Human risk assessment of ash soil after 2020 wildfires in Pantanal biome (Brazil)

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Abstract

Wildfires have increased in the last years and, when caused by intentional illegal burnings, are frequently run out of control. Wildfire has been pointed out as an important source of polycyclic aromatic hydrocarbons (PAHs) and trace elements (TEs) — such as, As, Ni, and Pb — to environmental compartments, and thus may pose a risk to human health and to the ecosystem. In 2020, the Brazilian biome, Pantanal, faced the largest losses by wildfires in the last 22 years. Ashes from the topsoil layer in Pantanal were collected after these wildfires at 20 sites divided into the sediment, forest, PF, PS, and degraded sites. Toxicity and associated risks for human health were also evaluated. The areas highly impacted by wildfires and by artisanal gold mining activities showed higher concentrations for TEs and PAHs than the protected areas. Pb varied from 8 ± 4 to 224 ± 81 mg kg⁻¹, and total PAH concentration ranged between 880 ± 314 and 1350 ± 70 ng g⁻¹, at sites impacted by anthropogenic activities. Moreover, health risk assessments for TE and PAH indicated a potentially great risk for children and adults, via ingestion, inhalation, and dermal pathway. The carcinogenic risks exceeded reference values, for both TE and PAH, suggesting harmful conditions, especially for vulnerable groups, such as children and the elderly.

Keywords Wildfire · Pantanal · Trace elements · Polycyclic aromatic hydrocarbons · Risk assessment

Introduction

Catastrophic wildfire events have increased around the world in the last years, due to climatic and accidental or criminal reasons (IPCC 2021). Extreme events, such as heatwaves, extreme temperatures, and increased frequency of droughts, which are consequences of climate change, are causing regional abrupt changes and are tipping points with severe impacts locally and globally (IPCC 2021).

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Soil plays an essential role in the forests and cooperates with climate regulation (Lal et al. 2021). It can control the emission and sequestration of greenhouse gases, volatile organic compounds (VOCs), and atmospheric particulate matter (PM), and biogeochemical cycles. These soil's actions may contribute positively and negatively to all of these processes (Datta 2021; Lal et al. 2021). Wildfires impact both vegetation and soil. Nevertheless, the effects of wildfire on soil are not yet totally understood, but they can affect soil diversity and stability (Datta 2021).

Wildfires occur under a combined set of conditions and are an environmental concern because of their adverse and spread impacts on the biosphere, with ecological, social, and economic consequences (Butt et al. 2020). The effects on deposition, mobilization, and fate of contaminants related to wildfires have been recognized as an important environmental question (Bodí et al. 2014; Pivello et al. 2021). Currently, wildfires have affected forests and land around the world, including Portugal, Australia, the USA, and Brazil (Aguilera et al. 2021; Alcasena et al. 2021; Hacon et al. 2021; Haque et al. 2021). Projections show that Brazilian biomes, such as Pantanal and Amazon, are one of the regions in the world



with the highest increase in wildfire throughout the present century. Pantanal experienced unprecedented wildfires in 2020 marking a record of burning the largest area registered over the past 20 years: almost 30% of the biome's area was on fire (Pivello et al. 2021).

The Pantanal is the largest continuous continental wetland in the world, located in the west central region of Brazil, comprising Mato Grosso (MT) and Mato Grosso do Sul (MS) states. There is relevance to Pantanal's geographical location because it is connecting the Cerrado and the Amazon biomes (central and north Brazil, respectively) and the Chaco (Bolivia) (Ikeda-Castrillon et al. 2020). The savanna portion of this wetland is fire-prone, but other non-savanna forest physiognomies are fire-sensitive areas (Primack and Vidal 2019).

Pantanal is home to more than 150 species of mammals, 300 species of fish, 177 species of reptiles, 600 species of birds, 41 species of amphibians, and 3500 species of plants (Primack and Vidal 2019), acting also as a regulator of several continental ecosystem services (da Silva et al. 2015). Human actions, such as touristic activities, and professional fishing, rely on climatic and ecosystem conditions (Bergier et al. 2018). Cattle breeding is the main economic activity in Pantanal, encompassing around 3.8 million cattle heads in the region (Oliveira et al. 2016).

The extension of the Pantanal wildfires highlights the proportion of fire impacts across the biome, regardless of the macrohabitat physiognomies. In 2020, uncontrolled wildfires occurred during the local dry season, which was the longest dry period in the region (Marengo et al. 2021), caused by anthropogenic and criminal actions. Deforestation, land degradation, increased soil erosion, and water resource contamination are some of the impacts that have been observed in the Pantanal region (da Silva et al. 2015; Schulz et al. 2019).

The literature has shown that wildfires modify the physical and chemical properties of the topsoil layer, by heating, combustion, and ash deposition (Fang et al. 2015; Verma et al. 2012) with effects on ecosystem services (Zavala et al. 2014), causing biodiversity damages and socioeconomic concerns (Leal Filho et al. 2021). Estimations indicated that around 17 million vertebrates were killed directly by the fires (Tomas et al. 2021), causing a collapse in the Pantanal's biodiversity (Silgueiro et al., 2021), and about 76% of the population of MT and MS were affected (Marengo et al. 2021). The Pantanal's wildfires intend to expand the borders to livestock, soybean, and sugarcane cultivation, the last one allowed by a federal decree in 2019 after a 10-year ban (Lima et al. 2020).

