoon and comparison with ecotoxicological thresholds (NOAA; CCME).

Contaminant group	Compound(s) detected	Maximum concentration (µg kg⁻¹, d.w.)	Ecotoxicological threshold (µg kg⁻¹, d.w.)	Reference	Exceedance of thresholds
PAHs (total)	Σ24 PAHs (9 detected; 6 > LOQ)	~ 1300	TEC (Σ_{PAHs}) = 1610	NOAA (Buchman, 2008)	No exceedance
PAHs (individuals)	Naphthalene	~ 200	TEL = 34.1	NOAA (Buchman, 2008)	TEL exceeded in upper layers
	Indeno[1,2,3-cd]pyrene	~ 220	LEL = 200	NOAA (Buchman, 2008)	Slight exceedance at depth
	Dibenzo[a,h]anthracene	~ 100	PEL = 135	CCME (1999)	No exceedance
PCBs (n = 7)	Only PCB 52 detected sporadically, always < LOQ	<LOQ	TEL (Σ_{PCBs}) = 34.1	NOAA (Buchman, 2008)	No exceedance
PBDEs (n = 7)	Not detected	–	–	–	–
Mercury (Hg)	Total Hg	85	TEL = 130	NOAA (Buchman, 2008)	No exceedance

Discussion

The sedimentary record of Nutrias Lagoon provides a valuable archive to reconstruct the recent history of contamination in a relatively pristine environment of southeastern Uruguay. This system, located within a protected landscape and characterized by limited local anthropogenic pressure, offers an ideal context to evaluate the influence of diffuse and long-range sources of pollutants. Unlike highly impacted sites where contaminant signals are dominated by local discharges, the Nutrias record highlights more subtle inputs, allowing for the identification of regional and global processes shaping contamination trends.

Mercury concentrations along the sediment core fluctuated within a narrow range, generally between 65 and 85 µg kg⁻¹. These values remained well below sediment quality guidelines proposed internationally (TEL = 130 µg kg⁻¹; Buchman, 2008), suggesting that Hg levels in Nutrias Lagoon sediments are unlikely to pose ecological risks under present conditions. The absence of clear peaks commonly associated with strong local inputs reinforces the interpretation that Hg in this system is mainly derived from atmospheric wet deposition, a phenomenon widely reported for remote lakes and lagoons across the globe (Cooke et al., 2020).

In the Uruguayan context, this interpretation is consistent with the national emissions inventory, which indicates that relevant Hg contributions may arise from diffuse or regional sources rather than point discharges within the lagoon basin (Cárcamo, 2018). Importantly, Uruguay does not rely on coal-fired power generation, but Hg releases to air have been associated with industrial activities where Hg is present as an impurity or emitted

during high-temperature processes, including cement production and pulp and paper manufacturing, as well as oil refining and biomass combustion. The same inventory also identifies the chlor-alkali industry historically using mercury-cell technology as a major national source of Hg releases, with Efice highlighted as the main contributor in Uruguay for the period assessed (Cárcamo, 2018). Such emissions are relevant because they can enter the atmospheric pool and contribute to regional deposition even in the absence of direct local sources.

Additionally, nationally recognized Hg sources include products with intentional mercury use (e.g., switches/relays, thermometers, lamps, batteries, catalysts, and some pharmaceuticals) and dental amalgams; inadequate end-of-life management can promote releases to air and water, further supporting a diffuse-input framework (Cárcamo, 2018). This broader national context aligns with Uruguay's implementation pathway under the Minamata Convention (Law No. 19,267 Approving the Minamata Convention on Mercury, 2014) and associated national initiatives aimed at reducing releases from mercury-containing products and wastes. Together, these considerations reinforce the relevance of interpreting Hg in Nutrias Lagoon primarily in terms of atmospheric deposition and diffuse regional pressures rather than local point-source contamination.

The organohalogen compounds exhibited a different pattern. PCBs were detected only occasionally, and PCB 52 was the sole congener consistently found in quantifiable amounts. This result is significant for two reasons. First, it indicates that Nutrias Lagoon is exposed to very low overall concentrations of PCBs, which is expected in the absence of direct local sources. Second, the discrete detection of PCB 52 at particular depths, mostly corresponding to the late 20th and early 21st centuries, aligns with the known period of widespread PCB use, production bans, and subsequent global redistribution.

