

Atmospheric Occurrence of Legacy Pesticides, Current Use Pesticides, and Flame Retardants in and around Protected Areas in Costa Rica and Uganda

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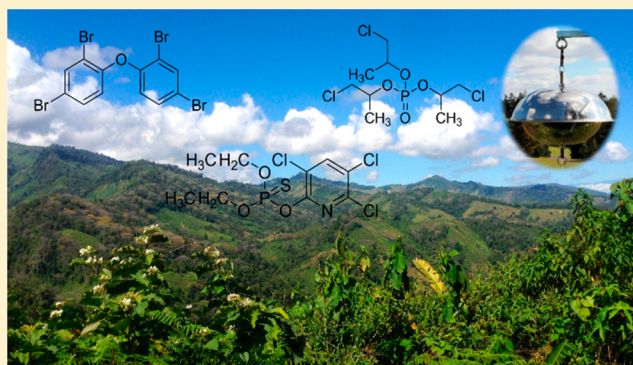
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Supporting Information

ABSTRACT: Protected areas have developed alongside intensive changes in land use and human settlements in the neighboring landscape. Here, we investigated the occurrence of 21 organochlorine pesticides (OCPs), 14 current use pesticides (CUPs), 47 halogenated flame retardants (HFRs), and 19 organophosphate esters (OPEs) in air around Las Cruces (LC) and La Selva (LS) Biological Stations, Costa Rica, and Kibale National Park (KNP), Uganda using passive air samplers (PAS) with polyurethane foam (PUF) discs (PAS-PUF). Significantly higher concentrations of CUPs were observed around LS, while LC had a higher concentration of OCPs. Land use analysis indicated that LS had a higher fraction of agriculture than LC (33% vs 14%), suggesting the higher CUPs concentration at LS was related to pesticide intensive crops, while higher OCPs concentration at LC may be attributed to the area's long agricultural history characterized by small-scale subsistence farming or long-range transport. In Uganda, CUPs and OCPs were generally lower than in Costa Rica, but high concentrations of HFRs were observed inside KNP, possibly due to human activity at research camps near the protected forest. This is the first study that documented the occurrence of anthropogenic chemicals in the air at protected areas with tropical forests.



INTRODUCTION

Throughout the tropics, the creation of protected areas to conserve biodiversity and ecosystems has developed alongside intensive changes in agricultural systems and human settlements. One overlooked effect of this juxtaposition is increased exposure to synthetic chemicals resulting from pest control, vehicle and building emissions, and passive diffusion from household products. Concern over the effects of anthropogenic chemicals became a major public issue with the publication of *Silent Spring* decades ago,¹ but the problem persists with the constant addition of novel chemicals to the environment. This problem may be particularly severe and overlooked in the tropics, where current rapid development and issues of temperature, humidity, rainfall, and pest diversity may promote use and long-range transport of these chemicals, particularly pesticides. Further, many tropical areas, including the sites examined in the current study, are biodiversity hotspots comprised of a high number of endemic species.² The potential endocrine disrupting effects of some of these

compounds are of particular concern for wildlife and humans.^{3,4} For example, thyroid hormone production can be inhibited by the pesticides cyhalothrin and fipronil.^{5,6}

Effects of pesticides have been documented across a diverse range of organism, including nonhuman primates.⁷ Primates and elephants living in mixed tropical forest-agricultural landscapes are of particular concern given their frequent interactions with human populations and agricultural systems via crop-raiding and exposure to anthropogenic chemicals used in agricultural and residential settings surrounding protected areas.^{8–11} For example, it has been suggested that exposure to agricultural pesticides has caused deformities in chimpanzees and baboons in western Uganda, including one of our study sites.^{12,13} It has also been suggested that agricultural pesticides