Ashes are produced by burnt soil and vegetation and show a very heterogeneous composition (Bodí et al. 2014). PM, which is present in ash, is constituted by different species, including toxic elements (arsenic, plumb, cadmium) and hazardous compounds, such as polycyclic aromatic hydrocarbons (PAHs). In ash produced by wildfires, carbonaceous species and trace metals are usually present (Bodí et al. 2014; Campos et al. 2015). Depending on chemical composition and concentration, exposure to trace elements (TEs) and PAHs is harmful to human and environmental health (Burton et al. 2016), becoming them relevant chemical species to be monitored in wildfires. TE composition depends on the type of plant, burn intensity, and soil origin (Bodí et al. 2014). TEs, such as cadmium (Cd), arsenic (As), and lead (Pb), are frequently found in wildfire ash (Burton et al. 2016), which can promote severe soil changes (Vassilev et al. 2013). Mercury (Hg) is a TE of particular concern because it is volatile, toxic, persistent, and neurotoxic (Campos et al. 2015).

PAHs are a group of major environmental concerns because some of them can be persistent, bioaccumulate in fatty tissues, and have been proven to their mutagenic, teratogenic, and carcinogenic behavior on living organisms (ATSDR 2009; IARC 2012).

Due to the importance of the Pantanal from an ecological, social, and cultural perspective and the need to quantify the risk posed by wildfires for humans exposed to this scenario, the aims of this study were to (1) identify TEs and PAHs present in ash samples from top layers of soils collected at twenty different sites from Pantanal during the wildfires that occurred in 2020, (2) compare the chemical profile between these sites, and (3) calculate risk exposure to the population. The present study will provide a fuller understanding of wildfires' impacts on the population living in Pantanal.

Methodology

Sampling

Pantanal's vegetation is a complex mixture of tropical savanna and semi-deciduous forest, far from river areas (Evans et al. 2014), with dense, low-canopy riparian forests near the streams and seasonally waterlogged woodlands and grassland in floodplains (Arruda et al. 2016). The forms of vegetation in the Pantanal are influenced by the soil.

The soil in the Pantanal was formed from loose sediment dating from the Quaternary period. Primarily soil contains sand and some areas of clay (Ivory et al. 2019; Pott et al. 2011). Related to chemical composition, Si, Al, Fe, K, Mg, Ca, and S are found in greater proportion throughout different Pantanal regions (Coringa et al. 2014; Oliveira et al. 2021; Sousa and Souza 2012) and high content of organic matter (Ivory et al. 2019; Pott et al. 2011). The main primary types of soil are Plinthosols, Planosols, and Gleysols (Galvanin et al. 2019).

Twenty sites in Pantanal (Fig. 1) were chosen to collect burned soil. The sampling points were carefully selected to include rural areas affected by wildfire disasters, locations inside ecological reserves, and a region impacted by artisanal gold mining. The locations were chosen to select distant points from each other to ensure the variability of the samples in different areas within the biome.

During the dry season of 2020, the temperature reached 40 °C in Corumbá (MS) and 38 °C in Cuiabá (MT) (INMET 2021). In the 2020 wet season (from June to September), the rainwater volume was 57% less than in previous years. This blend of hot, dry conditions pushed flammability indexes to their highest in 2020 (Libonati et al. 2020), and the fires were out of control. The consequence was unprecedented wildfires ripped through the region, including January and February, which is usually the wet season.

The sampling sites covered an area of around 114,000 km² and a radius of 190 km. Relating the twenty sites, they were classified into five groups (Fig. 1) according to their qualitative characteristics: (1) sites nearby riverside of different rivers in Pantanal, which represent sediment areas and were affected by wildfires (sites ID: 1, 3, 4, 5, 6, 13, 15, 16, and 17), this group was referred as sediment sites; (2) sites described as forest areas, predominantly ashes of burned vegetation (sites ID: 2, 7, 8, 9, 10, 11, 18, and 19), which were called forest sites; (3) forest inside a preservation area (site 12), the so-called protected forest (PF); (4) riverside into protecting area (site 14), named as protected sediment (PS); and (5) the last one, called degraded site, near an artisanal gold mining (site 20) exemplifying this other pollution source, which is growing quickly in the Pantanal (May Júnior et al. 2018). Information about each sampling site is summarized in Supplementary Material (Table S1).

The ash samples were collected between August and October in fire-affected sites 1 to 2 months after the disaster. At each location, a steel scoop was used to obtain a topsoil layer of 15 cm diameter on the surface. Between two and four samples were collected at each site. The aim was to collect mainly fresh ash from the soil; neither sample was collected below the top layer (Fang et al. 2015). The samples were placed in aluminum specimen boxes or paper containers with a capacity of 250 g and transported to the laboratory. The scoop was previously decontaminated with methanol to avoid any type of contamination. Following transport to the laboratory, the samples were dried, homogenized, sieved (<4 mm), and then stored at 5 °C until further analysis (Figure S1).

Cities and population description

The sampling sites are located in four municipalities, which are Barão de Melgaço, Cáceres, and Poconé, in MT, and Corumbá in MS. The cities of Barão de Melgaco and Corumbá show the largest area of their territory in the Pantanal, corresponding to 99.2% and 95.6% of its area, respectively, followed by Poconé (80.3%) and Cáceres (56.1%) (Silva and Abdon 2008).



