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Occurrence of current-use pesticides in sediment cores from lakes and peatlands in pristine mountain areas of Brazilian national parks☆

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ABSTRACT

This study assessed the occurrence of current-use pesticides in sediment cores from six lakes and peatlands in high-altitude (1952–2374 m) pristine areas within two southeastern Brazilian National Parks: Itatiaia National Park (IT-NP) and Serra dos Órgãos National Park (SO-NP). We sampled three sediment cores from lakes at IT-NP and three from peatlands at SO-NP, totaling 60 subsamples. Among the 38 current-use pesticides assessed, 17 were found in at least one sample, with 14 - including herbicides, insecticides, fungicides, and acaricides - identified in both parks. The most frequently detected pesticides were carbendazim and carbaryl (75–95%), followed by acetochlor, chlorpyrifos, diuron, metolachlor and tebuconazole (40–70%) and, to a lesser extent, terbuthylazine and malathion (10–30%). The organophosphates disulfoton (6.83 ± 20.18 ng g^{-1} dry weight) and chlorpyrifos (4.34 ± 6.81 ng g^{-1} dw) registered the highest concentrations across all compounds in the sediment layers, with chlorpyrifos showing the greatest relative abundance (65.9–92.8%) in four out of six sites. Risk characterization results revealed highest risk quotient (RQ) values (416–14,589) for chlorpyrifos, indicating potential ecological risks. High RQs were also obtained for acetochlor (5.76–94.6), carbaryl (0.4–4.08), carbendazim (0.09–3.46), diazinon (2048), disulfoton (34–569), diuron (1.45–35.0) and malathion (10.94). These results highlight the threat posed by long-range pesticide transport to pristine areas at National Parks. Urgent regulatory measures are needed to mitigate their impact and safeguard these ecosystems from degradation.

1. Introduction

The global consumption of pesticides has been increasing annually from 1990 to 2021, reaching over 3.5 million tons of pesticides sold in 2021 alone (FAO, 2023). Analyzing the ranking of countries with the highest pesticide usage, Brazil has been standing out as the top-consumer since 2011. In 2021, its consumption exceeded 700,000 tons, surpassing the 2nd place (United States) by 262,000 tons (FAO, 2023).

A major concern regarding the environmental behavior of pesticides, whether banned by national or international regulations or still in use, is their environmental persistence and tendency to spread beyond the areas of application over time. For instance, most pesticides can volatilize and enter the atmospheric circulation, being often mobilized from application sites to high-altitude and colder regions, where their precipitation through dry or wet deposition is favored (Daly & Wania, 2005; Gao et al., 2019).

Studies in mountainous regions suggest that colder temperatures enhance precipitation, promoting the deposition of pesticides over high altitudes (Daly & Wania, 2005). Moreover, mountains are often geographically closer to emission sources of these compounds than colder regions like those in extreme latitudes. Consequently,

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mountainous areas can serve as convergence zones for the dynamics of volatile and semi-volatile pesticides (Daly et al., 2007; Daly & Wania, 2005; Machate et al., 2022). In this context, several studies have reported the occurrence of pesticides in high-altitude areas across various regions in the northern and southern hemispheres. Studies have detected pesticides in various environmental matrices, including air (García-Solorio et al., 2022; Guida et al., 2018; Meire et al., 2012), water (Battaglin et al., 2018; Machate et al., 2022; Meire et al., 2016; Mtashobya, 2021; Rizzi et al., 2022), soil (Mtashobya, 2021), and sediment (Barrera H. et al., 2019; Battaglin et al., 2018; García-Solorio et al., 2022; Mtashobya, 2021).

Mountains account for over 30% of the Earth's surface, host approximately 23% of the world's forests, and are renowned for their exceptional biodiversity (UNESCO/UNEP, 2023). Of the 34 biodiversity hotspots identified globally, 25 are located entirely or partially in mountainous regions (UNESCO/UNEP, 2023). Additionally, the diverse habitats in these areas provide refuge for several amphibian, bird, and mammal species, including those of endemic occurrence (Zhang and Wang, 2023). In this context, pesticides and chemical mixtures can pose threats to the fauna and flora of these environments, by inducing acute or chronic toxicity in organisms and triggering cascading effects that can disrupt the entire mountainous ecosystem (Daly & Wania, 2005; Machate et al., 2022).

Recent studies have demonstrated the accumulation of pesticides in the tissues of fish (Battaglin et al., 2018) and frogs (Battaglin et al., 2018; Smalling et al., 2013; Sparling & Fellers, 2009) from alpine lakes. Research in these regions has also revealed declining air concentration trends of banned pesticides, such as chlordane (Shunthirasingham et al., 2011) and endosulfan (Meire et al., 2012; Van Drooge et al., 2014). In contrast, current-use pesticides in Brazil (CUPs) such as atrazine, metolachlor (Battaglin et al., 2018), chlorpyrifos (Guida et al., 2018), diazinon, and permethrin (Machate et al., 2022) have shown increasing concentrations in certain regions.

Although CUPs typically have shorter half-lives (ranging from days to months) compared to banned compounds such as dichloro-diphenyl-trichloroethane - DDT, lindane, dieldrin, chlordane, their continuous application results in a pseudo-persistent environmental presence. Furthermore, CUPs, often used as substitutes for pesticides banned or restricted under international agreements like the Stockholm Convention, can still be transported over long distances via atmospheric currents, ocean circulation, and migratory species, facilitating their global distribution (Gao et al., 2019; Machate et al., 2022).

Therefore, we aimed to investigate the occurrence of CUPs in sediment cores from lakes and peatlands at two protected mountain areas in southeastern Brazil: Serra dos Órgãos National Park and Itatiaia National Park. Furthermore, we aimed to assess potential ecotoxicological risks arising from the CUP concentrations found in the sediment cores to shed light on the challenges for biodiversity conservation due to the long-range transport of pesticides into protected high-altitude grassland fields.