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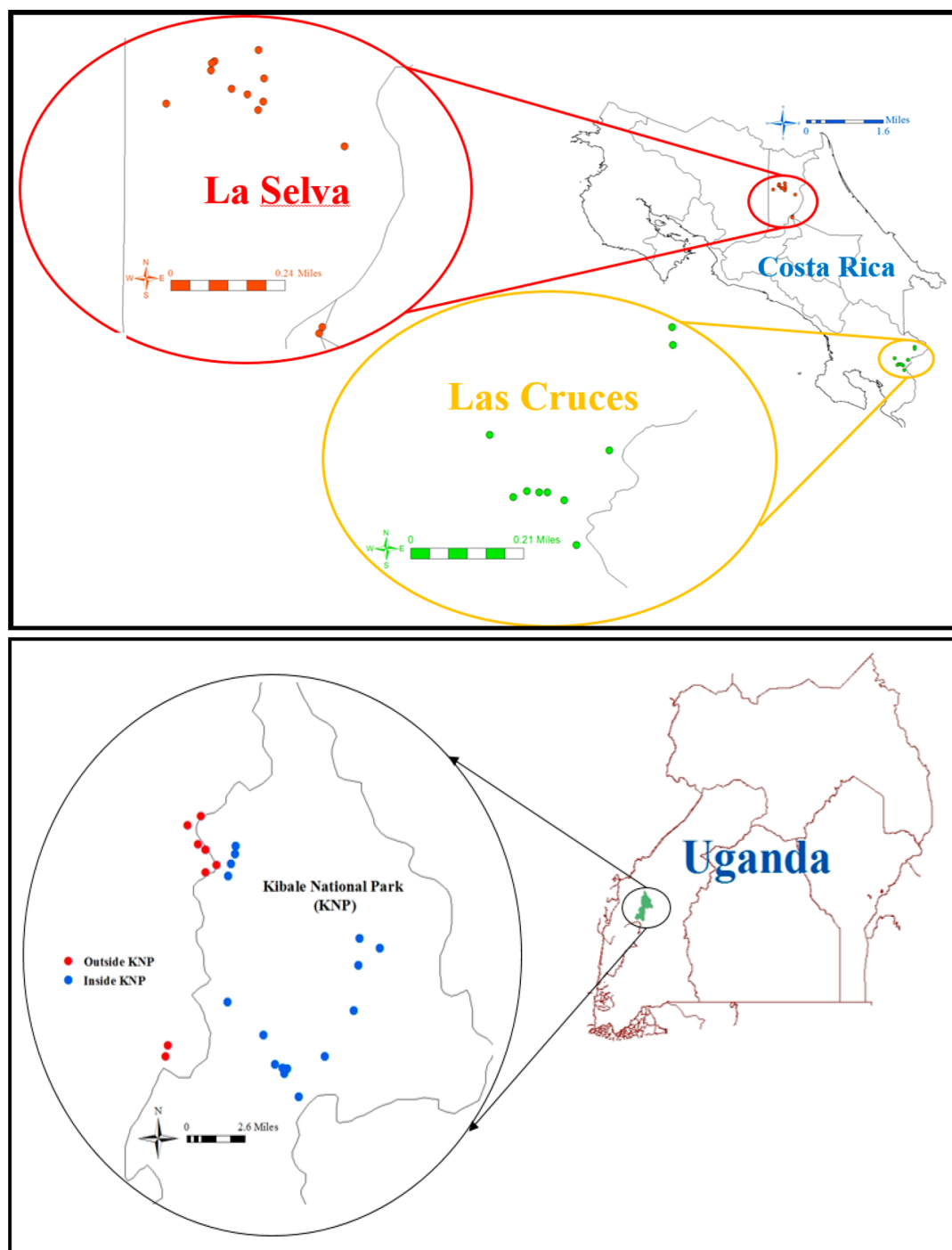


Figure 1. Sampling sites at La Cruces and La Selva in Costa Rica and at Kibale National Park in Uganda.

were responsible for changes in fur color in howler monkeys in Costa Rica, near one of our other study sites.¹⁴

While evidence for exposure to and effects of anthropogenic chemicals is scant for tropical vertebrates, the extent to which they are directly exposed to and affected by them may have major impacts on the ability of endangered species to maintain their population numbers. Examining the diversity and concentrations of anthropogenic compounds to which wild vertebrates are exposed through air in and around protected areas is an area of research that deserves much more attention than it currently receives.

Costa Rica and Uganda are two examples of tropical countries aiming to balance large-scale, pesticide-intensive agricultural approaches targeted to export crops, with small-scale subsistence farming and conservation of biodiversity. Furthermore, they are both rapidly developing, have high human population densities, and attract global tourists and international researchers based on their high levels of biodiversity and protected area infrastructure. Costa Rica is a global leader in both conservation and intensive tropical agriculture, where a fifth of the country has some type of protected status.¹⁵ Costa Rica has some of the highest yields per hectare of bananas and pineapples in the world, and the

use of pesticides per hectare is higher in Costa Rican agriculture than in most industrialized countries.¹⁶ For example, the application of chlorpyrifos was 130 t in 2010 in Costa Rica and 1800 t in 2012 in United States, respectively.^{17,18} In the past, Costa Rica mainly exported coffee, but bananas and pineapples became primary agricultural exports in the 1990s. Commercially grown bananas and pineapples are among the most pesticide-intensive crops.¹⁹ Unlike the agriculture industrialization of Costa Rica, Uganda is characterized as an “agriculture-based” country dominated by small scale farms. The three main types of agricultural land use in Uganda are tea, maize, and mosaic home gardens.^{20,21} Protected areas cover 16.1% of the total land area in Uganda.²² Uganda also has one of the fastest growing populations in the world with a 3.2% annual growth rate,²³ which is putting increasing pressure on these protected areas, as well as agricultural systems.²⁴

Therefore, we investigated the atmospheric distribution of anthropogenic chemicals, including organochlorine pesticides (OCPs), current use pesticides (CUPs), halogenated flame retardants (HFRs), and organophosphate esters (OPEs), in relationship with human activities around protected areas in Costa Rica and Uganda that conserve tropical forests and their high levels of biodiversity. This study provides useful information regarding overlooked ecological risk around protected areas triggered by land use changes that threaten tropical forest biodiversity.