Fig. 1 Map of sampling sites in Pantanal

The population characteristics of the four municipalities are summarized in Table 1. The traditional Pantanal population, such as indigenous people, resides in rural areas of the Pantanal (Ikeda-Castrillon et al. 2020; Rosseto 2009), which are normally remote regions. Additionally, the rural communities usually practice artisanal fishing and subsistence cultivation (Ikeda-Castrillon et al. 2020).

Chemical element analyses

Beringui et al. (2021) has described detailed methodology. Briefly, 200 mg of dried sample was extracted with 3.0 mL of HNO₃ (Vetec, 65%, bidestiled) and heated for 4 h at 120 °C in polypropylene tubes. After dilution with ultrapure water (Millipore, USA), each extract sample was analyzed in an inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer, NexIon $300 \times$, USA) system. ICP-MS parameters and standards solutions are described in Supplementary Material (S1).

An analytical six-point curve was prepared using multielement standard solutions (Perkin Elmer, USA), ranging from 1 to 100 μ g L⁻¹ for TEs. Samples that exceed the upper calibration limit were properly diluted to fit in calibration curve range. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated based upon the standard deviation of the calibration blanks: three times the standard deviation for the LOD (ten times for the LOQ), divided by the slope of the calibration curve. LOD varied from 0.001(Cd) to 0.149 (Cr) mg kg⁻¹. For LOQ, the values ranged between 0.003(Cd) and 0.491 Cr) mg kg⁻¹. To measure accuracy and precision, NIST SRM 1648a standard was used successfully.

PAH analyses

The extraction method was based on the EPA 3545A (SW-846) protocol. An aliquot of 10 g of sample was extracted by hot and pressurized solvent using the ASE 200 (Thermo Scientific, Germany) accelerated solvent extractor system (EPA 2007). After concentration, the extracts were purified by adsorption chromatography using alumina (Supelclean® LC-AL-N) and silica (Supelclean® LC-Si). The

fraction containing the PAHs was isolated by hexane: dichloromethane elution. PAH determinations were performed by gas chromatography (Thermo Trace-GC, Germany) coupled with mass spectrometry (Thermo ITQ 900, Germany), based on the EPA method 8270D (EPA 2014). A detailed description can be found in Supplementary Material (S1).

The analytical control of the process included checking the concentration of PAH contained in standard solutions prepared with different analyte concentrations (5, 10, 20, 50, 100, 200, 400, and 1000 ng mL⁻¹). Linear correlation coefficients > 0.990 were obtained for the calibration curves in all cases. In addition, for each group of 10 analyzed samples, a standard solution of the above compounds was injected to check instrumental calibration conditions. The LOD and LOQ were calculated considering the first calibration curve point and the mean extracted samples mass. The LOD was from 0.15 (Nap) to 0.48 µg kg⁻¹ (Chr), and LOQ was around 1.8 µg kg⁻¹. The accuracy was tested through successful analysis of SRM-NIST 1944.

Human health risk assessment

The hazard quotient (HQ) and carcinogenic risk (CR) were applied to assess the potential health risk posed by eight TEs (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and were calculated for each site. Detailed equations are in Supplementary Material (Table S2) (Pan et al. 2018; Zhaoyong et al. 2018).

The carcinogenic B[a]P equivalent (BaP_{EQ}^{C}) considers seven PAHs (PAH⁷) that present carcinogenic risk, and it was calculated in the present study (Bortey-Sam et al. 2014; Xia et al. 2013). The equation can be found in Supplementary Material (S2).

Incremental lifetime cancer risk (ILCR) was used to estimate the integrated lifetime risks that can occur in different age groups. In the present study, it was considered adults (19–70 years) and children (<14 years) for ILCR calculation through ingestion (IL_{ing}), dermal (IL_{der}), and inhalation exposures (IL_{inh}) (US EPA 1993). The equations are described in S2.

 Table 1
 Estimated inhabitants¹,

 percentage of children, elderly
 and rural residents¹, and

 population density¹
 Population density¹

Municipality	Total population	% children (<14 years)	% Elderly (> 60 years)	% rural residents	Population density (hab/ km)
Barão de Melgaço	8165	23.5	12.6	54.9	1.0
Cáceres	95,339	26.8	9.4	13.0	4.0
Corumbá	112,669	27.8	9.3	10.0	2.0
Poconé	33,386	27.2	10.9	27.4	2.0

¹IBGE, 2021a, b

Principal component analysis (PCA)

Statistical analyses were performed using software R, version 4.1.0. (R Core Team 2020) together with RStudio (RStudio Team 2015). Principal component analysis (PCA) was employed for the characterization of the source of chemical elements and the relation of all the sites. The analysis was carried out on 20 sites, described by 12 variables (Igeo of trace elements). The results of the PCA were graphically represented by chemical element correlation and cluster plot for sampling sites.

Results

Properties of soil in Pantanal

The physical and morphological features of the ash samples were not identified in the present study. The colors of the ash samples collected in the present study ranged from different shades of gray (Figure S1). For forest sites, light gray was predominant (Figure S1a), while for sediment sites, dark gray was the main color (Figure S1b). At the degraded site, the samples were off-black (Figure S1c). Lighter shades of ash indicate more complete combustion of the original material (Bodí et al. 2014).