2. Material and methods

2.1. Study area and sampling

The Itatiaia National Park (IT-NP) is a conservation unit located in the Atlantic Forest biome, which covers the municipalities of Resende and Itatiaia (Rio de Janeiro state), as well as Bocaina de Minas and Itamonte (Minas Gerais state), in southeastern Brazil (ICMBIO, 2024b). The IT-NP covers 40,029 ha within the Serra do Mar Ecological Corridor, which is in turn part of the Atlantic Forest Biosphere Reserve, an area of extremely high priority for biodiversity conservation. Its altitude ranges from 600 to 2791 m above sea level (m.a.s.l.) and it hosts typical Atlantic Forest vegetation, comprising dense montane ombrophilous forests (*floresta ombrófila densa montana*), dense ombrophilous high-montane forests (*floresta ombrófila densa altomontana*) and high-altitude grasslands (*campos de altitude*). The area has a humid climate with temperatures ranging from 15 °C to 18 °C during the winter season (June to August). However, at the highest summit landscapes (high--montane forest and high-altitude grasslands), average annual temperatures vary around 14 °C, and frost occurrence is relatively common (ICMBIO, 2013, 2024b).

The Serra dos Órgãos National Park (SO-NP) is a conservation unit also located in Rio de Janeiro state (RJ), covering 20,024 ha of Atlantic Rainforest and ranging from 200 to 2263 m.a.s.l. The SO-NP has high ecological importance, serving as a central corridor across the Serra do Mar and containing one of the largest remnants of Atlantic Forest. Its altitudinal variation contributes to a wide diversity of habitats and species richness (ICMBIO, 2008, 2024a). The climate corresponds to a highland tropical climate, characterized by short dry seasons and annual average temperatures ranging from 13 °C to 23 °C. However, at altitudes above 800 m.a.s.l., temperatures usually do not exceed 19 °C (ICMBIO, 2008; 2024a).

At each National Park, three sediment cores were collected from shallow lakes and peatlands along high-altitude gradients between 1952 and 2374 m.a.s.l. During the sampling campaign (August 2017), 7.0 cm diameter acrylic cores were used, and each sediment core was further divided into 10 transverse sections 1.0 cm each, from the top, resulting in a total of 60 subsamples kept in pre-cleaned aluminium foil and sealed in ziplock plastic bags. In IT-NP, sampling was carried in a peatland and two shallow lakes, located in Aiuroca (IT-NP-1), Cinco Lagos (IT-NP-2), and Prateleiras (IT-NP-3), respectively (Fig. 1; Supplementary material - Table S1). In SO-NP, all samples were collected from peatlands located in Abrigo Açu (SO-NP-1), Campo das Antas (SO-NP-2), and Abrigo Rebouças (SO-NP-3) (Fig. 1; Supplementary material - Table S2). Subsamples were transported to the *Laboratório de Estudos Ambientais Olaf Malm* (Biophysics Institute, Federal University of Rio de Janeiro, Brazil), where they were freeze-dried and stored in pre-cleaned aluminium foil, sealed in ziplock plastic bags, at −20 °C.

2.2. Sample preparation and chemical analysis

All chemical analyses were performed at the Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Brno, Czech Republic, accredited according to ISO/IEC 17025. The 60 freeze-dried subsamples of the six sediment cores were sieved using a stainless steel mesh to remove particles larger than 1 mm (mainly roots and stones).

A small portion of the sieved subsamples was used to determine the total organic carbon (TOC) fraction in each sediment layer. TOC was measured using a combustion-based method using a Vario TOC Cube (Elementar, Germany). Approximately 20–60 mg of freeze-dried sieved sediment was weighed on an analytical balance and placed onto a sheet of silver (Ag) foil. Two to three drops of concentrated hydrochloric acid (HCl) were added to the sample on the foil, ensuring that the surface of the sample was thoroughly wetted. The foil containing the sample was then placed in an oven at 75 °C for 1 h to evaporate the HCl. After drying, the Ag foil was formed into a capsule and introduced into a combustion tube. During combustion, carbon dioxide (CO2) was released and detected by an infrared (IR) detector. The software associated with the IR detector automatically converted the measured CO2 concentration into the total organic carbon (TOC) content, expressed as a percentage (Supplementary material - Table S3).

A total of 38 CUPs (acetochlor, alachlor, atrazine, azinphos-methyl, carbaryl, carbendazim, diazinon, dimethachlor, dimethoate, disulfoton, diuron, fenitrothion, fenoxaprop-ethyl, fenpropimorph, florasulam, fluroxypyr, fonofos, chlorpyrifos, chlorsulfuron, chlortoluron, isoproturon, malathion, metamitron, metazachlor, metolachlor, metribuzin, methyl parathion, pendimethalin, phosmet, pirimicarb, prochloraz, propiconazole, pyrazon, simazine, tebuconazole, temephos, terbufos, and terbutylazine) were assessed in sediment samples following a method previously described (Babić et al., 1998). Approximately 3 g of