MATERIALS AND METHODS

Sampling Sites. In Costa Rica, sampling was conducted around the Organization for Tropical Studies La Selva (LS) and Las Cruces (LC) Biological Stations (see Figure 1). LS and LC Biological Stations, established in 1968 and 1973, respectively, accommodate international research, environmental education, and tourist groups.^{25,26} Much of the land surrounding LS is used for growing bananas and pineapples.²⁷ In addition, the human population around LS has increased rapidly due to several factors, including the expansion of banana production and government settlement projects.²⁷ LC is surrounded mostly by cattle pasture, coffee plantations, and small forest fragments (typically less than 100 ha) often along the riparian zone and property lines.^{28,29} The study area included also two national parks, La Amistad and Braulio Carrillo, which are nuclear areas for high diversity sites.³⁰ In Uganda, sampling was conducted around Kibale National Park (KNP) in western Uganda (see Figure 1). KNP consists of a variety of ecosystems and vegetation types including mature, midaltitude, moist semideciduous and evergreen forest (57%), colonizing forest (19%), grassland (15%), woodland (4%), lakes and wetlands (2%), and plantations of non-native trees including *Eucalyptus spp* (1%).²¹ Much of the surrounding land is used for tea, maize, and mosaic subsistence gardens.³¹ In addition, two international research camps, Kanyawara (0°34'15.5" N, 30°21'39.6" E) and Ngogo (0°29'52.7" N, 30°25'30" E), are located inside KNP (Figure S1). Kanyawara is KNP's primary camp and the location of Makerere University Biological Field Station, established in 1970. Kanyawara consists of administrative offices, student and visitor housing, and long-term research laboratories. Ngogo serves as a smaller auxiliary camp, primarily utilizing tent housing and minimal electrical infrastructure. In addition to the research camps, KNP has one tourist camp, Kanyanchu, located near the southeast edge.³²

Air Sampling. Air was collected using passive air samplers (PAS) with polyurethane foam (PUF) discs as described elsewhere (PAS-PUF).³³ PUF discs (PUFs) were precleaned by Soxhlet extraction with hexane/acetone (1:1, v/v) for 24 h. PUFs were also dried in the fume hood covered in foil, with a small opening for solvent evaporation, and transferred to the sampling locations in sealed and cleaned aluminum foil. The PAS-PUFs were deployed at LS ($n = 13$) and LC ($n = 10$) in Costa Rica during January to July 2017 and at KNP ($n = 25$) in Uganda during May to October 2017. Air samplers were suspended by hanging them on tree branches using metallic chains at 1.5 to 2 m from the ground. After sampling, the PUFs were retrieved, individually covered with aluminum foil and sealed in Ziploc bags, shipped to the laboratory, and stored at $-20\text{ }^{\circ}\text{C}$ until extraction. The sampling air volume was calculated using a sampling rate of $4\text{ m}^3/\text{day}$, corrected for the median temperature obtained at each location during the sampling period, and adjusted for each target chemical.^{34,35} To make the calculations of volumes more tractable and since the temperature in each area was relatively stable during the duration of the sampling event, we used one value for each of the two areas: ($19.0\text{ }^{\circ}\text{C}$ for LC, $23.7\text{ }^{\circ}\text{C}$ for LS, $21.0\text{ }^{\circ}\text{C}$ for KNP).

Chemicals Analyses. The PUFs were added to accelerated solvent extraction cells (Dionex ASE 350, Sunnyvale, CA, USA), spiked with surrogate standards (for HFRs: BDE-77, BDE-166, and $^{13}\text{C}_{12}$ -BDE-209; for OPEs: d_{12} -TCEP and MTPP; for CUPs: d_{10} -chlorpyrifos and d_{14} -trfluralin; for OCPs: D-HCH and E-HCH), extracted using 50:50 hexane/acetone at $100\text{ }^{\circ}\text{C}$ and 1500 psi for three, 10 min static cycles, and concentrated to 1 mL under Rapidvap after solvent exchanging to hexane. The concentrated extracts were purified on a 3.5% water-deactivated silica column. The column was eluted with 12 mL of hexane, followed by 12 mL of a hexane/dichloromethane (DCM) mixture (1:1, v/v), and finally with 12 mL of an acetone/DCM mixture (7:3, v/v). All the fractions were blown down to 1 mL with N_2 and spiked with known amounts of internal standards (for HFRs: BDE-118 and BDE-181; for OPEs: d_{10} -anthracene, d_{12} -dibenz(a)anthracene, and d_{12} -perylene; for CUPs: BDE-181, for OCPs PCB-65). The hexane/DCM fraction was analyzed for legacy pesticides and CUPs, both hexane fraction and hexane/DCM fraction were analyzed for HFRs, while the acetone/DCM fraction was analyzed for OPEs. Details on the specific protocols can be found elsewhere.^{36,37}

Instrumental Analyses. Twenty-one OCPs, 14 CUPs, 47 HFRs, and 19 OPEs were selected as the targeted chemicals (see Table S1 for a complete list). The details of instrumental analysis are given in the Supporting Information. OCPs were analyzed by gas chromatography (GC) equipped with ^{63}Ni micro electron capture detectors and a DB-5 60 m column ($250\text{ }\mu\text{m}$ i.d. and $0.1\text{ }\mu\text{m}$ film thickness, Agilent, Santa Clara, CA). An Agilent 7890 gas chromatograph coupled to an Agilent 5975C mass spectrometer operating in the electron capture negative ionization mode with a Rtx-1614 capillary column ($15\text{ m} \times 250\text{ }\mu\text{m} \times 0.10\text{ }\mu\text{m}$ film thickness; Restek Corp., Bellefonte, PA) was used for HFRs and CUPs analysis. An Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer operating in electron ionization mode was used for OPEs analysis. Chromatographic resolution was achieved with a Rtx-OPPesticides2 capillary column ($30\text{ m} \times 250\text{ }\mu\text{m}$ i.d., $0.25\text{ }\mu\text{m}$ film thickness; Restek Corp., Bellefonte, PA) for OPEs.

