Large-scale spatiotemporal variations, sources, and risk assessment of banned OCPs and PAHs in suspended particulate matter from the Negro river, Argentina☆

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A R T I C L E I N F O

A B S T R A C T

Organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) threaten the environment due to their wide environmental resistance. Environmental paradigms coexist along the Negro River (NR) in Argentina, South America, which flows to the sea below the latitude of 40° S; however, this is the first environmental assessment of OCPs and PAHs in water of the NR for more than 15 years. With 21 sampling sites covering a range of 600 km of river extension, we assessed 16 OCPs and 16 PAHs in suspended particulate material (SPM) with regard to their levels, seasonality, sources, and potential biological risk assessment. Using gas chromatography–mass spectrometry and gas chromatography coupled with electron capture detection, we found an overall mean value for Σ_{16} OCPs of 648.56 ng. g^{-1}, d.w. Despite a ban spanning 25 years, an increasing trend of accumulation of hexachlorocyclohexanes (HCHs) and endosulfan was shown in the lower valley. The α-HCH/ɤ-HCH and β-HCH/(α + ɤ)-HCH ratios indicated a prevalent usage of technical HCH over lindane and recent HCH inputs. The most abundant compound, α-endosulfan, averaged 141.64 ng. g^{-1}, d.w. and DDX (Σ 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT) averaged 99.98 ng. g^{-1}, d.w. Winter OCP loads in the NR reflected the runoff of the heaviest pesticide application period. We estimated the total discharge of DDT into the Atlantic ocean was 96 g.day^{-1}, added to 458 g of HCHs and 257 g of endosulfans (α + β + epoxide) adsorbed by the SPM. PAHs occurred widely along the river (38.83 ± 43.52 µg. g^{-1}) and the highest levels coincided with locations with marked anthropogenic-related activity, such as petroleum/gas exploitation facilities. Risk quotient analysis showed a low risk posed by OCPs, but a high risk of potential effects on biota posed by the PAHs, highlighting the need for mitigation measures.

1. Introduction

Aquatic environments are easily polluted by persistent organic pollutants (POPs), including the world's most widespread organochlorine pesticides (OCPs): hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane and its isomers (DDXs), and chlordanes, including heptachlor, endosulfan, etc. In particular, OCPs have been included as part of the "dirty dozen" list of the Rotterdam Convention (2004) that severely prohibits their production, commercialization, and use. They are also prohibited for use by many national legislations, including Argentina (National Law 24.051, 1991). In parallel, the release and accumulation of polycyclic aromatic compounds (PAHs), a set of natural constituents of crude oil (up to 20%) and products of the incomplete high-temperature combustion processes of various types of organic matter (Shen et al., 2022), also commonly impact aquatic environments. Indeed, OCPs and PAHs have been

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reported to be widely distributed in freshwater bodies (Girones et al., 2020a; Xu et al., 2020; Chen et al., 2020a, 2020b). They also share distribution pathways and access to water: industrial/urban wastewater discharges, land runoff, irrigation channels, atmospheric deposition, and the cleaning of containers and agricultural equipment (Sousa et al., 2020).

The Negro River (NR) in Argentina, South America, has been noted as the most important river in the world, flowing into the sea below the latitude of 40° S (Pasquini and Depetris, 2007). It shows an estimated contribution of 20.10^6 tn/year of sediment to the Atlantic ocean and develops from the confluence of the Limay and Neuquén rivers, in an arid zone about 200 km east of the Andes. These are critical water resources under large-scale anthropogenic pressure (Kopprio et al., 2018).

On one hand, the level of agriculture production in their basins, which involves the spray application of 900 ton/year of chemicals (Anguiano et al., 2008), includes multiple families of pesticides over a long period that extends from October to April (Macchi et al., 2018). While the most used and currently marketed pesticides include carbamates, pyrethroids, organophosphates, and neonicotinoids, there is a group of legacy OCPs that have been widely used throughout the last century until their final prohibition in the 90's. Several precedents show the occurrence of organophosphates and OCP residues in the soil and groundwater in rural areas, with evidence of recent inputs of banned OCPs over the past two decades (Isla et al., 2010; Loewy et al., 2011; Miglioranza et al., 2013; Ondarza et al., 2014; LIBIQUIMA-CITAAC, 2016). In relation to this, there is a gross estimate of 50% loss to the environment during the application process, without reaching the intended targets (LIBIQUIMA-CITAAC, 2016). These pesticides will ultimately be transported to channels, lagoons, and streams due to drifting, runoff, washing by rain, and irrigation. On the other hand, this is the first report to address the levels and distribution of PAHs in the NR water.

Although SPM is an excellent repository of OCPs and PAHs, as defined by their *Kd* ranges in several aquatic environments around the world (Darwano et al., 2014; Cruzeiro et al., 2015), from a global point of view, the OCPs and PAHs transported in river SPM have received much less attention in recent decades compared to research on water (e. g., Belháčová-Minaříková et al., 2022; De Rosa et al., 2022) and sediments studies (e.g., Qazi et al., 2022). Connected to this, anthropogenic pressure has increased rapidly in the NR basin in recent times (Arias et al., 2021), including new cultivated land, crops, and petroleum products, such as nonconventional gas (shale or tight gas), raising environmental concerns. Therefore, one of the main aims of this study is to track the OCP and PAH levels in the SPM of the NR at 21 sampling points along >600 km of the length of the river; for the first time, this will determine the PAH levels transported by the NR while filling more than a decade of null information regarding OCP occurrence and distribution. As a second task, we tackle the hypothesis concerning the legacy of OCPs, addressing whether they persist as an environmental concern in the area after four decades of global prohibition, detailing their main inputs, seasonality patterns, and putative origins. Finally, we put our results into the river's global scenario, addressing the environmental ecotoxicological risks posed by these pollutants and estimating the bulk output of these compounds into the Atlantic Ocean.