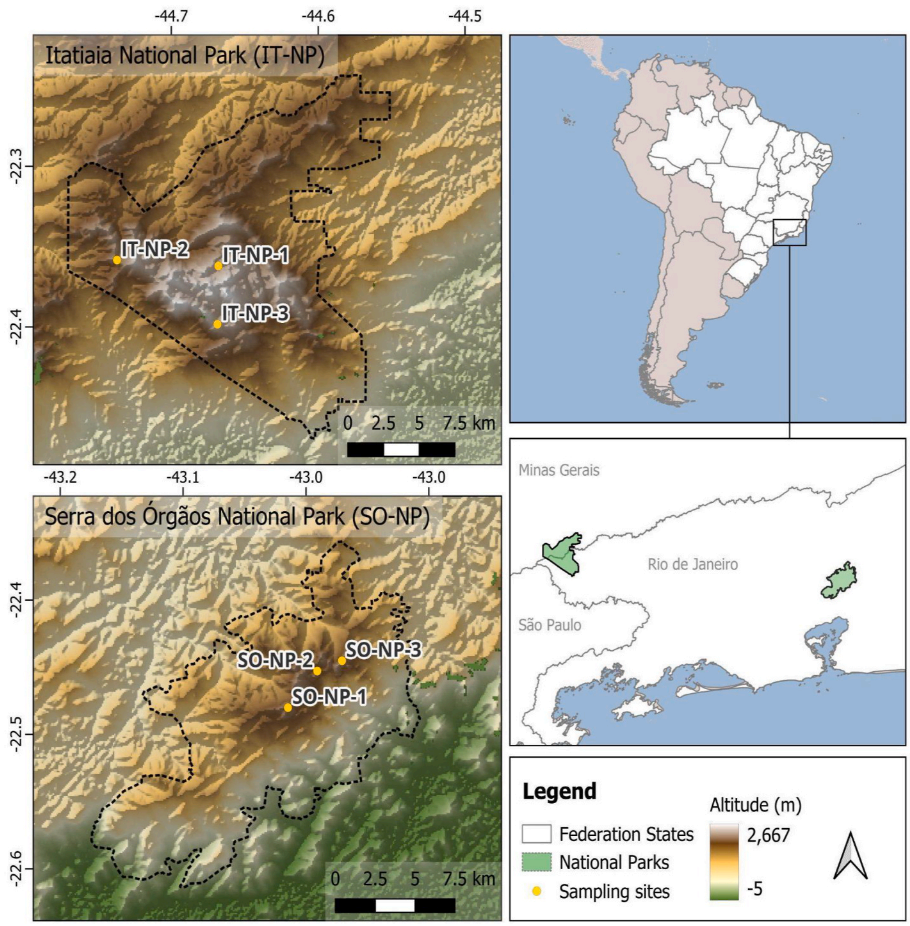

Fig. 1. Sampling points for sediment samples in the Itatiaia National Park (IT-NP) and the Serra dos Órgãos National Park (SO-NP), both located in Rio de Janeiro state, southeastern Brazil.

dried and sieved sediment samples were placed into a 15 mL centrifuge plastic tube and spiked with labelled standards covering all target CUPs investigated to quantify their contents by isotopic dilution (recovery corrected). Then, 5 mL of methanol was added in each tube. The tubes were closed and shaken intensively for about 1 min and placed under an ultrasonic bath for about 15 min. The supernatant was collected and placed in a new tube and the methanol extraction repeated two more times. Methanol extracts were manually shaken for about 1 min and filtered in a filter Whatman GF/D (47 mm diameter, No. 1823-047). Filtered extracts were placed into a 20 mL vial and evaporated to 1 mL under a gentle stream of nitrogen.

Native and labelled CUP contents were quantified as described elsewhere (Degrendele et al., 2022), using an Agilent 1290 High-Performance Liquid Chromatograph (HPLC, Agilent, USA) consisting of a vacuum degasser, a binary pump, a thermostated autosampler (10 °C) and a thermostated column compartment kept at 30 °C. The column was a Phenomenex Luna C-18 endcapped (3 μm) 100 × 2.0 mm i.d., equipped with a Phenomenex SecureGuard C18 guard column (Phenomenex, Torrance, CA, USA). The mobile phase consisted of 0.1% formic acid in water (A) and 0.1% formic acid in methanol (B). The binary pump gradient was non-linear (increase from 50% B at 0 min (after 3.5 min column equilibration) to 80% B at 3 min, then increased to 95% B at 6.5 min, and then 100% B for 1.5 min), with a flow rate of 0.25 mL min^{-1}. For the analysis, 5 μL of the individual sample-was injected. CUPswere quantified using a mass spectrometer (AB Sciex Qtrap 5500, AB Sciex, Concord, ON, Canada) with electrospray ionization (ESI+) in which ions were detected in the positive mode. The ionization parameters were as follows: capillary voltage, 5.5 kV; desolvation temperature, 400 °C; Curtain gas 15 psi, Gas1 40 psi, Gas2 30 psi. Identification of individual CUPs was based on a comparison of ion ratios and retention times with corresponding isotopically labelled standards and quantification was using internal standards (Degrendele et al., 2022).

2.3. Quality assurance and quality control

Field blanks (n = 6), consisting of granulate sodium sulfate, were open in the field and stored among the sediment subsamples in exactly the same way. Besides, one solvent blank was included into each analytical batch (n = 6). In general, most CUPs were below the detection limit or detected at low levels. The CUP concentrations reported in this study have been blank corrected by subtracting their contents measured in the respective analytical solvent blank and then by subtracting the average of the field blanks. Limits of quantification (LOQs) were determined as the maximum between the iLOQs and the average of solvent blanks plus three times their standard deviations (LOQb). All the procedural recoveries, measured by the labelled standards, were in the range of 70–120% and had a standard deviation lower than 20%, demonstrating acceptable results in regard to accuracy and precision.

2.4. Risk characterization

Considering the lack of specific datasets for ecotoxicological tests with CUPs in sediments, predicted no-effect concentrations (PNEC) on non-target sediment organisms were estimated from PNEC data for water organisms, based on the equilibrium partition method (European Commission, 2003; Parente et al., 2019; Wu et al., 2014) — as shown in Equation (1).

$$PNECsed = PNECwater \times Kd \quad \text{(Equation 1)}$$

Where: *PNECwater* was calculated based on ecotoxicological data available in the Pesticide Properties Database (PPDB - Pesticide Properties Database, 2024) referring to tests with freshwater invertebrates such as *Daphnia* sp., *Ceriodaphnia dubia* (Order: Anomopoda), *Americamysis bahia* (Order: Mysida), *Chironomus* sp. (Order: Diptera) and *Hyalella azteca* (Order: Amphipoda); as well as aquatic plants as *Lemna gibba* (Order: Alismatales), *Pseudokirchneriella subcapitata* and *Scenedesmus quadricauda* (Order: Sphaeropleales) - Table S5. The results of ecotoxicological tests must be divided by an assessment factor (AF) which considers inter-species variations: AF = 1000 for acute tests; and AF = 100 if based on chronic tests (European Commission, 2003).

The soil-water partition coefficient (*Kd* in L kg^{-1}) for each pesticide was derived from Equation (2), as previously described by Zhang et al. (2016).

$$Kd = Koc \times \left(\frac{foc}{100}\right) \quad \text{(Equation 2)}$$

Where: *Koc* (L kg^{-1}) is the organic carbon normalized octanol-water partition coefficient for each pesticide based on Comptox Chemicals Dashboard (USEPA, 2024) and *foc* (%) is the median of total organic carbon in sediment samples (20.95%), considering that no statistical difference was verified between the parks (Table S4).