Trace elements

The TE concentrations measured are presented in Supplementary Material (Table S2). The mean (\pm standard deviation) concentrations of sediment, forest sites, PF, PS, and degraded areas for some TEs determined are shown in Fig. 2 and Table S2. The results for sediment and forest sites impacted by wildfires were shown in the boxplot, while the level for PF, PS, and degraded area was presented in bar plots. The elements Cu, Cr, and V were dominant for sediment and forest sites. In PF area, Cu, V, and Ni showed the highest concentrations. For the PS site, V, Cr, and Pb were predominant. At the degraded site, Pb, Cu, and Cr were the major TEs.

The soil guideline values for agricultural and residential land use, given by the Canadian Council of Ministers of the Environment (CCME 2021), and the plant, avian, and mammalian screening levels recommended by EPA (US EPA 2011) for each TE were cited below, in attempt to compare the results of the present study and these two committees.

The mean concentration of As was 6.34 (\pm 1.50) mg kg⁻¹ at degraded site, 3.25 (\pm 1.92) mg kg⁻¹ at sediment sites, 2.31 (\pm 0.63) mg kg⁻¹ at PF, 1.60 (\pm 0.70) mg kg⁻¹ at forest sites, and 1.04 (\pm 0.33) mg kg⁻¹ at PS. As concentrations

were below the CCME reference $(12.0 \text{ mg kg}^{-1})$ (CCME 2021) for all sites, while the degraded area exceeded the EPA level (5.7 mg kg⁻¹) (US EPA 2011).

Cd varied from 13.10 (\pm 6.52) mg kg⁻¹ (degraded area) to 0.04 (\pm 0.01) mg kg⁻¹ (PS). For sediment sites (mean = 0.11 \pm 0.07 mg kg⁻¹), the values did not differ significantly (p > 0.05) between them, while for forest sites (mean = 0.18 \pm 0.10 mg kg⁻¹), the concentrations of each site were considerably different from each other (p < 0.05). The EPA screening level (0.002 mg kg⁻¹) (US EPA 2011) and CCME level (10.0 mg kg⁻¹) (CCME 2021) were shown in the plot area.

Cr levels were lower at the PF site $(7.83 \pm 1.67 \text{ mg kg}^{-1})$ and higher at the degraded site $(79.25 \pm 14.80 \text{ mg kg}^{-1})$. Neither sediment sites $(20.70 \pm 6.80 \text{ mg kg}^{-1})$ nor forest locations $(18.21 \pm 4.39 \text{ mg kg}^{-1})$ showed significant differences between the values (p > 0.05). The CCME recommended value for agricultural and residential land use was 64.0 mg kg^{-1} (CCME 2021).

Cu mean concentrations were 8.96 ± 5.78 mg kg⁻¹ (PS), 27.64 ± 13.67 mg kg⁻¹ (sediment sites), 37.84 ± 18.46 mg kg⁻¹ (forest sites), 40.51 ± 15.78 mg kg⁻¹ (PF), and 186.83 ± 71.50 mg kg⁻¹ (degraded area). Cu levels at all sites are above EPA value, and degraded area exceeded CCME level.

Ni concentrations ranged from $4.81 \pm 1.23 \text{ mg kg}^{-1}$ (PS) to 15.28 ± 5.23 (PF). At sediment ($12.96 \pm 6.90 \text{ mg kg}^{-1}$), the values of each site were not significantly different (p > 0.05), likewise at forest sites ($11.85 \pm 5.22 \text{ mg kg}^{-1}$). None of the sites exceeded the CCME value. However, 60% of the sediment and forest locations surpassed the EPA (13.6 mg kg^{-1}) recommendation (EPA 2011).

Pb levels ranged from 3.32 (\pm 1.12) mg kg⁻¹ (PF) to 223.72 (\pm 80.87) mg kg⁻¹ (degraded area). At sites impacted by wildfires, sediments (8.47 \pm 3.80 mg kg⁻¹), and forest (9.53 \pm 3.35 mg kg⁻¹), Pb concentration did not show a significant difference (p > 0.05). Except for the degraded area, the other sites showed Pb concentrations (Fig. 2) below the CCME value (CCME 2021). Furthermore, mercury (Hg) was detected only at two sites (degraded area=0.16 mg kg⁻¹ and forest site = 0.08 mg kg⁻¹).

A principal component analysis (PCA) was employed for the characterization of the correlation between TE concentrations and sampling sites (Fig. 3). About 77% of the total dataset variation is explained by the first two components. The first factor was predominated by Pb, Cd, Zn, Cr, and Cu in descending order (Fig. 3a, Figure S2). Due to Pb expressive concentration in the degraded area (site 20, Figure S3), compared to the other sites, site 20 comprised 80% of the total site contribution. The major elements in factor 2 were Ni, V, Ag, V, As, and Zn (Fig. 3a, Figure S2). The balanced distribution of site contribution (Figure S3) showed forest and sediment locations as dominant.



Fig. 2 Boxplot and bar plots of element concentration to sediment and forest sites, protected sediment and forest areas, and degraded sites comparing ash contents to the criteria obtained from the literature. The United States Environmental Protection Agency (EPA),

plant-avian-mammalian screening level (red line), and the Canadian Council of Ministers of the Environment (CCME), and soil quality guideline for agricultural and residential land use (blue line)

The cluster plot of all sampling sites (Fig. 3b) highlights the site with high concentration, which was the degraded site. The other sites did not present good separation from each other.