2. Materials and methods

2.1. Area of study

The NR is located in the west of Neuquén and Rio Negro provinces (Argentina). The area belonging to the Andes lakes region feeds the system from the precipitation loads that occur in the Andean zone in the form of snow and rain. Water flows towards the NR, the final and main drainage basin of the hydrographic system, which ends at the Atlantic ocean coast. Once it leaves the feeding basin in the Andean region, there is a section that can be identified as a water catchment area outside the

high-water sector. This section includes two important water courses: the Limay River to the south and the Neuquén River to the north, which are the main tributaries of the NR. The NR is located in the third part of this hydrographic system, transporting the water of the entire system that flows to the Atlantic Ocean through the upper, middle, and lower valleys. The NR runs from the confluence point through the valley to the east and crosses the entire Rio Negro province from west to east, including the plateaus, hills, islands, and plains throughout its length. Several economic activities are carried out in the valleys, with most of the population on its margins. The NR basin concentrates the production of 80% and 90% of the apples and pears in Argentina, respectively, and includes the production of small fruit, olives, nuts, and horticulture, among others (Argentine Ministry of Production, 2022). This is achieved by 2226 fruit production facilities on 45,000 ha of farmland. Also, the NR basin has an intensive petroleum industry (national and multinational based holdings), including the production of petroleum and conventional and shale gas (Argentine Ministry of Production, 2022). The NR flows through the departments of General Roca, El Cuy, Pichi Mahuida, Avellaneda, Conesa, and Adolfo Alsina, and its course is spatially structured in different valleys from the confluence point to the Atlantic (mouth): upper valley, middle valley, and lower valley.

2.2. Sampling

The field sampling was carried out in two seasons—austral winter (August 2018) and austral summer (December 2018)—on board National Prefecture vessels. Seasonal summer/winter sampling was chosen to cover the variability in the application of pesticides and river flow due to rain and the input of meltwater from the Andes in the warmer months. VanDoorn bottles were used to sample sub-superficial water, which was then filtered (Glassco system) using a peristaltic pump in situ through 0.45 μm mesh GF/F filters (Munktell) pre-ignited (in an oven at 450 °C for 4 h) and tared. A multiparametric probe was used at each sampling location to obtain water variables, such as temperature, dissolved oxygen, turbidity, conductivity, and pH. This is listed in Supplementary Table 1. The SPM is defined as a material that is retained by filtering through 0.45 μm mesh, which includes both suspended inorganic and organic particles. The SPM content was derived from the weight difference before and after filtration per unit of volume of filtered water. The OCP and PAH content in the SPM can be treated as the content of these pollutants in the particulate phase of the water column.

2.3. Extraction and purification

Samples were wrapped in muffled aluminum foil, stored at 4 °C in the field, and rapidly transported to the laboratory. The samples were then processed according to standardized protocols (EPA 3540C and IOC Nº 20; UNEP, 1993) and analyzed by capillary gas chromatography and mass spectrometry (GC Hewlett-Packard 68906C/MS Hewlett-Packard 5972). After lyophilization, the samples were extracted in Soxhlet devices (8 h) using a 1:1 hexane/acetone mixture. The volume of the extracts was reduced to approximately 5 mL by rotoevaporation (temperature <38 °C) and then transferred to pre-washed clean-up columns (silica gel/neutral alumina 63 μm mesh). The elution process was conducted with 60 ml of hexane (fraction 1), followed by 50 ml of hexane-ethyl ether (9:1), and 20 ml of hexane-ethyl ether (8:2) (fraction 2). Eluates were further evaporated down to 1 mL under a high purity N_2 stream. Prior to the chromatographic analysis, benzo-a-pyrene-d$_{12}$ was added to each sample to evaluate the corresponding recovery.

2.4. Instrumental analysis

PAHs: During the chromatographic analysis, the column used was HP-5MS, 30 m; 0.25 mm id; 0.25 μm layer thickness, the carrier gas was helium and the mass spectrometer was operated in the electron impact mode (EIM) (70 eV). The samples were injected by an auto-sampler

under a splitless mode at 250 °C and the temperature program was as follows: Initial temperature: 70 °C (2 min), heating up to 150 °C at a rate of 30 °C min^{-1}, heating up to 310 °C at a rate of 4 °C min^{-1}; finally, 310 °C for 10 min. The PAHs were monitored using a Selected Ion Monitoring (SIM) mass spectrometer. Each compound was confirmed by its retention time and quantification ion abundance relative to those obtained by authentic standards. The PAHs evaluated were: Naphthalene (Na), Acenaphthylene (Ac), Acenaphthene (Ace), Fluorene (Fl), Anthracene (An), Phenanthrene (Phe), Fluoranthene (Flu), Pyrene (Py), Benzo(a)anthracene (BaA), Chrysene (Cr), Benzo-b-fluoranthene (BbF), Benzo-k-fluoranthene (BkF), Benzo-a-pyrene (BaP), Dibenzo-ah-anthracene (DBA), Benzo-ghi-perylene (BghiP), Indenopyrene (IP). Quantification was performed using the external standard calibration method, which involves the simple comparison of the signal of the samples with the signal of the target compounds (EPA Method 8000D).

OCPs: The target OCPs were α-HCH, β-HCH, γ-HCH, δ-HCH, Heptachlor, Aldrin, Heptachlor exo-epoxide (isomer B), α-Endosulfan, 4,4′-DDE, Dieldrin, Endrin, β-Endosulfan, 4,4′-DDD, Endrin aldehyde, Endosulfan Sulfate, 4,4′-DDT, purchased from Supelco (USA). A Hewlett-Packard 5890 GC with ECD ^{63}Ni and HP-5 (30 m × 0.25 mm, 0.25 μm film thickness, 5% methyl-phenyl-silicon phase) capillary column was used with helium as the carrier gas and with nitrogen as the auxiliary gas. The GC instrumental conditions were as follows: injector temperature: 260 °C; detector temperature: 320 °C; initial oven temperature = 90 °C (2 min); ramp #1, 30 °C min^{-1}; temperature #2 = 180 °C (1 min); ramp #2, 30 °C min^{-1}; temperature #3 = 270 °C (35 min); purge time 0.75 min; injection split-splitless.

2.5. Quality assurance/quality control

The quality of the solvents was chromatographically pure for pesticide analysis (Merck, UVE). Silica and alumina were preheated at 450 °C for 4 h, activated in an oven, and deactivated with Milli-Q water (3% v/v), prior to use. Before and during the analysis, method blanks, instrumental blanks, and solvent blanks were implemented for each batch of six samples. Spiked matrices showed >95% recovery for both sets of compounds. The limit of quantification (LOQ) was set as three times the limit of detection (LOD), which ranged between 0.01 and 0.03 ng g^{-1} for chlorinated compounds and between 0.5 and 3.0 ng g^{-1} for PAHs.