Finally, according to the Technical Guidance on Environmental Risk Assessment (European Commission, 2003), the risk quotient (RQ) is estimated according to Equation (3).

$$RQ = \frac{MECsed}{PNECsed} \quad \text{(Equation 3)}$$

Where: *MECsed* is the concentration of each CUP in sediment samples (Supplementary material - Table S3). Given the amount of ecotoxicological data obtained, the inclusion criterion for the RQ calculation was the lowest value derived from the *PNECsed*, regardless of the type of assay used to determine the toxicity of the analyzed compound.

2.5. Data analysis

The limit of quantification (LOQ) for each pesticide was calculated as the mean of the analytical blanks plus three times the standard deviation. For concentrations < LOQ, values were estimated using the detection frequency in each park multiplied by the LOQ (Parente et al., 2020). All concentrations were normalized to the sediment's dry weight. Data normality was assessed using the Shapiro-Wilk test with a significance level of 5% ($p < 0.05$), which indicated data did not follow a normal distribution. Consequently, non-parametric tests were used for subsequent analyses. The Kruskal-Wallis test was applied to compare compound concentrations, while Spearman's test was used to assess the correlation between pesticides and TOC. This last analysis included only pesticides with a quantification frequency ≥50% in relation to the total samples analyzed. Statistical analyses and graph generation were performed using R software, version 4.1.2 (R Core Team, 2024).

3. Results and discussion

3.1. Pesticides in sediment samples from pristine areas

Out of the 38 targeted CUPs, 17 were quantified in at least one sediment subsample. A total of 14 CUPs were detected in both protected areas, comprising 6 herbicides, 7 insecticides, 4 fungicides, and 2 acaricides. It is important to note that some compounds can be classified into more than one category. Table 1 presents descriptive analyses for CUP concentrations measured in both protected areas, as well as their respective quantification frequencies.

Table 1
Descriptive analysis of pesticide concentrations (ng g^{-1} d.w.) in all sediment cores from Itatiaia National Park (IT-NP) and Serra dos Órgãos National Park (SO-NP) and frequency of quantification. Abbreviations = a: above the limit of quantification.

Pesticide (Samples ≥ LOQ)	Mean ± SD	Median	Min.	Max.	Frequency (>LOQ; n = 60)
Acetochlor (n = 60)	0.15 ± 0.18	0.07	0.03	0.82	66.7%
Atrazin (n = 30)	0.01 ± 0.02	0.01	0.01	0.07	8.33%
Carbaryl (n = 60)	0.46 ± 0.36	0.38	0.14	1.64	78.3%
Carbendazim (n = 60)	0.36 ± 0.43	0.21	0.02	2.44	93.3%
Chlorpyrifos (n = 60)	4.34 ± 6.81	2.72	0.01	43.66	61.7%
Chlorsulfuron (n = 20)	0.04 ± 0.07	0.01	0.01	0.26	5.00%
Diazinon (n = 10)	2.28 ± 3.10	1.30	1.30	11.10	1.67%
Disulfoton (n = 10)	6.83 ± 20.18	0.03	0.03	64.15	3.33%
Diuron (n = 60)	0.16 ± 0.19	0.08	0.06	1.21	60.0%
Malathion (n = 20)	0.04 ± 0.04	0.02	0.02	0.21	11.7%
Metolachlor (n = 60)	0.07 ± 0.011	0.01	0.00	0.43	51.7%
Pendimethalin (n = 10)	0.83 ± 1.27	0.43	0.00	4.44	1.67%
Pirimicarb (n = 10)	0.001 ± 0.002	0.00	0.00	0.01	1.67%
Prochloraz (n = 20)	0.08 ± 0.24	0.00	0.00	1.03	6.67%
Propiconazole (n = 30)	0.01 ± 0.01	0.00	0.00	0.06	5.00%
Tebuconazole (n = 60)	0.08 ± 0.01	0.04	0.01	0.52	40.0%
Terbutylazine (n = 40)	0.04 ± 0.04	0.03	0.03	0.21	23.3%

The most frequently detected CUPs (>LOQ) were carbendazim and carbaryl (75–95%); followed by acetochlor, chlorpyrifos, diuron, metolachlor, tebuconazole (40–75%); and, to a lesser extent, terbuthylazine and malathion (10–30%). Atrazine, chlorsulfuron, diazinon, disulfoton, malathion, pirimicarb, prochloraz and propiconazole were only detected below 10% of the subsamples.

In general, CUP concentrations measured across all sediment subsamples were largely dominated by chlorpyrifos, diazinon and disulfoton. Despite the high observed concentrations, the latter two compounds have revealed low quantification frequencies, considering the 60 subsamples (n = 1 and n = 2 for diazinon and disulfoton, respectively). The highest concentrations were detected for chlorpyrifos, diazinon and disulfoton (>10 ng g^{-1} dw), followed by pendimethalin, carbendazim, carbaryl, diuron, prochloraz (1–10 ng g^{-1} dw) and other target pesticides such as acetochlor and terbuconazole (0.9–0.01 ng g^{-1} dw) (Fig. 2).

Chlorpyrifos is an insecticide commonly detected in environmental samples from remote locations, ranging from mountainous areas (Ferrario et al., 2017; Guida et al., 2018; Santolaria et al., 2015) to polar regions (O'Connor et al., 2023). Indeed, previous studies have demonstrated that chlorpyrifos has the potential to be transported over distances of 200–400 km through the atmosphere before deposition or transformation occurs (Ferrario et al., 2017; Mackay et al., 2014; Muir et al., 2004). In a study conducted in Sierra Nevada, California, USA, the authors detected chlorpyrifos in all analyzed samples and estimated the annual wet deposition load at 9.4 kg in 1.6×10^9 m^2 to the Sequoia National Park (McConnell et al., 1998). Moreover, Rizzi et al. (2019) detected higher concentrations (max. 70.3 ng L^{-1}) and frequencies of chlorpyrifos compared to other target pesticides measured in alpine glaciers. On the other hand, fewer studies have identified disulfoton in pristine areas (Ding et al., 2023; Muir et al., 2007), including atmospheric air samples (max. 4.7 pg m^{-3}) and water (max. 4.9 ng L^{-1}) in the Canadian mountains.