Polycyclic aromatic hydrocarbons (PAHs)

A total of 18 PAHs from 2 to 6 fused rings were found above the limit of quantification, as follows: naphthalene (Nap), acenaphthylene (Acf), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k] F), benzo[e]pyrene (B[e]Py), benzo[a]pyrene(B[a]Py), perylene (Per), indeno[1,2,3-cd]pyrene (IdP), dibenz[a,h] anthracene (DB[ah]A), and benzo[ghi]perylene (B[ghi]Per).

The total concentrations of the 18 PAHs (\sum 18PAH) (Fig. 4) varied from 248 ± 60 (PS) to 1350 ± 70 ng g⁻¹ (degraded area). Relating to sites impacted by wildfires, sediment locations (880±314 ng g⁻¹) showed lower mean



Fig. 2 (continued)

concentration than forest sites $(1314 \pm 433 \text{ ng g}^{-1})$, and both ranges showed values considerably different (p < 0.05).

The total mean PAH concentration was determined in a previous study conducted at forest sites in South Korea $(\sum 16PAH = 1081 \text{ ng g}^{-1})$ (Kim et al. 2003), Portugal $(\sum 15PAH = 695 \text{ ng g}^{-1})$ (Campos et al. 2019), Nigeria $(\sum 16PAH = 713 \text{ ng g}^{-1})$ (Faboya et al. 2020), Switzerland $(\sum 16PAH = 167 \text{ ng g}^{-1})$ (Bucheli et al. 2004), China $(\sum 16PAH = 75 \text{ ng g}^{-1})$ (Xiao et al. 2014), Belém (Brazil) $(\sum 24PAH = 312 \text{ ng g}^{-1})$ (Lima et al. 2021), and California (USA) $(\sum 16PAH = 3640 \text{ ng g}^{-1})$ (Wan et al. 2021) which were plotted in Fig. 4.

The percentage contribution of the PAHs rings determined in ash samples was provided in Fig. 5. Nap was the dominant PAH in all samples (Fig. 5), ranging from 149 (PS) to 1267 ng g⁻¹ (degraded area). Phe and Pyr were the most abundant PAHs for sediment and forest sites. The values varied from 47 to 158 ng g⁻¹ (Phe) and from 10 to 233 ng g⁻¹ (Pyr), for sediments and forest, respectively.



Fig. 3 PCA variables for trace elements (a) and cluster plot for sampling sites (b) related to ash samples collected at Pantanal





Population characterization and health risk assessment

The health risk values determined through the calculation of non-carcinogenic and carcinogenic TEs for children and adult exposure were presented in Supplementary Material (Table S4). For non-carcinogenic TEs, HQ values lower than 1 indicate no adverse health effects, whereas values higher than 1 suggest probability of adverse health effects (Pan et al. 2018), by ingestion (HQ_{ing}) or dermal contact (HQ_{der}). For adults, HQ_{ing} mean ranged between 0.03 (forest sites) and 0.30 (degraded site) (Table S4). HQ_{der} values showed a minimum of 5.7×10^{-3} (sediment sites) and a maximum of 1.8×10^{-2} (degraded site) (Table S4). For children, HQ_{ing} means varied from 0.2 (forest sites) to 1.6 (degraded area). HQ_{der} average was between 2.2×10^{-2} (sediment sites) and 1.4×10^{-2} (forest sites).

For carcinogenic risk of TEs (CR), values $\leq 10^{-6}$ indicate lower effects, values $\geq 10^{-4}$ represent a potentially great risk, and the range between 10^{-6} and 10^{-4} suggests an acceptable total risk for regulatory purposes (Pan et al. 2018). Related to adult exposure for CR to ingestion (CR_{ing}), forest



Fig. 5 PAH contribution in ash samples at Pantanal sites



Fig. 6 Incremental lifetime cancer risk (ILCR) for ingestion, dermal and total exposure, and carcinogenic B[a]P equivalent (BaP_{EQ}) concentration at all sites in Pantanal ash samples

and sediment sites showed values around 10^{-5} , and in the degraded area, the mean was > 10^{-4} (Table S4); for CR to dermal contact (CR_{der}), no site exceeds the tolerable levels (Table S4) for adults. For children, CR_{ing} was > 10^{-4} at all sites, including the PF and PS areas; the degraded area was the most dangerous site (3.1×10^{-3}) (Table S4). The CR_{der} for children varied from > 10^{-6} (sediments and forest sites) to > 10^{-5} for the degraded area.

The BaP_{EQ}^{C} was calculated by considering adults' and children's exposure. Forest sites showed a risk of exposure varying from 127 to 2899 ng g⁻¹ (Fig. 6, Table S4). BaP_{EQ}^{C} for sediment sites ranged between 3.1 and 4569.0 ng g⁻¹ (Fig. 6, Table S4). Degraded area presented considerable value (1268.0 ng g⁻¹). If the Canadian soil quality guide's value for PAHs was considered (600 ng g⁻¹) (CCME 2021), 43% of forest sites and 40% of sediment locations surpassed this reference value for BaP_{EQ}^{C} , as well as degraded area; none of the protected areas exceeded CME value.