3. Results and discussion

3.1. Organochlorine pesticides

The overall mean value for the total OCPs (Σ16 OCPs) was 648.56 ng g^{-1}, SPM d.w. (4.68 ng.L^{-1} water particulate phase), with a peak of 3496.56 ng g^{-1}, SPM d.w. (15.97 ng.L^{-1}) recorded at PCOR (winter), and a minimum of 48.82 ng g^{-1}, SPM d.w. (0.17 ng.L^{-1}) for LNQN (summer). The median of the total dataset was 444.46 ng g^{-1}, SPM d.w. (2.65 ng.L^{-1}). The complete data set is shown in Supplementary Table 2. The results showed the highest levels for heptachlor, α-endosulfan (and its derivative as sulfate), and α-HCB. The sites with the highest concentrations—from west to east—were ORO (NR6), PCOR (NR10), POMO (NR16), CONE (NR17), PALO (NR20), and CPAT (NR21).

There is only one precedent accounting for OCP levels in the SPM of the NR, dating 15 years ago, which showed the occurrence of several POPs with a high predominance of HCHs, DDXs, and endosulfans (Miglioranza et al., 2013) (see Fig. 2). Although that study was performed before the global prohibition of endosulfan and eight years after the national DDT restriction (2006), the results indicated a continued use of that pesticide. Fig. 3 shows a comparison of our results with the closest precedent. At first sight, concentrations of the same order of magnitude were found for the OCPs. While a decrease in HCHs and endosulfan levels transported by SPM were recorded in the middle valley of the NR (the area with the highest levels of chlorinated pesticides), an increasing trend of HCHs and endosulfan was visible in the

lower valley. Concerning DDT, despite decades of bans and regulation, the detection of parental DDT and general DDX levels comparable to those measured in 2006 show that the use of DDT is still an environmental issue for the basin. A worldwide comparison with other rivers and freshwater systems showed higher OCP levels in the NR in terms of weight units (ng.g^{-1}, SPM d.w.); however, regarding the relatively low SPM levels, the amounts of transported OCPs considering the particulate fraction of the water column were below other rivers, such as the Yamuna (India), Gomti (India), Jinjiang, Daliao, Yangtze (China), and in the same order as the river Tiber (Italy, Supplementary Fig. 3).

3.2. HCHs

HCHs are a group of highly persistent contact pesticides that can persist for 14 years in sandy sediments and eight weeks in the water column before being absorbed in other organic phases (FAO and UNEP, 2021). They comprise a group of isomers that are frequently found in various commercial products, such as benzahex, dibenzoylhydrazine, dolmix, fortified benzene hexachloride, gammacide, gammacoid, gammexane, gamtox, gexane, hexablanc, hexachlor, hexachloran, 1,2,3,4,5,6-HCH, hexafor, hexamul, hexapoudre, hexyclan, isatox, kotol, lexone, lintox, and soprocide (https://oehha.ca.gov/air/chemicals/hexachlorocyclohexane-technical-grade). Our results show that all HCH isomers were found adsorbed by the SPM in the NR at different levels of concentration, with maximum values for α-HCH. The average levels of $\sum$HCHs (α + β+ γ) were 776.46 ng g^{-1}, SPM d.w. The detection frequency was α > β > γ and δ-isomer, with maximum values recorded at PALO (NR20, 915.27 ng g^{-1}, SPM d.w., winter) and ALLD (NR7, 195.55 ng g^{-1}, d.w. SPM, summer). The putative sources of HCHs in the environment involve the use of a technical product or lindane. While the typical congener distribution in the technical product includes 55%–80% α-HCH, 5%–14% β-HCH, 8%–15% γ-HCH, and 2%–16% δ-HCH, as is shown in diverse literature, the source distribution can be obtained from the isomer's ratios α-HCH/γ-HCH and β-HCH/(α+γ)-HCH (Zafarani et al., 2022; Hu and Tao, 2022). For instance, α-HCH/γ-HCH for technical HCH ranges from 4 to 7, whereas for lindane it is less than 0.1. This is mainly due to commercial lindane formulations, which frequently contain more than 99% of γ-HCH (Hu and Tao, 2022). Also, the ratio β-HCH/(α+γ)-HCH may be indicative of the age of the inputs; this is due to β-HCH stability under environmental conditions. Traditionally, a high β-HCH/(α+γ)-HCH coefficient indicates past use of technical HCH or lindane, whereas scores of this ratio of less than 0.5 may indicate recent use of both (Wang et al., 2013). On one hand, the mean α-HCH/γ-HCH ratio for the NR was 4.26, indicating a prevalent usage of technical HCH over lindane in the NR basin. On the other hand, the mean ratio β-HCH/(α + γ)-HCH was 0.24, pointing to its recent use. During winter, stations ORO (NR6), ALLD (NR7), PCOR (NR10), and PALO (NR20) showed recent contributions of technical HCH, while POMO (NR16) and CPAT (NR21) showed past use (historical/degraded). However, in summer 2018, a recent technical HCH contribution was seen at the following stations: CIPO (NR5), ORO (NR6), PCOR (NR10), CHEL (NR14), and PALO (NR20), whereas a past or residual pattern of HCH was found at ALLD (NR7), POMO (NR16), and CPAT (NR21). Besides the season, the stations ORO (NR6), PCOR (NR10), and PALO (NR20) showed a constant "recent input" signature of technical HCH, whereas the stations POMO (NR16) and CPAT (NR21) showed historical/degraded records. This contrasted with previous findings for the area, which showed a prevalence of lindane over technical HCH (Miglioranza et al., 2013). γ-HCH is regulated in Argentina for whole water (dissolved + particulate); however, SPM records could provide a sound proxy, since the highest proportion of HCH is commonly retained in the particulate phase (Miglioranza et al., 2013). While the nationally available chronic exposure limit for the protection of aquatic life by γ-HCH (20 ng.L^{-1}) was never exceeded in this study, an even more conservative guideline for freshwater life protection, the Canadian Council of Resource and Environment Ministers (10 ng.L^{-1} $\sum$HCH), has

never been exceeded for the NR.