Several CUPs have been detected in remote areas of tropical forests -

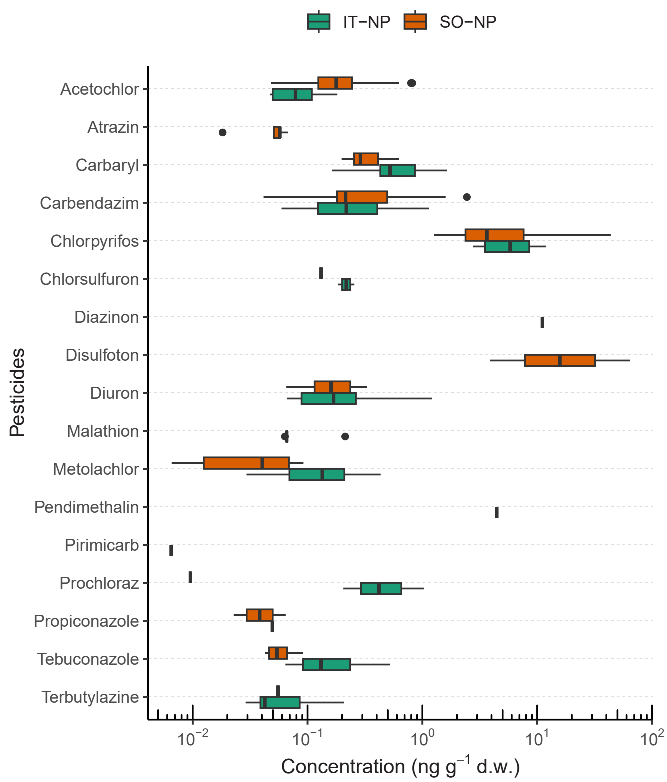

Fig. 2. Pesticide concentrations (ng g^{-1} d.w.) in sediment cores from Itatiaia National Park (IT-NP) and Serra dos Órgãos National Park (SO-NP).

e.g., carbaryl, carbendazim, metolachlor, chlorpyrifos, and pendimethalin (Guida et al., 2018; Meire et al., 2012; Shunthirasingham et al., 2011; Spirhanzlova et al., 2019), in temperate forests — *e.g.*, atrazine, chlorpyrifos, diazinon, and permethrin (Battaglin et al., 2018; Machate et al., 2022; Sparling & Fellers, 2009), and in glaciers — *e.g.*, chlorpyrifos, metolachlor, pendimethalin, and terbuthylazine (Ferrario et al., 2017; Rizzi et al., 2019). However, there are few reports on the occurrence of carbendazim, carbaryl, or diuron in remote areas. Both carbendazim and diuron have been identified in water samples collected from lakes in Kibale National Park, Uganda, and the Spanish Pyrenees, respectively (Santolaria et al., 2015; Spirhanzlova et al., 2019). In contrast, studies evaluating the presence of carbaryl in remote areas have analyzed surface water, rainfall, snow, and sediment samples. In this context, Mast et al. (2007) found in Rocky Mountain National Park and Glaciar National Park a higher frequency of carbaryl in rainfall samples (90%) compared to snow samples (8%). According to the authors, concentrations ranged from 7.9 to 95 ng L^{-1} (rainfall) and 0.82 ng L^{-1} (snow). The aforementioned studies (Battaglin et al., 2018; Rizzi et al., 2019; Santalorian et al., 2015; Spirhanzlova et al., 2019) also detected metolachlor in rainfall (ND – 6.8 ng L^{-1}), snow (ND – 1.2 ng L^{-1}), and surface water samples (<0.01–45 ng L^{-1}). Other studies have also detected metolachlor in surface water samples (<0.01–4.5 ng L^{-1}) (Machate et al., 2022; Muir et al., 2007; Usenko et al., 2005), in snow (0.07–3.1 ng L^{-1}) (Mast et al., 2007) and in atmospheric air (0.37–67.7 pg m^3) (Ding et al., 2023; Wang et al., 2018) in mountainous regions (Canada, France, and the USA) and at pristine areas (USA). In contrast, to the best of our knowledge, acetochlor, one of the most frequently detected pesticides in the present study, was only identified in water and snow samples analyzed by Mast et al. (2007) and Usenko et al. (2005).

According to Muir et al. (2007), limited precipitation and reduced concentrations of hydroxyl free radicals (OH) in the atmosphere may facilitate long-range transport of semi-volatile organic compounds (SVOCs) that would otherwise be radical-reactive and subject to wet deposition. Additionally, low temperatures in polar regions and cold lakes environments contribute to the persistence of these compounds. Usenko et al. (2007) suggest that the presence of SVOCs in remote mountains, as well as in the Arctic, indicates their capacity for atmospheric transport. However, high altitude mountains differ from the Arctic mainly because of two factors, first, they are located in the proximity to pollution sources and second, because they act as barriers to atmospheric transport. In this context mountains can influence wind and precipitation patterns, raising debates on the interference of the mountain in the cold trapping phenomena over long-range transport routes of pesticides (Vighi, 2006). In this regard, it could be argued that mountains could act as natural filters, slowing down or preventing the transport of chemicals to polar regions. On the other hand, the deposition and accumulation of pesticides in mountainous soils and sediments result in the formation of reservoirs for these pollutants in highland regions (Vighi, 2006).

3.2. *Abundance of pesticides in the national parks*

In terms of relative abundance (Fig. 3), chlorpyrifos stood out, occurring at a high relative percentage (65.8–92.8%) in 4 out of the 6 lakes/peatlands studied: Itatiaia National Park (IT-NP-2: 5.60 ± 4.33 ng g^{-1} d.w.; IT-NP-3: 5.82 ± 2.51 ng g^{-1} d.w.) and Serra dos Órgãos National Park (SO-NP-1: 2.77 ± 10.35 ng g^{-1} d.w.; SO-NP-2: 10.56 ± 11.04 ng g^{-1} d.w.). Additionally, diazinon was the most abundant compound in peatland IT-NP-1 (2.28 ± 3.10 ng g^{-1} d.w.), while disulfoton was the most abundant in peatland SO-NP-3 (6.83 ± 20.18 ng g^{-1} d.w.) (Table S5).