PCB 52 is recognized for its relatively high volatility and capacity for long-range atmospheric transport, which likely explains its sporadic detection in sediments of such a low-impact environment. Compared to higher chlorinated congeners, PCB 52 shows a greater tendency to partition into the gas phase, enhancing its capacity for long-range transport and deposition in remote environments with limited local sources. Indeed, several studies have reported that lower chlorinated PCB congeners, including PCB 52, can be relatively enriched in sediments or air samples from areas impacted primarily by diffuse, atmospheric inputs rather than direct local emissions, supporting the plausibility of this pattern in Nutrias Lagoon (National Research Council, 2001).

The temporal ranges where PCB 52 appears are also consistent with historical records, since PCBs, discovered in 1865 and first synthesized in 1881, began to be commercialized as mixtures for dielectric oils (Aroclor) in 1930 (Lammel & Stemmler, 2012; Ruiz-Fernández et al., 2012). In Uruguay, the dielectric oils most widely used were Aroclors 1242, 1254, and 1260 (Geymonat et al., 2017), in which the predominant tetrachlorinated congener is PCB 52 (Faroon & Olson, 2000). Although concentrations in the sediment were low and well below sediment quality thresholds, the presence of PCB 52 demonstrates the pervasive nature of these legacy contaminants, capable of reaching even remote or protected systems through atmospheric pathways.

Although PBDEs were not detected in the Nutrias Lagoon sediment core, this result is consistent with the limited documented use and environmental presence of PBDEs in Uruguay and the broader Latin American context. These compounds have been detected in environmental media globally, including air, dust, sediments, and biota, often reflecting historical use and global transport pathways (La Guardia et al., 2024; Rauert et al., 2018; Usenko et al., 2007). However, country-specific data for Uruguay are scarce, and existing monitoring efforts under international programs such as the UNEP/WHO Global Monitoring Plan indicate generally low

PBDE burdens in human and environmental samples in the region relative to industrialized countries (Schächtele et al., 2023). The absence of quantifiable PBDEs in Nutrias Lagoon sediments may therefore reflect a combination of limited PBDE-containing product use, effective regulatory controls under international conventions, and predominant incorporation of PBDEs into products with low emission potential in rural or low-impact settings. This interpretation aligns with findings from other low-impact environments where PBDEs occur at very low levels or below detection limits due to diffuse atmospheric inputs and long-range transport rather than local sources.

The integration of PCB and Hg data with previously reported PAH concentrations for the same core (Azcune et al., 2024) provides a more complete perspective on the contaminant history of Nutrias Lagoon. PAHs were consistently detected, reflecting their ubiquity and multiple atmospheric sources, including fossil fuel combustion, biomass burning, and industrial activities. Light PAHs, particularly naphthalene, were more abundant in surface sediments, indicating ongoing inputs from regional atmospheric deposition, potentially associated with construction activities linked to the Garzón Lagoon bridge, located approximately 30 km away, and related roadworks (Bremermann, 2018). By contrast, heavier compounds, such as dibenzo[a,l]pyrene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene, appear at the bottom of the core, possibly indicating smoke, associated to wildfires, supporting the hypothesis of a dry period linked to the final pulse of the Little Ice Age as discussed in Azcune et al. (2024). Notably, individual compounds exceeded international sediment quality guidelines in certain intervals: naphthalene concentrations surpassed the TEL of 34.1 μg kg^{-1} (CCME, 1999), while indeno[1,2,3-cd]pyrene exceeded the LEL of 200 μg kg^{-1} (Buchman, 2008). These exceedances indicate the potential for localized ecological risks, particularly to benthic organisms, despite the general perception of Nutrias Lagoon as a low-impact system.

The temporal coincidence between maximum ΣPAHs, sporadic detection of PCB 52, and the highest Hg concentrations within this core —though still low in absolute terms— is particularly relevant. These overlapping signals during the late 20th and early 21st centuries suggest periods of enhanced contaminant influx that may reflect broader regional or global emission events. For example, increased fossil fuel combustion, urban growth, or even biomass burning associated with land-use change could all contribute to synchronous increases in different contaminant groups. Although the concentrations observed in Nutrias Lagoon are substantially lower than those reported in heavily industrialized or urban-impacted lakes, their presence demonstrates the susceptibility of small, protected lagoons to global atmospheric processes.