Table 1. Median Atmospheric Concentration (Med, in pg/m³), Detection Frequency (DF), and the Contribution (%) of the Most Abundant Individual Compounds to the Total of Each Group of Chemicals in the Air of Costa Rica and Uganda^a

	Las Cruces (N = 10)			La Selva (N = 13)			Cost Rica (N = 23)			Kibale National Park-Inside (N = 17)			Kibale National Park-Outside (N = 8)			Uganda (N = 25)		
	Med	DF	%	Med	DF	%	Med	DF	%	Med	DF	%	Med	DF	%	Med	DF	%
OCPs																		
alpha-chlordane	0.65 ^B	80	4.5	1.6 ^A	100	33	1.3	91	21	0.32 ^b	82	0.89	0.61 ^a	100	5.6	0.34	88	2.4
gamma-chlordane	0.21	10	0.14	0.14	7.7	0.14	0.18	8.7	0.14	2.0 ^a	24	1.9	0.85 ^a	63	13	0.95	36	5.4
alpha-endosulfan	6.8 ^A	100	54	1.6 ^B	100	31	2.3	100	41				0.62	13	0.29	0.62	8.0	0.18
beta-endosulfan	2.3	90	9.9				2.3	39	4.3									
endosulfan sulfate	1.1	60	3.3				1.1	26	1.5									
HCB				0.87	31	3.5	0.87	17	2.0	26 ^a	88	81	22 ^a	88	78	25	88	80
heptachlor epoxide	1.6 ^A	30	4.2	2.0 ^A	7.7	1.2	1.6	17	2.5	0.43 ^a	59	1.3	0.95 ^a	63	2.6	0.55	60	1.7
<i>p,p'</i> -DDT	2.8 ^A	30	7.6	1.4 ^A	62	19	2.5	48	14									
Σ₂₁ OCPs (pg/m³)	19^A			6.3^B			8.0			27^a			25^a			25		
CUPs																		
chlorothalonil	2.9 ^B	100	11	37 ^A	100	4.0	7.0	100	7.2	0.46 ^a	35	1.2	0.71 ^a	63	2.8	0.71	44	1.7
chlorpyrifos	19 ^B	100	45	1111 ^A	100	95	82	100	74	8.7 ^a	100	90	1.4 ^a	100	94	9.3	100	92
pendimethalin	20 ^A	100	42	8.3 ^B	54	0.29	13	74	18									
cypermethrin	2.5	20	0.71				2.5	8.7	0.31	0.42 ^a	76	3.1	0.46 ^a	88	2.9	0.44	80	3.0
Σ₁₄ CUPs (pg/m³)	56^B			1174^A			135			9.3^a			15^a			9.5		
HFRs																		
BDE-30	0.88 ^B	100	28	2.0 ^A	100	61	1.2	100	47	0.24 ^a	24	1.0	0.29 ^a	25	4.2	0.25	24	2.0
BDE-47	0.60 ^A	100	19	0.43 ^A	100	16	0.53	100	18	8.1 ^a	100	57	2.4 ^b	100	51	7.8	100	55
BDE-99	0.19 ^B	90	5.9	0.80 ^A	15	2.2	0.19	48	3.8	2.6 ^a	100	20	0.86 ^b	100	18	2.2	100	19
BDE-209	0.19 ^A	100	8.3	0.06 ^B	77	2.7	0.14	87	5.1				0.21	38	1.5	0.21	12	0.49
total DPs	0.22 ^A	100	10	0.16 ^A	92	10	0.18	96	10	0.022 ^a	59	0.45	0.018 ^a	63	0.37	0.019	60	0.42
Σ₄₇ HFRs (pg/m³)	3.0^A			3.4^A			3.1			14^a			4.2^b			12		
OPEs																		
TNBP	370 ^A	100	43	233 ^A	100	20	248	100	30	53 ^b	100	19	98 ^a	100	18	93	100	19
TCEP	214 ^B	90	13	1024 ^A	100	71	711	96	45	67 ^b	88	17	116 ^a	75	16	92	84	17
TCIPP	68 ^B	100	6.5	117 ^A	100	9.7	96	100	8.3	42 ^b	94	13	66 ^a	75	9.2	52	88	12
TPEP	75	80	6.9				75	35	3.0	43 ^a	88	9.1	41 ^a	100	8.3	43	92	8.9
Σ₁₉ OPEs (pg/m³)	1089^A			1452^A			1193			408^a			688^a			477		

^aANOVA results using logarithmically transformed concentrations are also included; concentrations sharing the same letter are not significantly different at a $p < 0.05$ level. N is the number of samples at the given sites.

QA/QC. The recovery of surrogate standards was in the range 50–120%, which is acceptable according to EPA standards (see Table S2 for a summary).³⁸ The exception was ¹³C₁₂ BDE-209, which showed average recoveries of 42% in Costa Rica samples and 32% for Uganda samples. Since BDE-209 is not expected to be present at high concentrations in PAS-PUF samples because of its tendency to partition mostly in the particle phase,³⁹ these results were considered acceptable, and data were not corrected for recovery. Both field blanks and lab blanks were collected. Field blanks were travel blanks briefly exposed to the air outside the research station at each of the four locations in both countries. Lab blanks consisted of precleaned PUFs processed with a batch of samples. Lab blank levels for all compounds were generally low and were not subtracted from sample levels. Sample concentrations below the average site-specific field blank concentrations on a mass basis were treated as nondetects, and replaced by blank cells for statistical analysis.