3.3. DDXs

DDXs detected levels in water, comprising the sum of 4,4′-DDE, 4,4′-

DDD, and 4,4′-DDT, averaged $1,24 \pm 0.13$ ng.L^{-1} (99.98 ng g^{-1}, SPM d. w.). The frequency of detection was 52%, 21%, and 19% for DDD, DDT, and DDE, respectively. The summary of parental DDT and its isomers represented approximately 9% of the total organochlorines detected in the river water. The maximum value for DDT was recorded at POMO

Sampling Station		Lat/Long	Land Use/Land Cover
NR1	ARRO	Lat: 39° 07'S Long: 68° 56'W	Residential high density
NR2	VALE	Lat: 38° 44'41''S Long: 68° 18'20''W	Recreational Area. Fruits Production
NR3	NNQN	Lat: 38° 44'41''S Long: 68° 18'20''W	Residential high density
NR4	LNQN	Lat: 38° 59'20''S Long: 68° 00'24''W	Main Sewage discharge. Residential High density
NR5	CIPO	Lat: 38° 59'20''S Long: 67° 59'13''W	Former Recreational (presently banned)
NR6	ORO	Lat: 38° 59'49''S Long: 67° 57'18''W	Industrial discharge, fruits production
NR7	ALLD	Lat: 39° 01'35''S Long: 67° 51'36''W	Industrial Discharge. Residential medium density
NR8	ALLG	Lat: 39° 01'35''S Long: 67° 50'37''W	Gas duct. Fruits production
NR9	ALLT	Lat: 39° 01'56''S Long: 67° 50'27''W	Water intake point for human comsuption
NR10	PCOR	Lat: 39° 06'32''S Long: 67° 37'48''W	Recrational. Residential medium density
NR11	ROCA	Lat: 39° 04'23''S Long: 67° 31'54''W	Waste Water Discharge. Fruit Production
NR12	REGI	Lat: 39° 10'27''S Long: 67° 06'25''W	Recreational. Residential medium density
NR13	CHIC	Lat: 39° 07'56''S Long: 66° 49'57''W	Waste Water Discharge. Residential low density
NR14	CHEL	Lat: 39° 05'29''S Long: 66° 31'50''W	Recreational. Residential low density
NR15	CHOE	Lat: 39° 18'07''S Long: 65° 39'46''W	Industrial Discharge. Residential medium density
NR16	POMO	Lat: 39° 29'17''S Long: 65° 39'28''W	Recrational. Residential medium density
NR17	CONE	Lat: 40° 06'18''S Long: 64° 27'84''W	Recreational. Residential low density
NR18	MITR	Lat: 40° 27'21''S Long: 63° 47'09''W	ship traffic, goods transportation
NR19	VIED	Lat: 40° 52'32''S Long: 62° 54'34''W	Water intake point for human comsuption. Vegetables production
NR20	PALO	Lat: 40° 49'74''S Long: 62° 56'57''W	Waste Water Discharge. Residential low density
NR21	CPAT	Lat: 40° 48'05''S Long: 63° 00'42''W	Waste Water Discharge. High density

Fig. 1. Map showing the area of study along the NR, the sampling stations, and their references.

(NR16, 1.14 ng.L^{-1}, summer), for DDE at ORO (NR6, 0.91 ng.L^{-1}, summer), and for DDD at CPAT (NR21, 1.45 ng.L^{-1}, winter). Commercial DDT usually contains 75% 4,4′-DDT, 15% 4′-DDT, 5% 4,4′-DDE, <0.5% 4,4′-DDD, <0.5% 4′-DDD, <0.5% 4′-DDE, and 5% unidentified compounds (WHO 1979). DDT isomers have a high persistence in the environment and gradually degrade to DDE and DDD under aerobic and anaerobic conditions (Allen-Gil et al., 1997; Arias et al., 2011). Once released into the environment, 4,4′-DDT degrades to 4,4′-DDE, and the relative abundance of the parent compound and its metabolite is used to distinguish recent use (DDT/DDE >1) from those released in the past (DDT/DDE <1) (Pozo et al., 2009; Yatawara et al., 2010; Verhaert et al., 2013). Previous reports point to high inputs of DDT in the NR due to intense ongoing agricultural activity (Ondarza et al., 2010, 2011; Gonzalez et al., 2010; Miglioranza et al., 2013). In particular, in addition to water SPM and sediment resuspension transport, Miglioranza et al. noted a west–east direction of wind transport carrying DDT loads, which explains the high DDT levels at Viedma (VIED, NR19) (Miglioranza et al., 2013). Similarly, in this study, we found DDT/DDE>1 ratios mainly at the west stations, namely PCOR (NR10), ROCA (NR11), REGI (NR12), CHOE (NR15), POMO (NR16), MITR (NR18), PALO (NR20), and CPAT (NR21), with maximum parental DDT levels recorded at POMO (NR16) (Fig. 1). This indicated recent entry of DDT from primary sources (land application and washing) or secondary sources (e.g., sediment resuspension and maintenance dredging). Additionally, DDD showed a high detection frequency (52% of sampling stations), pointing to the wide use of commercial DDT in the past that could have undergone anaerobic degradation processes in the river. Regarding guidelines for freshwater quality protection, there are varying criteria. For instance, a value of 1 ng.L^{-1} was originally established by the Canadian Water Quality Guidelines, whereas a value of 0.4 ng.L^{-1} for DDT, 0.13 ng.L^{-1} for DDE, and 2 ng.L^{-1} for DDD was established by the Texas Commission on Environmental Quality (USEPA, 1980). Australia and New Zealand state a 10 ng.L^{-1} (95% protection) as a recommended trigger value for slightly–moderately disturbed systems (https://www.waterquality.gov.au). Then, according to the range of DDX levels in the NR and considering the particulate phase of the water column, exceedance of various current international protection levels persist after two decades of bans, which, in connection to the evidence of recent inputs to the river, raise environmental concerns.

3.4. Endosulfan

Technical grade Endosulfan is a mixture that usually contains 95% of the two diastereoisomers, known as α-endosulfan and β-endosulfan in proportions from 2:1 to 7:3, and 5% of impurities and degradation products (GFEA-U, 2007; Hu et al., 2009; Tombesi et al., 2018). Both isomers decompose in the environment, producing endosulfan sulfate with a similar structure to the parent compound but more toxic (Stadler et al., 2006). α-endosulfan was one of the most abundant organochlorine compounds detected in the NR water, with a general mean of 1.18 ng.L^{-1} water (particulate phase, 141.64 ng g^{-1}, d.w. SPM), and a median of 0.62 ng.L^{-1}. The maximum α-endosulfan level was detected at PCOR (NR10, summer, 10.93 ng.L^{-1}); however, the general levels detected ranged from 1.29 ng.L^{-1} to below the detection limit. The frequency of detection was high, accounting for 50%, 52%, and 61% of the samples for α, β, and sulfate-endosulfan. The latter compound was the degradation product of α+β-endosulfan, endosulfan sulfate (mean = 0.89 ng.L^{-1}), which is more toxic and more persistent, and was found at 61% of the stations, suggesting widespread usage and persistence along the river. In fact, endosulfan has been one of the most widely used chlorinated pesticides in Argentina as a broad-spectrum insecticide and acaricide in fruits, vegetables, and cereal production; for example, it has been widely used in soybean production. Since 2013, its import and use have been prohibited in Argentina (Res. SENASA 511/11). Despite this, it has recently been detected in various scientific studies of air and sediments in the area. For example, 3400 pg/m^3 of Σendosulfans were detected in the air in the southwest of Buenos Aires (Tombesi et al., 2014) and there was a maximum of 26.2 ng g^{-1} of α-endosulfan in the Bahía Blanca estuary (sediments) (Arias et al., 2011). Furthermore, a study involving atmospheric OCP levels in the Negro basin, conducted between 2011 and 2013, concluded that endosulfan and DDTs were the most prevalent pesticides in the NR watershed at that time (Miglioranza et al., 2021), demonstrating the continued use of endosulfan and technical DDT. Total endosulfan concentration (α+β+sulfate) averaged 2.30 ± 0.49 ng.L^{-1} (213.16 ng g^{-1}, d.w. SPM), which is much lower than the national water guideline for biota protection in Argentina of 20 ng.L^{-1}, (National Law N° 24.051). Finally, the acute exposure criterion developed by the Canadian Environmental Council (CCME) for the protection of aquatic life is even higher, 60 ng.L^{-1} for endosulfan (CCME, Canada) which was never exceeded in the NR particulate phase; however, the CCME chronic exposure guide level (3 ng.L^{-1}) was occasionally exceeded in this study.