The occurrence of chlorpyrifos in both parks is consistent with the findings reported by Guida et al. (2018), who detected this pesticide in atmospheric samples from IT-NP and SO-NP. Additionally, Bradford et al. (2013) detected chlorpyrifos in sediment samples collected at Yosemite National Park (USA). However, the median concentration identified by the authors (0.048 ng g^{-1} d.w.) was around 90 times lower than the median found in our study, while the maximum concentration (0.78 ng g^{-1} d.w.) was about 55 times lower compared to this study. Relative abundance of diazinon (53.43%) in IT-NP-1 and disulfoton (68.29%) in SO-NP-3 also stood out. Although carbendazim had a low relative abundance, it was quantified at all sampling points, with the highest mean concentration observed in peatland SO-NP-1 (0.48 ± 0.60 ng g^{-1} d.w.). Additionally, it is noteworthy that atrazine (0.01 ± 0.01 ng g^{-1} d.w.), disulfoton (6.83 ± 20.17 ng g^{-1} d.w.) and pendimethalin (0.83 ± 1.27 ng g^{-1} d.w.) were detected exclusively in SO-NP samples. Meanwhile, diazinon (2.27 ± 3.1 ng g^{-1} d.w.), malathion (0.04 ± 0.04 ng g^{-1} d.w.), pirimicarb (0.001 ± 0.001 ng g^{-1} d.w.), and prochloraz (0.08 ± 0.24 ng g^{-1} d.w.) were identified only in sediments collected in IT-NP. The difference in pesticide occurrence between the two parks

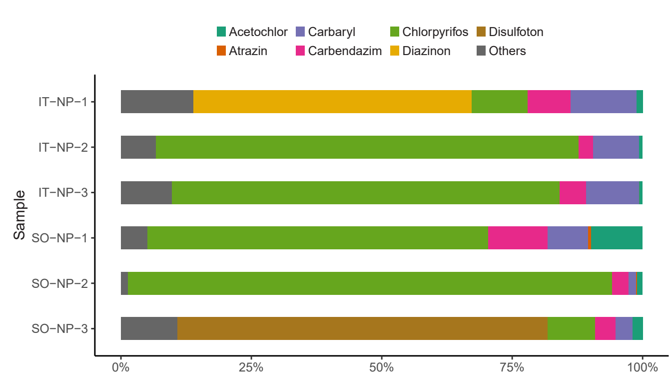

Fig. 3. Relative abundance of pesticides in each sediment core from Itatiaia National Park (IT-NP) and Serra dos Órgãos National Park (SO-NP). Others: Chlorsulfuron, Diuron, Malathion, Metolachlor, Pendimenthalin, Pirimicarb, Prochloraz, Propiconazole, Tebuconazole and Terbutylazine.

may be linked to surrounding activities. According to Guida et al. (2018), intensive agricultural activity in Rio de Janeiro's "green belt" region, near SO-NP, leads to significantly higher concentrations of most analyzed pesticides compared to those found in IT-NP.

In regard to chemical groups, the herbicides acetochlor, diuron, and metolachlor were quantified in all lakes/peatlands. Herbicides are applied to control unwanted vegetation growth, being designed to exhibit significantly higher toxicity to plants than to other organisms (EPA, 2023). Currently, herbicides are the most widely used CUPs worldwide (FAO, 2023), which is related to the development of herbicide-resistant crops, whether through traditional breeding methods or genetic modifications (GMOs). The development of a crop-resistant technology led to an increase of 239,000 tons in herbicide use in the United States between 1996 and 2011, especially due to the massive increase in the use of glyphosate (Benbrook, 2012).

Most of the pesticides quantified in the subsamples act systemically within plants. This means that once absorbed through the cuticle, these pesticides can move through the vascular tissue (phloem) to reach the site of action, which may be close to or distant from the point of application (Carvalho, 2013; Marchi, 2008). Generally, these compounds interfere with biological functions, *i.e.*, specific biochemical reactions (Au, 2003). Their mode of action is strongly associated with growth regulators, such as inhibitors of photosynthesis, pigments, lipid synthesis, cell wall synthesis, amino acid synthesis, and cell division, as well as cell membrane disruptors (Holt, 2013).

Among the most abundant pesticides found in both parks, chlorpyrifos, diazinon and disulfoton are organophosphate insecticides, while carbaryl is a carbamate. As of 2020, disulfoton, pirimicarb, and diazinon are banned in Brazil (ANVISA, 2024). Following the ban on organochlorines, organophosphate and carbamate insecticides have been widely adopted as substitutes due to their lower persistence in the environment and lower toxicity compared to organochlorines (Colović et al., 2013). Although structurally distinct, organophosphates and carbamates share a similar mechanism of action: both bind to the enzyme cholinesterase at synaptic junctions, preventing the inactivation of acetylcholine and resulting in prolonged action of this neurotransmitter in cholinergic synapses (Fukuto, 1990). The key difference between them is the reversibility of inhibition. Organophosphates are irreversible cholinesterase inhibitors, requiring the synthesis of new enzymes to restore normal function, whereas carbamates are reversible inhibitors, dissociating from the enzyme within 12–48 h (Fukuto, 1990; Sousa et al., 2009).

3.3. *Pesticide depth profiles*

Acetochlor measurements showed distinct distribution patterns for the compound between sediment cores from IT-NP and SO-NP. In the former environment, concentrations were predominantly low and punctual, with limited detection in specific points of intermediate and deep layers. This was verified with the exception of the sediment core from IT-NP-2, where acetochlor exhibited a more uniform distribution through the layers. In SO-NP, concentrations were more homogeneously distributed through the sediment cores, with the exception of SO-NP-2, where acetochlor was detected only in superficial and intermediate layers. The low percentage of TOC (9.3–19%) may have contributed to the lower retention of the pesticide in SO-NP-2. In the lakes (IT-NP-2 and 3), this dynamic may have occurred more pronouncedly due to the solubility of the compound in water (282 mg L^{-1}).