Statistical Analysis. Basic and descriptive statistics were calculated using Minitab 18 and Microsoft Excel 2016. Plots were generated using SigmaPlot 13 (Systat Software Inc.). For LC and LS, land use analysis was generated by using land cover classification data from NASA's Earth Observing System Data and Information System (EOSDIS) layer in ArcMap 10.4.1 (ESRI, Redlands, CA, USA). The land use categories were combined in the following three groups: agriculture, forest, and other. The forest category included evergreen, deciduous, tropical, and mixed rainforests, as well as inland water, and the other category included areas that are developed and utilized for residence purposes. Each area analyzed for land use covered over 2000 km² to include all sampling sites and the existing different land use and forest types. For Uganda, the sampling sites maps and calculation of distance from sampling sites to the research camps were conducted using ArcMap 10.4.1 (ESRI, Redlands, CA, USA). To identify the potential impacts of human activities on the chemical's distribution around KNP, samples were grouped into two categories based on sampling location: inside KNP (KNP-In) and outside KNP (KNP-Out) (see map in Figure 1). Distances between sites were calculated as spherical distances using the site coordinates.

RESULTS AND DISCUSSION

Table 1 gives the summary statistics for the most abundant chemicals in terms of the detection frequency and contribution to each group of chemicals across the sampling sites, as well as the total concentration of each group of chemicals (Σ_{21} OCPs, Σ_{14} CUPs, Σ_{47} HFRs, and Σ_{19} OPEs). Figure 2 shows box-plots for the air concentrations of targeted chemicals at each location. Table S3 gives the minimum and maximum concentration for the most abundant chemicals at each site.

Pesticides: Costa Rica. The two most frequently detected OCPs at both LC and LS were alpha-endosulfan and alpha-chlordane, with detection frequencies of more than 80% (Table 1). Median concentrations of these two pesticides were 2.3 pg/m³ and 1.3 pg/m³, respectively. One of the most widely used pesticides in the past, *p,p'*-DDT, was detected in about half of the samples at a median concentration of 2.5 pg/m³. Among CUPs, chlorpyrifos and chlorothalonil were detected in all the samples, while pendimethalin was detected in 74% of the samples. Chlorpyrifos showed the highest concentration among all pesticides with a median of 82 pg/m³.

The ANOVA results ($p < 0.05$) showed that Σ_{21} OCPs concentration was significantly higher at LC than at LS (Figure

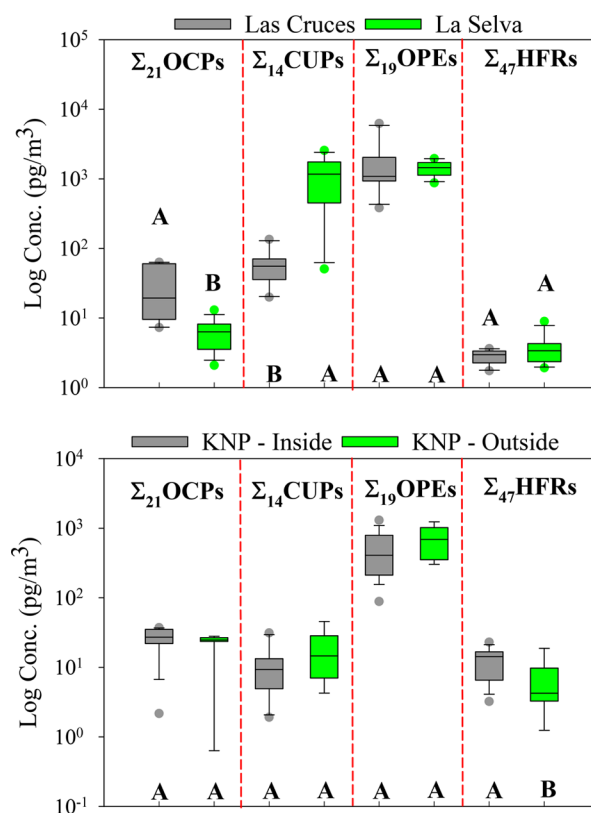


Figure 2. Total concentrations (pg/m³) of atmospheric OCPs, CUPs, OPEs, and HFRs in Costa Rica and Uganda. The boxes represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles, and the black horizontal solid line inside each box represents the median. The letters represent the ANOVA results of the logarithmically transformed concentrations among the sites in Uganda or Costa Rica, respectively. The site name is abbreviated as follows: KNP-In, inside of the Kibale National Park; KNP-Out, outside of the Kibale National Park.

2). Specifically, Σ_{21} OCPs concentration ranged from 7.3 to 64 pg/m³ at LC and 2.1 to 13 pg/m³ at LS, with a median of 19 and 6.3 pg/m³, respectively (Table 1 and Table S3).

Significantly higher concentration of alpha-endosulfan was observed at LC, while the level of alpha-chlordane was higher at LS. The levels of *p,p'*-DDT at LC were statistically indistinguishable from those at LS. In a previous study using PAS-XAD, alpha-endosulfan was also the most abundant atmospheric legacy pesticide across Costa Rica in 2005¹⁷ with concentrations in the range of 12 to 440 pg/m³. This level was higher than our measured concentrations at LC (3.8–53 pg/m³) and at LS (0.45–2.9 pg/m³).

The concentration of alpha-chlordane was in the range of 0.053–11.0 pg/m³ across Costa Rica during the period of 2004 to 2005,⁴⁰ these values were consistent with our findings at LC and LS, where the concentrations ranged from 0.39 to 1.1 pg/m³ and 0.60 to 3.1 pg/m³, respectively. Gamma-chlordane concentration acquired by PAS-XAD across Costa Rica in 2004/2005 was in the range of 0.42–20 pg/m³,⁴⁰ which was higher than our median measurements at LC (0.21 pg/m³) and at LS (0.14 pg/m³).