When compared systematically against international guideline values, most contaminants in Nutrias Lagoon sediments remained below thresholds of concern. This is consistent with the lagoon's protected status and the limited local anthropogenic pressure in its basin. However, the repeated exceedances of PAH guideline values underscore that ecological risks cannot be entirely excluded, particularly when considering additive or synergistic effects among different contaminants. It is well known that mixtures of PAHs, PCBs, and metals can exert cumulative effects on benthic fauna, even when individual compounds are below guideline thresholds. Moreover, sediment quality guidelines, while useful for risk screening, are inherently conservative and may not fully capture the complexity of ecological responses.

From a management and conservation perspective, these findings reinforce the importance of monitoring programs that include protected or remote ecosystems. While such systems may not face immediate local threats, their sediments provide essential baselines against which to evaluate regional and global

contamination trends. The presence of guideline exceedances for PAHs in Nutrias Lagoon, coupled with sporadic PCB 52 detection and persistent Hg deposition, highlights the need to account for diffuse inputs in environmental assessments. Moreover, under scenarios of global change, with potential alterations in atmospheric circulation, climate, and land-use patterns, the vulnerability of small coastal lagoons to contamination may increase. Thus, Nutrias Lagoon serves not only as a reference system for Uruguay but also as a sentinel site for understanding the broader dynamics of contaminant transport and deposition in the South Atlantic region.

Conclusions

The sedimentary record of Nutrias Lagoon provides concrete evidence of the historical behavior of persistent and semivolatile contaminants in a low-impact coastal ecosystem of southeastern Uruguay. The sporadic detection of PCB 52, the absence of PBDEs throughout the core, the slight enrichment of mercury during the mid-20th century, and the increase in light PAHs in recent sediments together indicate that contaminant inputs to this system have been low in magnitude and primarily driven by regional to long-range atmospheric deposition rather than by local sources. These patterns are consistent with the protected status of the lagoon and with the absence of direct anthropogenic pressures in its catchment.

The occurrence of PCB 52 as the only PCB congener detected in quantifiable amounts supports the interpretation of diffuse atmospheric inputs, in line with its physicochemical properties and historical patterns of use in Uruguay and the region. Similarly, mercury concentrations remained consistently below international sediment quality guidelines, reinforcing the notion that atmospheric wet deposition represents the dominant pathway for Hg input in this coastal lagoon. In contrast, the non-detection of PBDEs suggests limited atmospheric influence of these compounds in southeastern Uruguay during the period represented by the sediment record.

The integration of PCB, Hg, and PAH data for the same sediment core allows identification of periods of enhanced contaminant influx, particularly during the late 20th and early 21st centuries, when maximum ΣPAHs, sporadic PCB 52 detection, and higher Hg concentrations coincide. Although concentrations remained generally low, exceedances of sediment quality guidelines for specific PAHs indicate that ecologically relevant thresholds can be reached even in systems considered relatively pristine, highlighting the sensitivity of small coastal lagoons to cumulative atmospheric inputs.

From a regional perspective, this study provides one of the few paleoenvironmental reconstructions of organic contaminants and mercury in coastal lentic systems of Uruguay, contributing baseline information for southeastern South America. These results demonstrate the value of protected lagoons as reference systems for assessing background contamination levels, validating the role of atmospheric transport in shaping sedimentary contaminant records, and supporting future comparative studies aimed at evaluating spatial variability and cumulative impacts across the region.

Declarations

All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors.

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Author Contribution

G. Azcune was responsible for the overall conceptualization of the study, conducted the investigation, performed data analysis, and wrote the original draft of the manuscript.C. M. Alonso-Hernández contributed to mercury analysis and provided access to analytical resources.N. Gerez contributed to the development and implementation of gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) methodologies and participated in analytical work.H. Heinzen contributed to GC–MS/MS methodological development and provided access to analytical resources.L. Fornaro contributed to the conceptualization of the study, supervised the research, participated in manuscript review and editing, and provided access to resources.A. Pérez Parada contributed to the conceptualization of the study, supervised the research, participated in manuscript review and editing, and provided access to resources.