The ILCR was chosen as the standard to analyze probabilistic cancer risks that can arise from PAH exposure for children and adults. This calculation considered three different pathways, which were ingestion, inhalation, and dermal contact (Huang et al. 2018), and was called ILCR_T. For adults, the results ranged from 10^{-5} to 10^{-2} , at sediment sites, and from 10^{-4} to 10^{-2} at forest sites (Fig. 6, Table S4). Children's risk varied between 10^{-5} and 10^{-2} at sediment areas and between 10^{-3} and 10^{-2} at forest locations. Related to each pathway of exposure, the dermal was significantly higher for adults (p < 0.05) than for children. The order of exposure for the three pathways for adults and children is dermal contact > ingestion > inhalation.

Discussion

Levels and risk assessments of TEs

The analyses of the portion of ash composition in the topsoil layers of the Pantanal biome were useful for measuring impacts on fauna, flora, and humans. The wide sampling site enabled us to classify them according to similar characteristics, which comprised sediment locations (9 sites), forest areas (8 sites), PS, PF, and degraded area (one site each) and access to the risk of exposure to the residents and communities near these sites.

Understanding whether wildfire increases the risk exposure to the population is of utmost importance to provide scientific evidence to better inform policymaking to protect public health, especially in the most vulnerable segments of the population. Wildfire events can impact elements and organic matter availability in soil by volatilization, charring, or complete oxidation (Oliveira et al. 2021), contributing to growth risk factors and causing harmful damage to the environment and inhabitants.

In general, the levels of As at each sediment site did not show significant differences between them (p > 0.05), as well as between each forest site (p > 0.05) (Fig. 2). Except for the degraded area, As concentrations for the other sites did not exceed EPA level (5.7 mg kg⁻¹) (US EPA 2011). Related to Cd levels, all sites exceeded the EPA screening level (US EPA 2011), and only the degraded area had been above the CCME. For Cr concentration, the degraded area surpassed the CCME recommended value for agricultural and residential land use (64.0 mg kg⁻¹) (CCME 2021).

During the wildfire process, some chemical bonds of humic substances presented in soil organic matter are broken; releasing Cu and Ni (Manahan 2000), both were identified in large concentrations, especially at sites directly impacted by wildfires, which were sediment and forest areas. Cu levels exceeded EPA recommendations at all sites, demonstrating a potential danger to ecological receptors, even at ecological reserves (Fig. 2). Ni presented considerable percentage contribution to total carcinogenic risk (CR) exposure in the samples, varying from 38.3 (sediment sites) to 42.0% (forest sites) related to children and from 38.0 (sediment sites) to 41.5% (forest sites) to adults. Since more than 20% of the total population corresponds to children in the municipalities where the samples were collected, Ni should be considered a potential hazard element, especially to children, and its concentration needs to be monitored.

As, Cd, and Cr are harmful to humans and animals (Garba and Abubakar 2018; Yang et al. 2019). All of them showed concentrations higher than screening levels to plant, avian, and mammalian (US EPA 2011). Then, the astonishing number of dead vertebrate animals immediate after the 2020 wildfires (Tomas et al. 2021) did not reflect the complete picture of mortality because of modifications in soil composition, cover the land, and reduction of food and water availability (Silgueiro et al. 2021) have caused late mortality in the Pantanal. Mortality also may have occurred due to increased predation during dislocation from affected home ranges (Andersen et al. 2012), which was a negative impact stronger for small animal populations that were living endangered and will require more time to recover (Tomas et al. 2021).

Pb is one of the most widespread element pollutants (Alexakis 2020) and may be emitted by anthropogenic activities, such as mining and coal combustion (Medunić et al. 2018), causing bioaccumulation on living beings (Pandey and Tiwari 2021). Since the degraded area (site 20) is near artisanal gold mining, the extreme Pb levels observed at that location can be associated with this anthropogenic activity. Relating to the non-carcinogenic hazard (HQ), Pb posted a strong influence at the degraded site, contributing to 46.2% for children and 38.0% for adults of the total risk. This site is around 4 km away from Poconé downtown, where 27.2% and 10.9% of the population represent children and elderly people, respectively. In Poconé, more than 800 mil ha were burned during the 2020 wildfires, including conservation areas, which charred whole houses and plantations of riverside, forcing indigenous communities, such as the Guató and Bororo ethnic groups, to leave their lands (Silgueiro et al. 2021). Additionally, the concentrations of TEs, especially Pb, were above the plant, avian, and mammalian screening level (US EPA 2011) and the reference value for agricultural and residential land use (CCME 2021), confirming that this site is quantitatively degraded.

Many of the TE content in ash samples may have been volatilized during the wildfires, and concentrations can be underestimated to these elements. The low frequency of Hg widely studied in atmospheric particulate matter in Pantanal due to its harmful potential (Webster et al. 2016) suggested effective evaporation to the atmosphere at the sampling sites.