Although *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, and *o,p'*-DDD were observed at LS in 2004, here we detected only *p,p'*-DDT and at lower concentrations (2.5 pg/m³ in 2004 vs 1.4 pg/m³ in our study). This decline is consistent with a halving time of

~8 years measured in the Great Lakes region.⁴¹ DDT had been banned for application in Costa Rica since 1988, and the lack of detection of DDE and DDD, which are its degradation products, suggests that the atmospheric concentration of DDT is slowly approaching background concentration, despite being highly persistent.⁴⁰

Unlike legacy pesticides, the concentration of Σ_{14} CUPs was significantly higher at LS than at LC (Figure 2), with medians of 1174 pg/m³ and 56 pg/m³, respectively. Among Σ_{14} CUPs, chlorpyrifos was the most abundant compound measured at LS, representing 95% of the total with a median concentration of 1111 pg/m³; at LC its contribution was much lower, at 45% of total with a median concentration of 19 pg/m³. The atmospheric concentrations measured here are significantly higher than those reported across Costa Rica for samples collected in 2004 using PAS-XAD, which were in the range of 7.3–17 pg/m³ but comparable to those measured in San Antonio de Belen, Costa Rica in 2005–2006 using both PAS-PUF and high volume samplers (annual mean concentrations were 2200 ± 707 pg/m³ and 600 ± 480 pg/m³, respectively).^{17,42} Since chlorpyrifos is used in the control of insect pests in Costa Rica, such as the coffee berry borer⁴³ and banana plantation pests,⁴⁴ the elevated atmospheric concentrations are consistent with its usage in the banana plantations that dominate the agricultural activity in the vicinity of LS. Chlorpyrifos is an organophosphorus cholinesterase inhibitor after metabolism, allowing acetylcholine to accumulate at cholinergic synapses. Low-dose exposure to chlorpyrifos resulted in neurological changes for rats, with larger effects on emotional processing and cognition than on motor skills.

The median atmospheric concentration of chlorothalonil was also significantly higher at LS (37 pg/m³) than at LC (2.9 pg/m³). In previous studies at this site, the atmospheric concentrations for chlorothalonil in samples collected using PAS-XAD ranged between a mean of 1707 pg/m³³⁴⁵ in 2004/2005 and a mean of 26 pg/m³ for 2005/2006 using PAS-XAD.¹⁷ Chlorothalonil is widely applied in Costa Rica as a fungicide in banana, coffee, and pineapple productions.^{46,47} The annual average import of chlorothalonil was more than 750 tons in 2001 to 2005, decreasing to 300 tons between 2006 and 2010.¹⁷ Chlorothalonil was shown to dissipate rapidly in the environment, with half-lives of 2.2 days in banana plantation soils in Costa Rica.⁴⁸ The relative short half-lives and the decreasing application of chlorothalonil in Costa Rica indicate that its environmental concentrations are expected to decrease with time, potentially reaching the concentrations of remote sites with low or background concentrations.

Pendimethalin was the only compound among CUPs for which the atmospheric concentrations were higher at LC than at LS (median of 20 pg/m³ and 8.3 pg/m³, respectively). Previous studies reported mean pendimethalin atmospheric concentrations of 9.5 pg/m³ in San Antonio de Belen, Costa Rica using PAS-PUF in 2008⁴² and of 3.4 pg/m³ at LS using PAS-XAD in 2005–2006.¹⁷ Pendimethalin, a pre-emergent herbicide, is used in Costa Rican rice and sugar cane production.^{49,50}

Overall, we found higher concentrations of legacy pesticides at LC and higher concentrations of current use pesticides at LS (Figure 2). We hypothesize that these atmospheric concentrations are significantly connected to the historical land use around the sampling sites, with the LS region characterized by more intensive, industrial agricultural crops such as banana and pineapple plantations and the LC area characterized by more

traditional, small scale crops, coffee, and pastures. Results from land use analyses show that 33% of the land around LS was used for agriculture, compared to 14% around LC. The amount of land covered by forest as broadly defined above was similar for both sites at ~70%, although it is more fragmented around LC. The region around LC had a significantly higher fraction of land developed and used for residential purposes than that around LS (16% vs 1%). These results suggest that high concentrations of CUPs found around LS are likely related to pesticide intensive crops, whereas the high concentrations of legacy pesticides at LC are likely the result of a long agricultural history in the region characterized by small scale, subsistence farming coupled with pastures. From a conservation perspective, human and wildlife exposure to a high environmental abundance of CUPs resulting from such large-scale agricultural expansion may pose significant health risks.^{12,51} Moreover, given their persistence and long-range transport capacity, the influence of OCPs residues still in the environment cannot be ignored.

Pesticides: Uganda. In Uganda, the three most frequently detected OCPs were hexachlorobenzene (HCB), alpha-chlordane, and heptachlor epoxide, which were detected in more than 50% of the samples (Table 1). Median concentrations ranged between 0.34 pg/m³ for alpha-chlordane to 25 pg/m³ for HCB. Chlorpyrifos was the most abundant among CUPs, with a detection frequency of 100% and a median concentration of 9.3 pg/m³, followed by cypermethrin with a detection frequency of 80% and a median concentration of 0.44 pg/m³.