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Data Availability

The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

References

1. Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. J. (2003). Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and “Dispersive Solid-Phase Extraction” for the Determination of Pesticide Residues in Produce. *Journal of AOAC International*, *86*(2), 412–431. https://doi.org/10.2478/s11687-011-0011-9
2. Anastassiades, M., Scherbaum, E., Taşdelen, B., & Štajnbaher, D. (2007). Recent Developments in QuEChERS Methodology for Pesticide Multiresidue Analysis. In *Pesticide Chemistry* (pp. 439–458). Wiley. https://doi.org/10.1002/9783527611249.ch46

3. Anual, Z. F., Maher, W., Krikowa, F., Hakim, L., Ahmad, N. I., & Foster, S. (2018). Mercury and risk assessment from consumption of crustaceans, cephalopods and fish from West Peninsular Malaysia. *Microchemical Journal*, *140*, 214–221. https://doi.org/10.1016/j.microc.2018.04.024
4. Appleby, P. G., & Oldfield, F. (1978). The calculation of lead-210 dates assuming a constant rate of supply of unsupported 210Pb to the sediment. *CATENA*, *5*(1), 1–8. https://doi.org/10.1016/S0341-8162(78)80002-2
5. Aquino-López, M. A., Blaauw, M., Christen, J. A., & Sanderson, N. K. (2018). Bayesian Analysis of 210 Pb Dating. *Journal of Agricultural, Biological, and Environmental Statistics*, *23*(3), 317–333. https://doi.org/10.1007/s13253-018-0328-7
6. Aquino-López, M. A., Ruiz-Fernández, A. C., Blaauw, M., & Sanchez-Cabeza, J.-A. (2020). Comparing classical and Bayesian 210Pb dating models in human-impacted aquatic environments. *Quaternary Geochronology*, *60*(November 2019), 101106. https://doi.org/10.1016/j.quageo.2020.101106
7. Arocena, R. (Ed.). (2016). *Principios y métodos de limnología : ejemplos de Uruguay* (2nd ed.). DIRAC – Facultad de Ciencias.
8. Azcune, G., Griffero, L., Pareja, L., Ríos, J. M., Galbán-Malagón, C., & Pérez-Parada, A. (2022). Trends in the monitoring of legacy and emerging organic pollutants in protected areas. *Trends in Environmental Analytical Chemistry*. https://doi.org/10.1016/j.teac.2022.e00165
9. Azcune, G., Puerto, L. del, Blasi, A., Castiñeira, C., Pérez, L., Inda, H., Parada, A. P., & Fornaro, L. (2024). Paleoenvironmental characterization and historical trends of polycyclic aromatic hydrocarbons (PAHs) of Nutrias Lagoon, Uruguay. *Chemosphere*, *53*, 143617. https://doi.org/10.1016/j.chemosphere.2024.143617
10. Birch, G. F. (2011). Indicators of Anthropogenic Change and Biological Risk in Coastal Aquatic Environments. In E. Wolanski & D. McLusky (Eds.), *reatise on estuarine and coastal sciencie, Vol 4: Geochemistry of estuaries and coasts* (pp. 235–270). Elsevier Academic Press Inc.
11. Bolaños-Alvarez, Y., Ruiz-Fernández, A. C., Sanchez-Cabeza, J.-A., Asencio, M. D., Espinosa, L. F., Parra, J. P., Garay, J., Delanoy, R., Solares, N., Montenegro, K., Peña, A., López, F., Castillo-Navarro, A. C., Batista, M. G., Quejido-Cabezas, A., Metian, M., Pérez-Bernal, L. H., & Alonso-Hernández, C. M. (2024). Regional assessment of the historical trends of mercury in sediment cores from Wider Caribbean coastal environments. *Science of The Total Environment*, *920*(December 2023), 170609. https://doi.org/10.1016/j.scitotenv.2024.170609
12. Bremermann, E. (2018). *Cómo cambió la vida alrededor del puente Garzón tras su construcción*. El Observador. https://www.elobservador.com.uy/nota/como-cambio-la-vida-alrededor-del-puente-garzon-tras-su-construccion-201816500
13. Buchman, M. F. (2008). *Screening Quick Reference Tables (SQuiRTs)*. https://repository.library.noaa.gov/view/noaa/9327
14. Campos, M. D. R., Gonçalves, P. B., & Bizon, L. (2022). Mercury variation over the last century in dated sediment cores across Brazil: a systematic review of literature. *Environmental Forensics*, *0*(0), 1–11. https://doi.org/10.1080/15275922.2022.2047837
15. Cárcamo, M. I. (2018). *Informe sobre la situación del mercurio en Uruguay*. http://www.rapaluruguay.org/agrotoxicos/COPs/Informe_sobre_la_situacion_del_mercurio_en_Uruguay.pdf
16. CCME. (1999). Canadian Sediment Quality Guidelines for the Protection of Aquatic Life - Polycyclic Aromatic Hydrocarbons. *Canadian Council of Ministers of the Environment*, 1–16. http://ceqg-