PCA results showed that only the eigenvalues of the first two components (PC1 = 5.94 and PC2 = 1.75) were > 1. According to the varimax rotation results (Fig. 3), PC1 and PC2 explained 77% of the total variance. PC1 showed a strong positive loading for Pb, Cd, Zn, Cr, Cu, and Co

(Figure S1) and moderate positive loading for As and Ni indicating the presence of anthropogenic impute. Related to site contribution, the degraded site (site 20) accounted for 80% of the total contribution (Figure S3). Pb, Cd, Cu, and As have been found in wildland fires (Burton et al. 2016; Garba and Abubakar 2018; US EPA 2019), but also it may be emitted in mining activities, including the processing and transportation of ores and wastewater around mines (dos Santos et al. 2016; Tepanosyan et al. 2018), and the degraded site was mainly impacted by artisanal gold mining activities. It can be the predominant source related to factor 1 (Fig. 3). In the last decades, illegal gold extraction activities have impacted the Pantanal environment (May Júnior et al. 2018) and can cause intensive landscape change, threatening many environmental processes such as sediment control and storage and interfering with the cycle and storage capacity of metals (Tepanosyan et al. 2018).

Ni, V, and Ag showed great contribution to factor 2 (Figure S1), and As, Zn, Cd, and Pb presented moderate associations. Previous studies have reported increased concentration of Ni (Alexakis 2020) and V (Huang et al. 2021) after wildfires, as well as As (Wan et al. 2021) and Cd (Campos et al. 2016). The site's contribution was more balanced than factor 1, showing a strong contribution of forest and sediment sites. Therefore, factor 2 was assigned to the predominance of biomass burning, i.e., wildfires as a source contribution to metals (Fig. 3a). The clusters of sampling sites were clearly separated (Fig. 3) for the degraded site from the other ones because the dominant source at site 20 was mainly linked to mining activities. Therefrom, protected areas, sediment, and forest sites were associated due to a principal source of TEs, which have impacted these locations and probably is wildfires.

The total index of adverse health effects (HQ) of TEs did not exceed the reference value among the sites (Table S4). All locations showed low values for children and adult exposure, indicating that direct contact via ingestion or dermal ways did not pose relevant health risks associated with TE levels determined in this study. As levels pose the greatest threat to HQ calculation, even though their levels were not higher than Cu or Zn concentrations. As has been associated with vascular and nervous system abnormalities, reduced DNA repair, abortion, pregnancy hypertension, and endocrine disruption (Alexakis 2020; Milton et al. 2005; Rahman et al. 2016).

The total CR of TEs indicates acceptable risk for regulatory purposes for adults, via ingestion and dermal contact. CR suggested potentially great risk for children, for both ways of exposure. Since dermal and oral contacts are more related to local communities, i.e., indigenous, and rural groups, the people are the most impacted by these risks. Some of TEs have been associated with different cancers. Cd is related to liver, kidney, lung, prostate, and other systems cancer (Pecina et al. 2021), while Pb is associated with lung, kidney, stomach, and brain cancers (Boskabady et al. 2018), and As may cause skin, lung, prostate, liver, kidney, and bladder cancers (Abdul et al. 2015). Then, based on the increased rate of deforestation and wildfires in the Pantanal region in the last years (Reid and Maestas 2019), the effects of human exposure are expected to be significant in vulnerable groups, such as children, the elderly, and people with comorbidity.

PAH concentrations and carcinogenic risks

The total PAH concentrations (Fig. 4) at sediment, forest, and degraded sites were higher than in studies piloted in other regions affected by wildfires, such as in South Korea, where ash soil samples were collected 1 month after a wildfire, which burned more than 20,000 ha over several days (Kim et al. 2003); in Portugal, during the burning of pine forest (Campos et al. 2019); in Nigeria, at a tropical rain forest in Nigeria, where seasonal wildfires occurred (Faboya et al. 2020); in Switzerland, after a wildfire in Alpine soils (Bucheli et al. 2004); in China, from rural forest areas (Xiao et al. 2014); and for sediment samples collected around Pará River, which is the most populated area in the coast of the Brazilian Amazon (Lima et al. 2021). Only, total PAHs in ash samples from wildfires that occurred near farming areas, in California (USA), showed high value (Fig. 4) (Wan et al. 2021) than those observed in sediment, forest, and degraded areas. The low PAH concentrations at the PS site (Fig. 4) may be attributed to transport into the underground river through leaching and percolation since leaching and percolations of organic compounds occur commonly in surface systems (Alam et al. 2014).

In the present study, Nap was the highest PAH at all sampling sites (Fig. 5). Despite its highest vapor pressure (Abdel-Shafy and Mansour 2016), the great concentration can be attributed to Nap behavior in organic matter-rich soils because it has hydrophobic interactions with aromatic fragments of humic and fulvic acids (Vasil et al. 2008), which increase its bioavailability in soils or sediments (Abdel-Shafy and Mansour 2016). Additionally, Phe showed great concentration at sediment and forest sites; this PAH is produced under fast heating and high temperature (Tsibart and Gennadiev 2013). PAH concentrations showed similar profiles for sediment and forest sites (Fig. 5), evidencing the same major source of these organic compounds in the region. According to previous studies, PAH profile in the soil varies widely among the protected areas in Brazilian landscape zones even without anthropogenic interference (Tsibart and Gennadiev 2013; Wilcke et al. 2003).

At sites impacted by burnings, the fire intensity is crucial to determine the PAH profile and concentration in ash samples. Higher proportions of 2–3 ring PAHs (Nap, Acf, Ace, Flu, Phe, and Ant) in ash soils post-fire have been observed previously (Campos et al. 2015; Harper et al. 2019; Simon et al. 2016; Wan et al. 2021), and then the predominance of LMW-PAHs (Fig. 5) in the present study might be attributed to the high production of 2–3 ring PAHs after moderateand high-intensity wildfires (Chen et al. 2018; Yang et al. 2022). Both fire intensities favor greater volatilization and mineralization of organic matter, which benefit LMW-PAH production (Chen et al. 2018).