For chlorpyrifos there was high variability in concentrations. In IT-NP, the pesticide was found in higher concentrations in the intermediate and deep layers of the cores from lakes (IT-NP-2 and 3). In contrast, in sample IT-NP-1, chlorpyrifos was detected only in the 10 cm layer. In SO-NP, the compound showed a wide distribution throughout the layers in SO-NP-1, while in cores SO-NP-2 and 3, chlorpyrifos was restricted to the upper and intermediate layers.

With regard to TOC concentrations, there was a high percentage in the peatland sediment samples (IT-NP-1, SO-NP-1, 2 and 3: 29.3 ± 9.40%) compared to the %TOC in sampled lakes (IT-NP-2 and 3: 18.7 ± 2.02%). In fact, studies indicate that peatlands can have much higher organic carbon concentrations than lakes, as well as higher acidity, due to their organic matter-rich environments (Arsenault et al., 2022). Investigations on possible significant correlations between pesticide concentrations in sediments and TOC revealed a positive correlation for acetochlor ($R = 0.65$; $p = <0.001$) and a negative correlation for chlorpyrifos ($R = -0.60$; $p = <0.001$) — Supplementary material (Fig. S1). Both pesticides have octanol-water partition coefficients that indicate a high bioaccumulation capacity: acetochlor log $Kow = 4.14$ and chlorpyrifos log $Kow = 4.96$ (Sangster, 2024). The negative correlation between chlorpyrifos and TOC may be related to the higher rate of microbial degradation associated with organic matter (Chishti et al., 2013).

Carbaryl exhibited a heterogeneous concentration profile in both parks, with distinct patterns among cores. In IT-NP-1, the highest concentration was recorded in the intermediate layer (5 cm: 1.64 ng g^{-1} d.w.), while in IT-NP-3 a sharp peak was observed in deeper layers (9 cm: 1.55 ng g^{-1} d.w.). On the other hand, in the SO-NP cores, carbaryl presented lower concentrations and less variability across layers, indicating a more homogeneous and limited distribution compared to the IT-NP cores. The distribution of carbendazim in the cores revealed a consistent pattern, characterized by higher concentrations in the superficial layers, with a gradual decrease towards the deeper layers. This pattern was observed for both parks, although SO-NP presented more pronounced peaks. Metolachlor concentrations were detected in almost all cores. In IT-NP, the lacustrine samples IT-NP-2 and IT-NP-3 presented the highest values, with peaks recorded in the upper layers (1 cm: 0.40 ng g^{-1} d.w.; 2 cm: 0.43 ng g^{-1} d.w., respectively). In contrast, in the peatland (IT-NP-1), concentrations were significantly lower and distributed in a dispersed manner (max. 0.15 ng g^{-1} d.w.). In SO-NP, metolachlor concentrations were even lower and presented an irregular distribution throughout the cores (max. 0.09 ng g^{-1} d.w.). Tebuconazole was detected in both parks, with higher concentrations in IT-NP. In the IT-NP-1 subsamples, the compound showed a higher incidence in the intermediate and deep layers. In IT-NP-2, the distribution was more homogeneous throughout the layers, while in IT-NP-3 an irregular pattern was observed, with higher concentrations in the superficial layers. In the SO-NP cores, the presence of tebuconazole was sporadic and recorded in lower concentrations.

Regarding terbutylazine, in IT-NP the distribution of the compound occurred irregularly in IT-NP-1 and 3, while in IT-NP-2 the pesticide was present only in the surface layer of the core. The presence of terbutylazine was also limited in SO-NP, with very low concentrations.

Measurements of atrazine, chlorsulfuron, diuron, disulfoton, diazinon, malathion, pirimicarb, prochloraz and propiconazole in IT-NP and SO-NP samples revealed specific distribution patterns, characterized by low detection frequency and localized concentrations. The compounds chlorsulfuron, diuron, disulfoton and diazinon were found in more superficial layers (1–3 cm), which may be a consequence of their fast degradation in the environment (W-S DT50: 26, 48, 15 and 10 days, respectively). Furthermore, diazinon is a volatile compound (VP: 11.97 mPa) and chlorsulfuron has high solubility in water (Sol. 12,500 mg L^{-1}) (PPDB - Pesticide Properties Database, 2024), characteristics that do not favor the retention of these pesticides in sediment layers. Atrazine was also found only in superficial layers (1–3 cm) of the cores. Malathion was detected in the intermediate layer (4 cm). The punctual detection in low concentrations can be attributed to its rapid degradation (W-S DT50: 0.4 days) and low persistence in the sediments. Pirimicarb and prochloraz were also detected in intermediate layers of the core (4–7 cm), the latter also reaching deeper layers (10 cm). However, these compounds present a slower degradation (W-S DT50: 168 and 359 days, respectively) and prochloraz has high lipophilicity (Log Kow: 3.5), which provides a greater affinity with organic matter and favors its retention. The degradation time and lipophilicity of propiconazole (W-S DT50: 561

days; Log Kow: 3.72) may also have contributed to the compound being found in deep layers (9 and 10 cm) of the cores.

According to Lourençato et al. (2023), sedimentation rates in IT-NP and SO-NP peatlands are very low, with mean values of 0.26 and 0.37 cm year^{-1}, respectively. Therefore, considering the reported half-life of these analytes, our data suggest that CUP concentrations detected along the profile do not directly reflect a chronological record of deposition, but a process of vertical mobility. Phenomena such as diffusion, bioturbation or chemical redistribution over time may be involved in this dynamic. In addition, these areas have high acidity, which can directly impact the behavior and stability of pesticides in the environment.

3.4. Risk characterization

The ecological risk associated with pesticides can be evaluated using the risk quotient (RQ), calculated based on ecotoxicological assays that assess acute or chronic toxicity. RQ values are classified into a range of low (<0.1), medium (0.1 ≤ RQ < 1), and high (≥1) ecological risk (Parente et al., 2019). Among the 17 pesticides identified in the sediment samples, eight presented high-risk to aquatic biota (acetochlor, carbaryl, carbendazim, chlorpyrifos, diazinon, disulfoton, diuron, and malathion) (Fig. 4).

Chlorpyrifos exhibited the highest RQ values, ranging from 416 to 14,589, highlighting its potential for significant environmental impact. According to Huang et al. (2020), the toxic effects of chlorpyrifos on aquatic organisms include histopathological alterations, behavioral changes, oxidative stress, neurological damage and genotoxicity. The authors also noted that their toxicity tends to be more pronounced in freshwater environments and at lower temperatures, which exacerbates its risk in high-altitude lakes.