rcqe.ccme.ca/download/en/243

17. Cooke, C. A., Martínez-Cortizas, A., Bindler, R., & Sexauer Gustin, M. (2020). Environmental archives of atmospheric Hg deposition – A review. *Science of the Total Environment*, *709*, 134800. https://doi.org/10.1016/j.scitotenv.2019.134800
18. de Álava, D., Piñeiro, G., & Panario, D. (2013). *Sistema de toma de decisión para apertura artificial de la barra de la Laguna de Rocha. Contribución desde la geomorfología costera. Informe final grupo – GEO*. 30. https://doi.org/10.13140/RG.2.2.19947.13606
19. European Commission. (2021). *Analytical quality control and method validation procedures for pesticides residues analysis in food and feed. SANTE 11312/2021 v2. Implemented by 01/01/2024* (pp. 1–55).
20. Faroon, O., & Olson, J. (2000). *Toxicological Profile for Polychlorinated Biphenyls (PCBs)*. U.S. Department of Health & Human Services. https://www.ncbi.nlm.nih.gov/books/NBK587429/
21. Geymonat, E., Mangarelli, A., & Barboza, N. (2017). 8085UY - Determinación de bifenilos policlorados (PCB) en muestras de aceites dieléctricos. In *Manual de procedimientos analíticos para muestras ambientales* (p. 7).
22. Green, C. S., Morris, J. M., Magnuson, J. T., Leads, R. R., Lay, C. R., Gielazyn, M., Rosman, L., Schlenk, D., & Roberts, A. P. (2025). Exposure to the Polychlorinated biphenyl mixture Aroclor 1254 elicits neurological and cardiac developmental effects in early life stage zebrafish (Danio rerio). *Chemosphere*, *371*(October 2024), 144023. https://doi.org/10.1016/j.chemosphere.2024.144023
23. Gros, M., Zilkey, D. R., Griffiths, K. T., Pham, J., MacKeigan, P. W., Taranu, Z. E., Aulard, C., Baud, A., Garner, R. E., Ghanbari, H., Lachapelle, M., Monchamp, M.-È., Paquette, C., Antoniades, D., Francus, P., Smol, J. P., & Gregory-Eaves, I. (2023). Long-term environmental changes in the Canadian boreal zone: Synthesizing temporal trends from lake sediment archives to inform future sustainability. *Environmental Reviews*, *31*(3), 509–526. https://doi.org/10.1139/er-2023-0006
24. Hung, H., MacLeod, M., Guardans, R., Scheringer, M., Barra, R., Harner, T., & Zhang, G. (2013). Toward the next generation of air quality monitoring: Persistent organic pollutants. *Atmospheric Environment*, *80*, 591–598. https://doi.org/10.1016/j.atmosenv.2013.05.067
25. Kruk, C., RodrÍguez-Gallego, L., Meerhoff, M., Quintans, F., Lacerot, G., Mazzeo, N., Scasso, F., Paggi, J. C., Peeters, E. T. H. M., & Marten, S. (2009). Determinants of biodiversity in subtropical shallow lakes (Atlantic coast, Uruguay). *Freshwater Biology*, *54*(12), 2628–2641. https://doi.org/10.1111/j.1365-2427.2009.02274.x
26. La Guardia, M. J., Mainor, T. M., Luellen, D. R., Harvey, E., & Hale, R. C. (2024). Twenty years later: PBDEs in fish from U.S. sites with historically extreme contamination. *Chemosphere*, *351*(August 2023), 141126. https://doi.org/10.1016/j.chemosphere.2024.141126
27. Lammel, G., & Stemmler, I. (2012). Fractionation and current time trends of PCB congeners: Evolvement of distributions 1950-2010 studied using a global atmosphere-ocean general circulation model. *Atmospheric Chemistry and Physics*, *12*(15), 7199–7213. https://doi.org/10.5194/acp-12-7199-2012
28. Law No. 19,267 Approving the Minamata Convention on Mercury (2014). https://www.impo.com.uy/bases/leyes/19267-2014
29. Long, E. R., & MacDonald, D. D. (1998). Recommended Uses of Empirically Derived, Sediment Quality Guidelines for Marine and Estuarine Ecosystems. *Human and Ecological Risk Assessment: An International*