The BaP_{EQ}^{C} values obtained in the present study (Fig. 6) exceed the value recommended by the Canadian guide of 600 ng g^{-1} (CCME 2021) for more than 40% of forest and sediment sites, the highest concentration (4569.0 ng g^{-1} , sediment site) was seven times above the reference value. Additionally, the reference ILCR was 10^{-6} (US EPA). For adults and children via inhalation, ingestion, and dermal pathway of all the PAHs, the ILCR results (Fig. 5) were higher than the EPA value at all sediment and forest fires, as well as in the degraded area and denote a non-negligible risk. Children can easily ingest contaminated soils during play activities and around their homes leading to a higher cancer risk. The wildfire events have combined acute exposure over many years for Pantanal inhabitants, which can have a noteworthy impact considering all those different pathways and the period of exposure since wildfires have increased in the last years in the region (Marengo et al. 2021). Moreover, the risks of contamination posed by wildfires are not limited to the in situ, burnt soils and might be potentiated in surface and groundwater bodies within and downstream of a burnt area.

Environmental and population impacts

The wildfires can cause socioeconomic damage, which can be observed in several levels of severity and spatiotemporal scale, affecting local communities, firefighters, and more vulnerable groups such as children and the elderly (Fiocruz 2020). The Fiocruz (2020) technical report observed that the PM and toxic gases produced by burned vegetation can spread over long distances, with the capacity of reaching populations hundreds of kilometers from the wildfires (Fiocruz 2020).

The present study calculated the risk of acute exposure for the population, and the results were related to wildfires that occurred during the 2020 dry season. However, the Pantanal is burning systematically throughout the dry season every year, which was intensified in 2019. Then, the local communities have been facing chronic exposure, which may increase the risk assessment, especially for rural residents, who accounted for 30% of the total population in some Pantanal municipalities (IBGE 2021a, b) and the indigenous people. In 2020, these populations have been forced to leave their homes due to fire disasters impacting their routine, culture, and habits. Several studies have shown that the high rates of illiteracy influence the conditions of unhealthy living environment for mainly the rural and remote communities in Pantanal (Gaudioso et al. 2020; Gonçalves et al. 2018; Marengo et al. 2021), and these factors may contribute to getting worse the negative impacts of wildfire exposure, due to the low perception of that population related to the impacts of fire expose during the dry period in Pantanal.

The drought situation and warm conditions, when mean temperature reached 41 °C, establish a new record-breaking level for the region (Libonati et al. 2022), favoring the propagation of fires in the Pantanal in 2020 (Marengo et al. 2021). Several burned areas did not have easily accessible locations, making firefighting difficult (Leal Filho et al. 2021). Furthermore, the COVID-19 outbreak affected fire management in 2020, further reducing the number of firefighters for the Pantanal dry season. Firefighters needed to follow social distancing during the pandemic, and several brigades had been working overwhelmed, under great pressure, and risking their lives daily (Garcia et al. 2021).

The challenge to access the burned locations and collect samples immediately after the wildfires limited the present study; the lack of other parameter measures, such as temperature and pH of the soil, was also a limiting factor.

Conclusion

The Pantanal's 2020 wildfire was the result of a complex interaction among meteorological/climatic, land use, and anthropogenic activities. Uncontrolled fires destroyed massive vegetation and killed wildlife, putting one of the world's most diverse ecosystems in danger. From the results described in this study, wildfires caused a complex combination of chemical species and organic compounds determined in the ash samples from topsoil layers across the biome.

Since element contents of ash exceed the plant-avian-mammalian screening levels and agricultural and residential reference, the sites impacted by wildfires are at potential risk. Human health risk assessment showed that the elemental non-carcinogenic and carcinogenic risks to adults and children were associated with the Cu, Ni, and Pb contents. Moreover, the level of total carcinogenic risk was greater for children than adults, exceeding the reference value.

The health risk assessments for PAHs indicated that the population, especially more vulnerable groups, has been exposed to high amounts of carcinogenic compound concentration via ingestion, inhalation, and dermal contact pathways. The total BaP_{EQ} surpassed the value recommended by guidelines for 40% of the sites, and PAH exposure at all sites presented severe lifetime cancer risks for residents (children, and adults).

After wildfires, the Pantanal region has been negatively impacted by biodiversity losses, with millions of dead animals, modifications in the soil–plant–organism system, and considerable risk assessment for humans, especially among the susceptible populations, such as children, the elderly, and rural communities. This study reveals that the intensive and extensive fires in this biome are a potential threat to the population, the wild animals, and the ecosystem services from Pantanal.

This disaster faced by the Pantanal biome has clearly been a central topic of public debate around the world since its long-term environmental consequences and recovery are highly uncertain. And this study can justify the urgent need for actions of prevention and mitigation of the occurrence of wildfires and should be combined and implemented in an integrated way by policymakers and community actors. Additionally, the federal and state governments, decisionmakers of the organizations that respond to the planning of wildfire prevention and fight, must take effective positions.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary material.

Code availability Not applicable.

Declarations

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