3.5. Heptachlor

Heptachlor is a cyclodiene compound constituent of technical-grade chlordane with approximately 10 percent by weight. Chlordane was used and formulated in Argentina (available information shows 220 tons
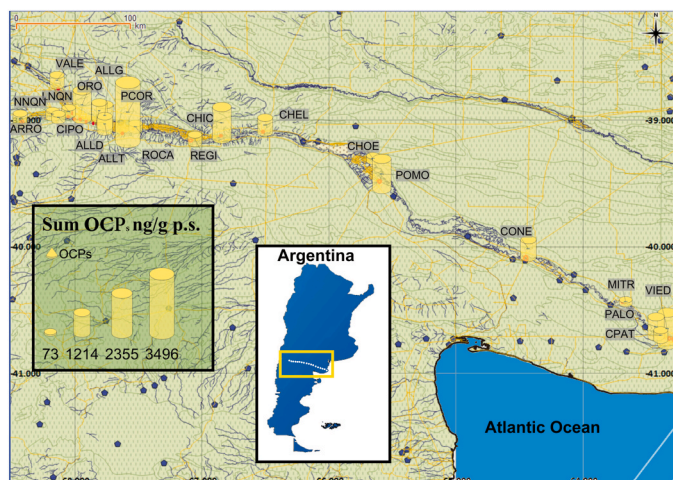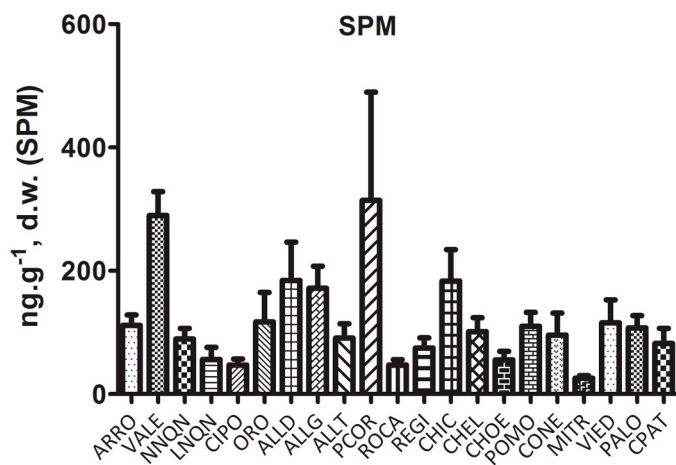

Fig. 2. Spatial distribution of SPM organochlorine compounds at 21 locations along the NR, Argentina. SPM total organochlorine concentrations (sum of the 16 target compounds) at the sampled stations (box = mean, bar = standard error of the mean).
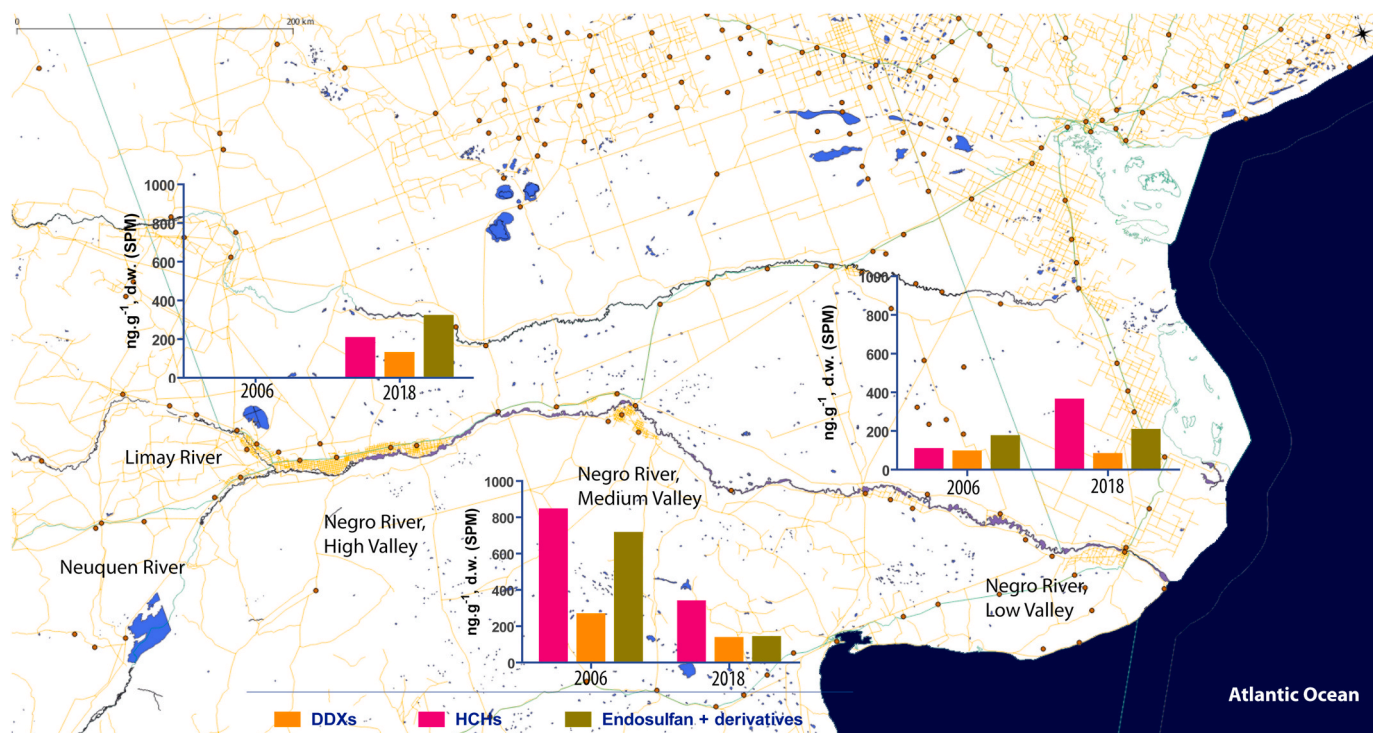
Fig. 3. Past and present organochlorine distribution in the upper, middle, and lower reaches of the NR, according to the chemical groups hexachlorocyclohexanes, dichlorodiphenylchloroethanes, and endosulfans (Miglioranza et al., 2013).