The second highest risk was identified for diazinon (RQ: 2048), followed by disulfoton (RQ: 34–569). Diazinon is widely recognized for its toxic effects, both acute and chronic, being particularly harmful to aquatic invertebrates (Ccanccapa et al., 2016; Kandie et al., 2020), underscoring the need for strict monitoring and control of this compound in aquatic environments. Considering that the cited pesticides, as well as carbaryl (RQ: 0.40–4.08) and malathion (RQ: 3.12–10.94),

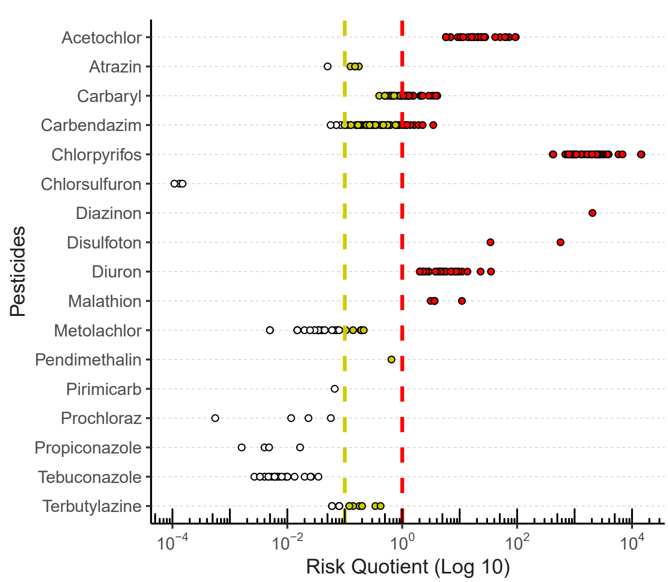

Fig. 4. Risk quotient (RQ) based on pesticides occurrence in sediment samples from Itatiaia National Park (IT-NP) and Serra dos Órgãos National Park (SO-NP). RQ values below the yellow dashed line indicate low ecological risk, values between the yellow and red lines are classified as medium risk, while values above the red line indicate high risk. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

belong to the organophosphate and carbamate groups, their toxic effects are directly associated with the stimulation of nerve impulses. This continuous stimulation can result in serious toxic effects, including prolonged muscle contractions, seizures, and, in severe cases, respiratory failure (Fukuto, 1990; Sousa et al., 2009).

Acetochlor also presented a high-risk to aquatic biota (RQ: 5.77–94.6). Previous studies (Guo et al., 2020; Huang et al., 2021; Saleh et al., 2022) indicate that this pesticide is highly toxic to fish, being associated with deformities, hormonal disruptions, neurological malformations, and mortality. Additionally, acetochlor has the potential to disrupt ecological interactions and trophic webs in freshwater ecosystems (Wang et al., 2023, 2024). Diuron (RQ: 2.03–35.01), in turn, can inhibit the abundance and activity of algae, compromising the recovery capacity of microbial communities, even under favorable environmental conditions (Pesce et al., 2006). Regarding carbendazim (RQ: 0.09–3.47), some authors have observed that it alters swimming patterns and reduces fish aggressiveness, which can contribute to increased predation rates (Andrade et al., 2016; Shuman-Goodier & Propper, 2016; Oliveira et al., 2024). In microcrustaceans, carbendazim has been associated with potential DNA damage, especially when multiple generations are continuously exposed (Silva et al., 2017).

Another important aspect to consider is that pesticide toxicity may be underestimated when analyzing individual compounds, disregarding synergic effects of chemical mixtures. Wacksman et al. (2006) demonstrated that, although atrazine exhibited low toxicity to *Xenopus laevis* on its own, its combination with chlorpyrifos significantly increased acute toxicity. Similarly, atrazine combined with diazinon resulted in a significant increase in toxicity to *Ceriodaphnia dubia* (Banks et al., 2005) and *Hyalella azteca* (Anderson and Lydy, 2002). Furthermore, Pérez et al. (2013) observed that *Danio rerio* larvae exposed to atrazine and terbuthylazine exhibited changes in swimming behavior and balance; and exposure to chlorpyrifos intensified acetylcholinesterase inhibition, suggesting a synergistic effect.

4. Conclusions

This study reveals the widespread occurrence and persistence of multiple pesticides in high-altitude pristine environments within two Brazilian National Parks. The occurrence of 17 CUPs, including herbicides, insecticides, fungicides, and acaricides, in sediment samples from both IT-NP and SO-NP emphasizes the vulnerability of these remote areas to contamination from long-range transport of pesticide. The high-risk quotient values observed for chlorpyrifos, acetochlor, and other compounds demonstrate the potential ecological threats these substances pose to sensitive freshwater ecosystems. The findings underscore the need for urgent action to mitigate the impact of pesticide contamination, particularly in highly biodiverse regions. Enhanced regulatory measures, coupled with sustainable agricultural practices, are crucial to safeguarding these invaluable ecosystems from further degradation.

CRediT authorship contribution statement

Patrícia C.G. Pereira: Writing – original draft, Methodology, Data curation. **Cláudio E.T. Parente:** Writing – original draft, Supervision, Methodology, Data curation, Conceptualization. **Yago Guida:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Raquel Capella:** Writing – review & editing, Methodology, Formal analysis, Data curation. **Gabriel O. Carvalho:** Writing – review & editing, Formal analysis, Data curation. **Pavlína Karásková:** Writing – review & editing, Validation, Methodology, Data curation. **Jiří Kohoutek:** Writing – review & editing, Validation, Methodology, Data curation. **Karla Pozo:** Writing – review & editing, Supervision. **Petra Přibylová:** Writing – review & editing, Validation, Methodology, Data curation. **Jana Klánová:** Writing – review & editing, Validation, Methodology, Data curation. **João P.M. Torres:** Writing – review & editing, Supervision, Funding acquisition. **Paulo R. Dorneles:** Writing –

original draft, Supervision. **Rodrigo O. Meire:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.126005.

Data availability

Data will be made available on request.

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