To explore the potential for protected areas to act as buffers to chemical pollution entering from neighboring agricultural fields and human settlements but also the possibility that even these areas are exposed to anthropogenic compounds from human use far from the forest edge, we examined variation in chemicals inside and outside KNP. The concentrations of Σ_{21} OCPs at KNP-In and KNP-Out were indistinguishable (median of 27 and 25 pg/m³, respectively; Table 1 and Table S3). HCB was the most abundant OCPs at both locations, contributing to 80% of Σ_{21} OCPs. Although direct application of HCB was stopped globally, it was reported to be a byproduct in the manufacturing of other major pesticides, including lindane, chlorothalonil, and pentachlorophenol.^{52,53} Also, uncontrolled combustion, especially municipal waste and biomass burning, was reported to be a significant source of HCB.^{52,54} Surprisingly, we did not detect *p,p'*-DDT, as a previous study conducted at KNP demonstrated the presence of DDT and chlorpyrifos in primate dietary items and other environmental matrices, excluding air.¹² However, given our methods were able to detect the presence of *p,p'*-DDT at locations in Costa Rica, the differences between these studies were likely due to the type of matrix analyzed between studies; *p,p'*-DDT is a highly persistent compound, and its half-life is higher in soil and sediments than air.⁵⁵ It is also possible that local variation in *p,p'*-DDT exists around the KNP area given it encompasses 795 km², and the previous study was conducted in a different part of the protected area.

Atmospheric measurements of pesticides in the African continent are very limited,^{12,53,56–62} and only one publication specifically relates to Uganda.⁵³ HCB has been detected in samples collected in 2010 at Entebbe, on the northern side of Lake Victoria, Uganda, using a high volume air sampler with a mean of 8.0 pg/m³,⁵³ which is lower than our median measurements at both KNP-In (26 pg/m³) and KNP-Out (22

pg/m³). The mean concentration of gamma-chlordane at the same site in Uganda⁵³ was 4.34 pg/m³, which is higher than our findings at KNP. Interestingly, the mean concentration of alpha-chlordane measured at Entebbe in 2010 was 4.0 pg/m³, which is significantly higher than our median value at 0.34 pg/m³.

Similar to legacy pesticides, higher Σ_{14} CUPs concentrations were observed at KNP-Out (15 pg/m³, median) than at KNP-In (9.3 pg/m³), although the differences were not statistically significant. Chlorpyrifos was the predominant CUP, representing >90% of Σ_{14} CUPs with median concentrations of 8.7 pg/m³ and 14 pg/m³ at KNP-In and KNP-Out, respectively. One previous study reported average chlorpyrifos concentrations in Uganda ranging from 10 pg/m³ to 29800 pg/m³.⁵³ Chlorothalonil was previously detected in the atmosphere in Uganda at concentrations ranging from 0.1 to 24 pg/m³,⁵³ which is comparable with the median concentrations at KNP (0.46 pg/m³ at KNP-In and 0.71 pg/m³ at KNP-Out).

In general, the atmospheric concentrations of CUPs and OCPs were similar at both locations, KNP-In and KNP-Out. These findings suggest that human activities, and in particular agriculture, do not influence the atmospheric concentrations of pesticides around Kibale as much as they do in Costa Rica. Unlike the industrial scale agriculture found in Costa Rica, especially around LS, KNP is surrounded by small-scale subsistence farming, resulting in more limited pesticide application. Small-scale farmers generally cannot afford to buy pesticides for their crops,⁶³ and companies growing tea for export have progressively moved toward more sustainable methods that do not rely as heavily on pesticides as in the past.⁶⁴ It should also be noted that this study only included air samples, which provide a partial picture of the presence of pesticides in this environment. Future studies should investigate the occurrence of pesticides, particularly herbicides which are used on all agricultural farms, in plants, water, and soil, as well as biological samples, to look further into their potential impacts on the ecosystem in and around KNP. Also, the list of target pesticides should be expanded after collecting more information on the ground about specific products used locally.

Flame Retardants: Costa Rica. BDE-30, BDE-47, BDE-209, and total-DP were the most abundant FRs with detection frequencies higher than 75%. The median concentration for Σ_{47} HFRs was 3.1 pg/m³. TNBP, TCEP, and TCIPP were the most frequently detected OPEs, with the detection frequencies >90%, and the median concentration of Σ_{19} OPEs was 1193 pg/m³.

The median Σ_{47} HFRs concentrations between LC and LS were comparable (3.0 pg/m³ and 3.4 pg/m³, respectively), as well as their congener pattern. Data on HFRs concentrations in Costa Rica are limited, with the exception of the Global Atmospheric Passive Sampling (GAPS) project.^{65,66} Data from GAPS showed that the median concentration of BDE-47 at a background site of Tapanti in Costa Rica was 0.2 pg/m³, which is lower than our median measurements at LC (0.60 pg/m³) and LS (0.43 pg/m³). However, the corresponding BDE-99 concentrations (1.6 pg/m³) were higher than those measured at LC (0.19 pg/m³) and LS (0.80 pg/m³). On a broader scale, the atmospheric concentrations for BDE-47 and BDE-99 measured at these two sites are significantly lower than those measured at two remote sites (Sleeping Bear Dunes and Eagle Harbor) in North America, where the geometric mean for each one was around 2.0 pg/m³.⁶⁷ To the best of our knowledge,

this study, for the first time, revealed the occurrence of HFRs at two major national parks, La Amistad (3.3 pg/m³) and Braulio Carrillo (2.1 pg/m³), in Costa Rica.