formulated in 1967) as a soil and seed treatment to control ants, cutworms, maggots, termites, and other pests in agriculture and in domestic applications; however, although prohibited worldwide, several formulations still seem to be in use (58.5 tons were imported by Venezuela between 1975 and 2003; Girones et al., 2020b). It is a persistent organic pollutant (Stockholm Convention) with a half-life of ~1.3–4.2 days (air), ~0.03–0.11 years (water), and ~0.11–0.34 years (soil), poorly soluble in water (0.056 mg.L^{-1} at $25\,^{\circ}C$); thus, it tends to be adsorbed by soil particles and it evaporates. Heptachlor and its degraded compound, heptachlor epoxide, were frequently detected in our surveys in the NR, with a general average SPM concentration of 172.4 ng g^{-1}, d.w. and 89.1 ng g^{-1}, d.w., respectively, showing a parental/degraded compound

ratio of 2:1. This contrasts with precedents for the area (Miglioranza et al., 2013; Ondarza et al., 2014), suggesting that despite decades of prohibition, recent usage of any of its technical mixtures has occurred in the area over the last 15 years. This is consistent with other recent reports on Argentine rivers (e.g., the Uruguay river; Williman et al., 2017), where heptachlor has been found at higher concentrations than the aquatic life protection limits, demonstrating the current availability and usage of this compound in the country.

The seasonal OCPs loads in the NR were different, with higher amounts of OCPs reaching the river in winter than in summer ($p < 0.05$). The NR winter OCP loads could reflect the runoff of pesticide application from January to April when the water supply to the irrigation channels
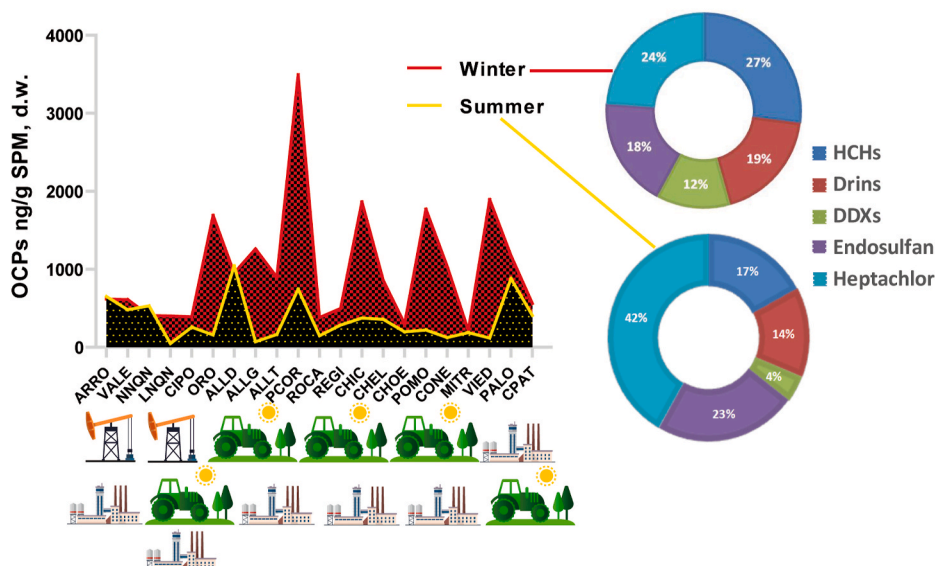

Fig. 4. Organochlorine pesticide load in the SPM of the river Negro during the winter and summer seasons, showing the main land use/cover at peak zones.

ceases during and after harvest (Macchi et al., 2018). As the irrigation network may act as a transport route for the applied pesticides to the river, a diminished flow in the channels would lead to a delay in the flow of OCPs to the river. Also, lower air and water temperatures contribute to lower evaporation losses of these compounds. During the fall (April, May, and June), the highest rainfall period increases the flow of the irrigation channels, allowing the translocation of OCPs from the river into the SPM; this could be the rationale for the winter season peak of organochlorine compounds at the NR (Fig. 4). In contrast, pesticide loads were lower during the summer. While the December OCP loads of SPM could reflect the small fruit period and pre-harvesting crop spraying (INTA, 2020), higher environmental temperatures and evaporation rates of pesticides should favor the water–air transition processes, implying less transportation through the river water.

We applied a principal components analysis (PCA) to dimensionally reduce the multivariate OCPs dataset. The PCA allowed us to extract three principal components that explained more than 60% of the total variance. Significant loading that contributed to each component (marked in red circles in Supplementary Fig. 1) resulted in their classification, with a group of compounds contributing to each variation vector. As a result, Factor 1 was driven by the use of technical HCH and aldrin and the past use of heptachlor; Factor 2 was driven by heptachlor, lindane, dieldrin residues, and the past use of DDT (DDE), while Factor 3 was noted as past/degraded use of endosulfan and DDT (Supplementary Fig. 1). The distribution of the factor scores allowed us to ordinate sampling locations for these three factors, explaining the distribution of the OCPs along the river. On one hand, the highly agricultural locations, such as ALLD (NR7), ALLG (NR8), PCOR (NR10, located in the upper reach of the river), POMO (NR16, at the middle reach), and VIED (NR19, lower reach), showed a signature for the occurrence of technical HCH, aldrin, and evidence of past use of heptachlor. On the other hand, CIPO (NR5), ORO (NR6, upper reach), and CONE (NR17, lower reach) correlated with the use of heptachlor, lindane, and dieldrin and evidence of degraded DDT. Finally, Factor 3 was interpreted as a degraded OCP signature for endosulfan and DDT, which correlated with ALLD (NR7), ALLG (NR8), and ROCA (NR11) locations in the upper reach, POMO (NR16) at the middle, and PALO (NR20) and VIED (NR19) locations in the lower reach, following an east–west direction. Although SPM is a moving phase that can integrate several OCP inputs into the river, the PCA led us to conclude that the upper reach (stations NR3–NR10, Fig. 1) showed evidence of technical HCH, drines, and heptachlor (degraded and parental) usage accessing the system. Also, a signature for degraded DDT and endosulfan was widespread in the three basins as a sign of the extensive usage of these compounds in crop production areas over recent decades. Finally, as shown in Fig. 3, the lower valley showed higher endosulfan records than the 2006 precedents (Miglioranza et al., 2013). In light of the PCA results—the lower reach highly coordinated with Factor 3—we conclude that this endosulfan degraded signature, even with higher levels than 2006, could be a positive consequence of the endosulfan prohibition by law in 2013.