Journal, *4*(5), 1019–1039. https://doi.org/10.1080/10807039891284956

30. Ministerio de Vivienda Ordenamiento Territorial y Medio Ambiente. (2010). *Decreto 61/010 - Aprobación de la selección y delimitación del área natural protegida "Laguna de Rocha."* https://www.impo.com.uy/bases/decretos/61-2010
31. Muir, D. C. G., & de Wit, C. A. (2010). Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations. *Science of the Total Environment*, *408*(15), 3044–3051. https://doi.org/10.1016/j.scitotenv.2009.11.032
32. National Research Council. (2001). PCBs in the Environment. In *A Risk-Management Strategy for PCB-Contaminated Sediments*. National Academies Press. https://doi.org/10.17226/10041
33. Nipen, M., Vogt, R. D., Bohlin-Nizzetto, P., Borgå, K., Mwakalapa, E. B., Borgen, A. R., Schlabach, M., Christensen, G., Mmochi, A. J., & Breivik, K. (2022). Increasing Trends of Legacy and Emerging Organic Contaminants in a Dated Sediment Core From East-Africa. *Frontiers in Environmental Science*, *9*(January), 1–13. https://doi.org/10.3389/fenvs.2021.805544
34. Okuthe, G. E., Dube, E., & Mafunda, P. S. (2025). Effects of Pharmaceuticals and Endocrine-Disrupting Chemicals on Reproductive Biology of Aquatic Fauna: Penguins as Sentinel Species. *Journal of Xenobiotics*, *15*(4), 110. https://doi.org/10.3390/jox15040110
35. Oregel-Zamudio, E., Alvarez-Bernal, D., Franco-Hernandez, M. O., Buelna-Osben, H. R., & Mora, M. (2021). Bioaccumulation of PCBs and PBDEs in Fish from a Tropical Lake Chapala, Mexico. *Toxics*, *9*(10), 241. https://doi.org/10.3390/toxics9100241
36. Pareja, L., Pérez-Parada, A., Azcune, G., Muela, A., & Colazzo, M. (2022). Determination of multiclass emerging contaminants using QuEChERS method. In *Emerging Contaminants in the Environment* (pp. 335–380). Elsevier. https://doi.org/10.1016/B978-0-323-85160-2.00003-2
37. Rauert, C., Schuster, J. K., Eng, A., & Harner, T. (2018). Global Atmospheric Concentrations of Brominated and Chlorinated Flame Retardants and Organophosphate Esters. *Environmental Science and Technology*, *52*(5), 2777–2789. https://doi.org/10.1021/acs.est.7b06239
38. Ruiz-Fernández, A. C., Sprovieri, M., Piazza, R., Frignani, M., Sanchez-Cabeza, J. A., Feo, M. L., Bellucci, L. G., Vecchiato, M., Pérez-Bernal, L. H., & Páez-Osuna, F. (2012). 210Pb-derived history of PAH and PCB accumulation in sediments of a tropical inner lagoon (Las Matas, Gulf of Mexico) near a major oil refinery. *Geochimica et Cosmochimica Acta*, *82*, 136–153. https://doi.org/10.1016/j.gca.2011.02.041
39. Sanchez-Cabeza, J.-A., Díaz-Asencio, M., & Ruiz-Fernández, A. C. (2012). Radiocronología de Sedimentos Costeros Utilizando 210Pb: Modelos, Validación y Aplicaciones. In J.-A. Sanchez-Cabeza, M. Díaz-Asencio, & A. C. Ruiz-Fernández (Eds.), *Organismo Internacional de Energía Atómica, Centro Internacional de Viena*. International Atomic Energy Agency.
40. Schächtele, A., Malisch, R., Hardebusch, B., van Leeuwen, F. X. R., Moy, G., Tritscher, A., van Duursen, M., van den Berg, M., Šebková, K., Klánová, J., & Kalina, J. (2023). WHO- and UNEP-Coordinated Exposure Studies 2000–2019: Findings of Polybrominated Substances (PBDE, HBCDD, PBB 153, PBDD/PBDF). In *Persistent Organic Pollutants in Human Milk* (pp. 299–342). Springer International Publishing. https://doi.org/10.1007/978-3-031-34087-1_9
41. Smol, J. P. (2008). Pollution of lakes and rivers: a paleoenvironmental perspective. In *Library*. Blackwell Pub. https://books.google.com.uy/books?id=A2rxAAAAMAAJ