We calculated the OCPs' ecological risk using the risk quotient (RQ) approach; for this, each RQ was computed as follows:

$$RQ = \frac{C}{PNEC} \quad (1)$$

where C is the individual congener concentration, and PNEC is the Probable No-Effect Concentration estimated for each OCP congener. Each PNEC value was obtained from the ECOTOX database (www.epa.gov/ecotox). PNEC and calculated RQs for each sampling station and season are summarized in Supplementary Tables 3 and 4 Traditionally, for RQ values < 1.0 the environmental risk after exposure to the recorded OCP levels are low. In this survey, RQs were <0.01 in all cases, indicating a very low risk to biota posed by the exposure to OCPs.

Considering an outlet discharge of 550 m^3.seg^{-1} (EVARSA 2004) and our average SPM records for the lower reach (27 g m^{-3}) with the average

OCP levels measured at the lower reach, we estimated the total discharge of DDT at 96 g.day^{-1}, added to 458 g of HCHs and 257 g of endosulfans (α + β + epoxide) adsorbed onto the SPM. These values are in the order of those estimated by Miglioranza et al. (2013), showing that despite decades of prohibition and law regulations, there is a prevalence and present concern about these compounds, which are still transported into the NR.

4. Polycyclic aromatic hydrocarbons

The SPM showed detectable concentrations of PAHs at all sampling locations of the NR. The overall mean concentration for total PAHs for the study area was 38.83 ± 43.52 μg g^{-1}, SPM d.w. (n = 42), with a minimum of 4.82 μg g^{-1}, d.w. and maximum values from west to east at NNQN (NR3, 193.48 μg g^{-1}, d.w.), ORO (NR6, 91.36 μg g^{-1}, d.w.), ALLD (NR7, 199.36 μg g^{-1}, d.w. [the highest record in this study]), ALLG (NR8, 30.04 μg g^{-1}, d.w.), ALLT (NR9, 45.25 μg g^{-1}, d.w.), REGI (NR12, 83.36 μg g^{-1}, d.w.) and PALO (NR20, 118.01 μg g^{-1}, d.w.). This distribution is schematized in Figs. 1 and 5. The highest records of PAHs at the SPM matched locations with marked anthropogenic-related activity, such as petroleum/gas exploitation facilities (Neuquén, Fernandez Oro, and Allen) and major urban developments (Regina, Viedma, and Patagones; Fig. 5). The most abundant compounds were BaA, Cr, Py, and Phe (Fig. 5A). The most frequently detected compounds were Ace, Py, Phe, Ac, Flu, and Na.

In comparison to other large rivers worldwide, the PAHs concentrations in the SPM were higher than other rivers such as the Tibet, Seine, and Mississippi rivers (Supplementary Fig. 3; Fernandes et al., 1997; Mitra and Bianchi, 2003; Patrolecco et al., 2010); however, considering the relatively low SPM levels in the NR, the amounts of PAHs transported by the SPM were in the low range when considering the particulate fraction of the water (mean 352.7 ng.L^{-1}), i.e., below the values reported for the Yellow river (Sun et al., 2009), Dliao river basin (Guo et al., 2009), and Pearl river (Deng et al., 2006), and similar to those reported for the Sarno river (Supplementary Fig. 3; Montuori and Triassi, 2012).

Although the geo-spatial distribution of the SPM should be interpreted as a snapshot of the river, SPM is the transport vector for innumerable compounds and the preferential partition matrix for organic compounds with high K$_{ow}$ values, such as PAHs and other hydrocarbons (Mackay et al., 1992). Seasonal analysis showed a highly dynamic system with slightly higher average PAH flows in summer than in winter. It is noteworthy that there is a difference in the river flow between the cold and warm seasons, which could influence the load of PAHs due to higher runoff. In our study, this seasonal difference was particularly driven by high PAH records at Neuquén (NQNN, NR3), Fernandez Oro (ORO, NR6), and Allen (ALLD [NR7], ALLT [NR8], and ALLG [NR9]), all locations that support intensive industrial/oil/gas facilities in the area as potential sources.

To further evaluate the potential ecological risk posed by PAHs adsorbed by the SPM of the NR, RQs were calculated following Kalf et al. (1997), Cao et al. (2010), and Zhang et al. (2016) as follows:

$$RQ = \frac{CPAHi}{CQV} \quad (2)$$

where CPAH$_i$ is the individual concentration of a certain compound in the SPM, and CQV is the corresponding quality value. For these, we used negligible concentrations (NCs) and maximum permissible concentrations (MPCs) referenced by Cao et al. (2010) and Wang et al. (2016), and then the RQs for the NR were calculated as follows:

$$RQNCs = CPAHi/NCi \quad (3)$$

$$RQMPCs = \frac{CPAHi}{MPCi} \quad (4)$$

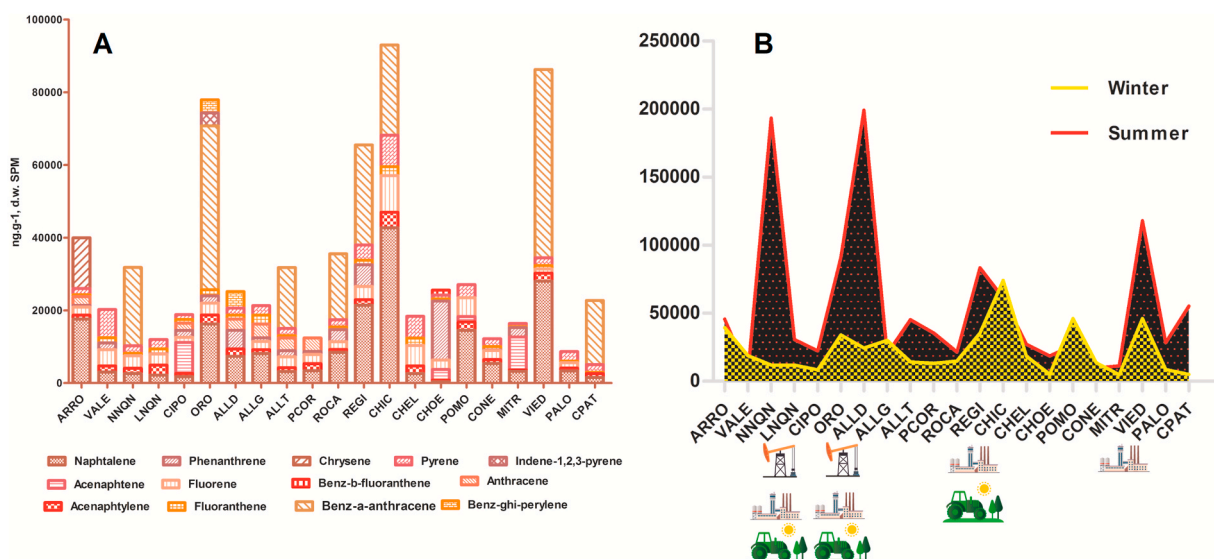The calculated RQs and NC$_i$ and MPC$_i$ of the NR used for the quotient

Fig. 5. A. Averaged cumulative distribution of PAHs along the different NR regions (units: ppb, ng/g, d.w.) and B. Total PAH seasonal distribution showing the main land use/cover at the peak zones.

calculus are listed in Supplementary Table 5. All the computed $RQsNC_i$ were >1, which indicated that there are no areas with negligible concern in regard to PAHs. Also, nine $RQMPC_i$ were >1 (Naph, Ac, Ace, Flu, Phe, An, Py, Chry, and BbF), which indicates a high risk of potential effects to biota and a need for mitigation actions (Wang et al., 2016).

The compositional pattern of PAHs was dominated by compounds with two, three, and four rings in their structure, in that order, with percentage averages ranging from 41% to 19% relative abundance. Occasionally, six-ringed PAHs were detected above LOQs, particularly at ALLG (NR7) and ALLD (NR8) locations close to gas/petroleum facilities. The most abundant mass groups (two and three rings) were represented by Na, Ac, Fl, and Phe. These compounds are characterized as low molecular weight compounds, characteristic markers of petrogenic sources. The group of four benzene rings, markers of mixed origin commonly indicative of fuel combustion and organic matter, was represented by Flu, Py, and Cr. The detection of six-ringed PAHs (e.g., benzo-fluoranthenes) suggests an additional contribution of high-temperature pyrolytic processes (ALLG [NR8] and ALLD [NR7]). We applied traditional molecular indices to further assess the potential sources and classify sites (Yunker et al., 2002; Budzinski et al., 1997), including Flu vs. Flu + Py (Fl/202), An vs. An + Phe (An/178), and the low/high molecular weight (LMW/HMW) index. On one hand, while Fl/202 < 0.40 is often a marker of petrogenic origin (non-combusted petroleum, diesel, coal, oils), >0.40 and < 0.50 points are commonly attributed to a combustion origin (combustion of fossil fuels, such as road traffic, engines, etc.), and values above 0.50 are commonly attributed to the burning of pasture, wood, and coal. On the other hand, while An/178 values > 0.10 indicate pyrolysis and <0.10 non-combusted petroleum sources, the LMW/HMW<1 suggest a load of pyrolytic PAHs, while higher values indicate petrogenic sources (Yuan et al., 2001).

SPM PAHs in the NR mainly showed mixed contributions from non-combusted petroleum, oil, and fuels to oil and gas combustion and biomass burning (Supplementary Fig. 2). In agreement with the observations stated in the above paragraphs, the upper reach of the river showed a mixed imprint of PAH's signature, with contributions from non-combusted fuels and combusted petroleum derivatives indicating a strong anthropogenic pressure in the area.

5. Conclusion

After tracking the levels and distribution of OCPs and PAHs in the SPM of the NR, we conclude that some legacy OCPs are still an

environmental concern in the highly agro-industrial basin of the river, while PAHs pose a certain risk to freshwater biota in all areas. As mentioned, the limitations of our study rely on the variability of the SPM phase and river hydraulic conditions; however, the high number of samples involved, and the seasonal sampling under different flow and temperature conditions, helped to strengthen our conclusions. We concluded that despite years of prohibition, an increasing trend of accumulation of HCHs and endosulfan was shown in the lower valley, with evidence of a prevalent usage of technical HCH over lindane and recent HCH inputs into the river. Moreover, according to the measured DDX range, we found that exceedance of various current international protection levels persists even after two decades of the national ban on these pesticides, while evidence of recent inputs of DDT to the river raises an alert. We also demonstrated the prevalence of endosulfan, a compound banned in 2013 (Resolution Nº 511/11, SENASA Argentina), and its derivatives in the SPM of the NR; this shows remarkable chemical pressure on freshwater ecological systems. Indeed, we estimated the daily total discharge of DDT (96 g), HCHs (458 g), and endosulfans (257 g) adsorbed by the SPM, which was in the order of that estimated in 2006.

With regard to PAHs, we reported their widespread occurrence and distribution along the entire river for the first time. We concluded that the maximum levels occurred in highly anthropogenic locations, peaking at major urban conglomerates with oil/gas extraction facilities. Indeed, at those locations, we found that a major contribution of PAHs originated from non-combusted petroleum, oil, and fuels, and oil and gas combustion. Additionally, we performed an RQ analysis for the PAH levels transported by the SPM particles in the river and concluded that in regard to PAHs there were no areas with negligible concern; moreover, they predicted a high risk of potential effects on the biota, which would need urgent control/mitigation actions, for instance, the treatment of urban effluents that flow into the river and the urban/industrial atmospheric emissions in the NR basin. As previously mentioned, there are limitations to our study, since the SPM should be interpreted as a snapshot of river transport, which is also subjected variations in river flow. In this study, this variability was reduced by a high number of sampling points and different seasons throughout the year. The future scope should address regular monitoring of environmental levels of OCPs, which can be an effective control measure to decrease the illegal application of these products along the valleys. Additionally, we suggest addressing air emissions and the control and monitoring of urban wastewater treatment plants along the NR basin to mitigate potential

hydrocarbon inputs to the river.

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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.

Data availability

Data will be made available on request.

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We dedicate this research *in memoriam* to Dr. Mariza Abrameto and Juan Carlos Del Bello.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121067.

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