42. Smol, J. P. (2019). Under the radar: long-term perspectives on ecological changes in lakes. *Proceedings of the Royal Society B: Biological Sciences*, *286*(1906), 20190834. https://doi.org/10.1098/rspb.2019.0834
43. UN Environment. (2019). *Global Mercury Assessment 2018*. UN Environment Programme, Chemicals and Health Branch Geneva. http://www.unep.org/gc/gc22/Document/UNEP-GC22-INF3.pdf
44. United Nations Environment Programme. (2013). *Global Mercury Assessment: Sources, emissions, releases, and environmental transport* (p. 44). UNEP Chemicals Branch. https://wedocs.unep.org/20.500.11822/7984
45. Usenko, S., Landers, D. H., Appleby, P. G., & Simonich, S. L. (2007). Current and Historical Deposition of PBDEs, Pesticides, PCBs, and PAHs to Rocky Mountain National Park. *Environmental Science & Technology*, *41*(21), 7235–7241. https://doi.org/10.1021/es0710003

Figures

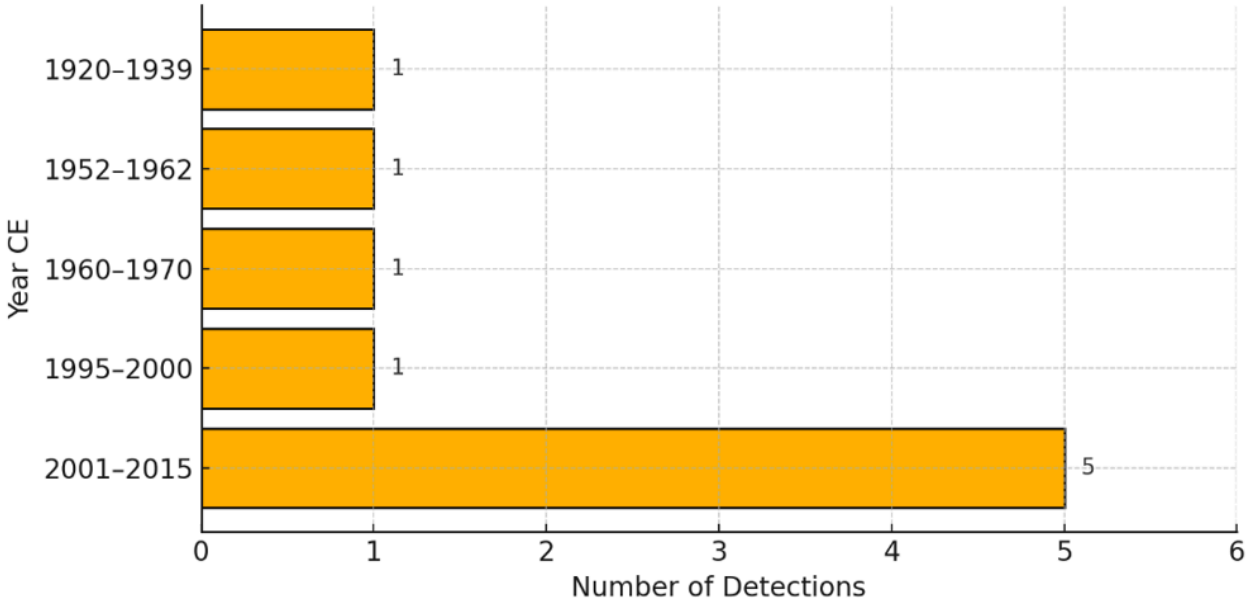


Figure 1

Detections of PCB 52 across different time ranges

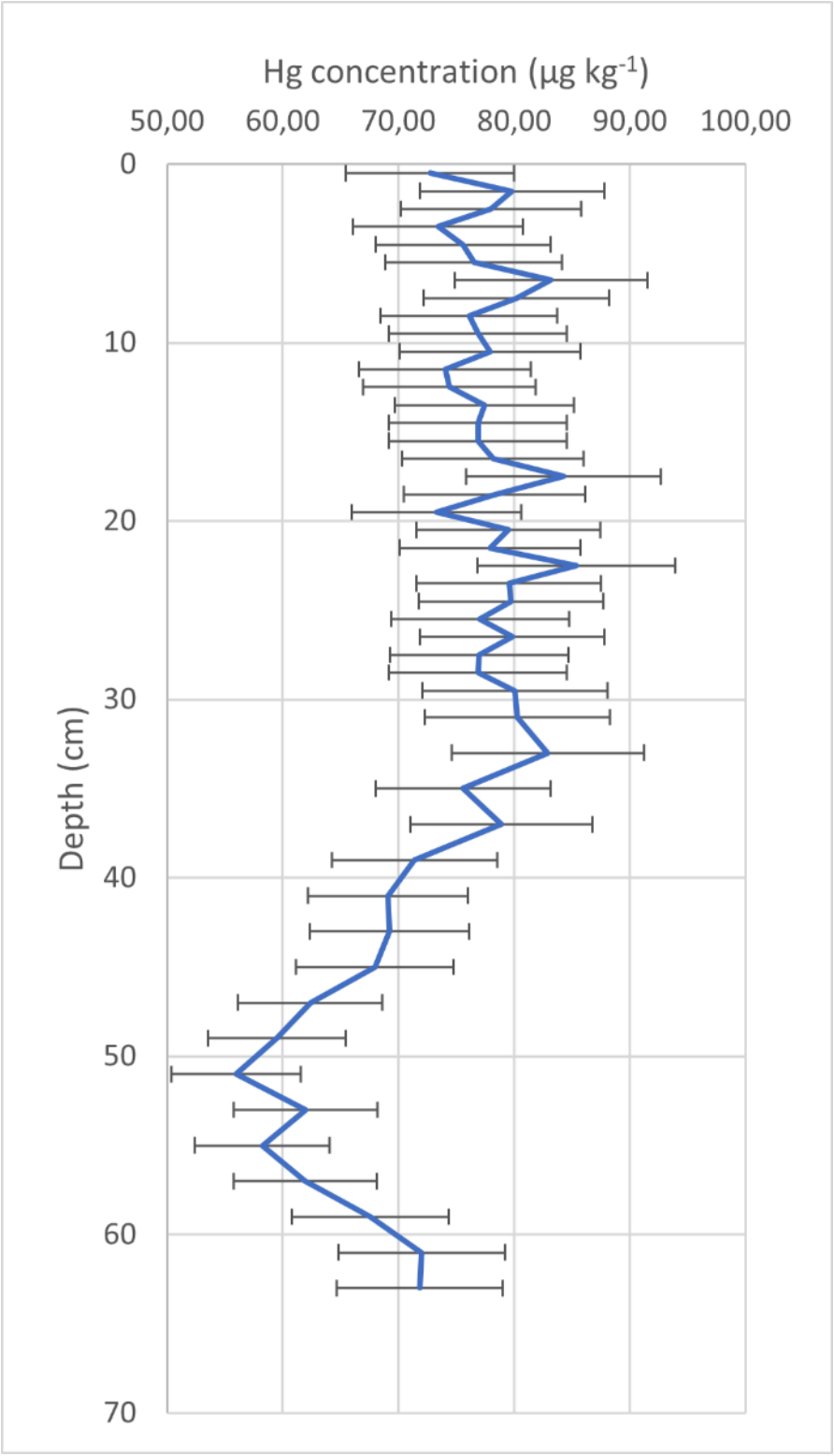


Figure 2

Total mercury concentration profile