At both locations, OPEs concentrations were 2 orders of magnitude higher than those of HFRs, which is consistent with the OPE-BFR ratios reported for the Arctic atmosphere⁶⁸ and the North American Great Lakes basin.⁶⁹ The median Σ_{19} OPEs at LC (1089 pg/m³) was indistinguishable from that at LS (1452 pg/m³). Significantly higher concentrations were observed for TCEP and TCIPP at LS than at LC. OPEs, including TCEP and TCIPP, are frequently used as plasticizers. The significantly higher concentration of TCEP and TCIPP at LS can be potentially attributed to the larger presence of industrial scale agriculture operations which inherently involve more items that could be sources of flame retardants and plasticizers or to its closer proximity to urban sprawl where the capital, San Jose, is located, which is the most densely populated area across Costa Rica.

Limited data are available on the occurrence and abundance of OPEs in Costa Rica.^{65,66,70} One study reported that at Tapanti TCEP and TCIPP were the most abundant chemicals, consistent with our findings.⁷⁰ The concentrations of TCEP and TCIPP were generally similar to those reported here but not for TNBP. Interestingly, the median TNBP concentration was 370 pg/m³ at LC and 233 pg/m³ at LS, but TNBP was not detected in Tapanti. In general, our measured Σ_{19} OPEs concentrations were within the range of those measured in Latin America and the Caribbean for samples collected in 2014 using PAS-PUF where the mean was in the range of 80–1660 pg/m³.⁶⁶

Flame Retardants: Uganda. The most frequently detected HFRs were BDE-47 and BDE-99, with detection frequencies of 100% at KNP and median concentrations of 7.8 and 2.2 pg/m³, respectively. TNBP, TCEP, TCIPP, and TPEP were the most frequently detected OPEs at both locations, with detection frequencies >75% and median concentrations of 93, 92, 52, and 43 pg/m³, respectively.

Interestingly, Σ_{47} HFRs concentration was significant higher at KNP-In than at KNP-Out (Figure 2), with median concentrations for Σ_{47} HFRs being 14 pg/m³ and 4.2 pg/m³, respectively. Unsurprisingly, BDE-47 and BDE-99 were the predominant congeners, with median concentrations of 8.1 and 2.6 pg/m³ at KNP-In and 2.4 and 0.86 pg/m³ at KNP-Out. BDE-47 and BDE-99 combined contributed 77% and 69% of the total at KNP-In and KNP-Out, respectively. HFRs were measured in the atmosphere only in one study in Uganda, around Lake Victoria.⁷¹ The median concentration of BDE-47 and BDE-99 was 9.8 and 1.9 pg/m³, respectively, which is comparable with our measured concentrations. Surprisingly, the measured concentration for BDE-47 at KNP-In was comparable with the geometric mean concentrations of 9.2 pg/m³ in samples collected at Chicago, one of the urban sites of the Integrated Atmospheric Deposition Network (IADN), using the same sampling method.³³ These results indicate a rather large source of HFRs inside or near KNP, such as research and tourist camps. BDE-47 and -99 were the main congeners used in the penta-BDE commercial mixture, which was withdrawn from the market in the early 2000s. We suspect that these camps are stocked with older pieces of furniture, which are more likely to contain penta-BDE congeners, including BDE-47 and -99.⁷²

Σ_{19} OPEs was the most abundant chemical among the four groups of compounds measured at KNP. Median Σ_{19} OPEs

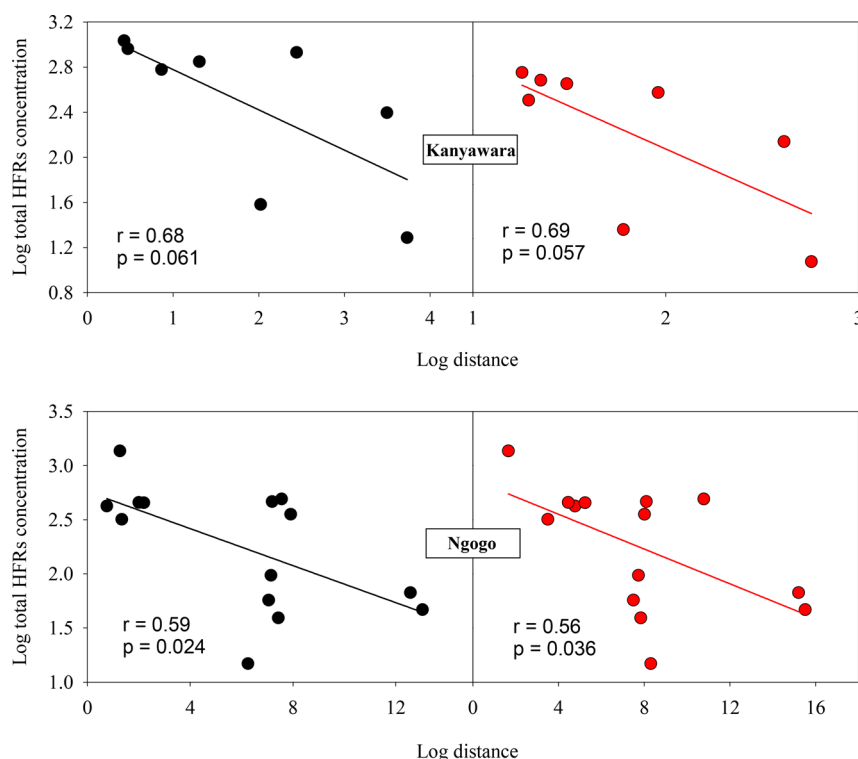


Figure 3. (left) Correlation between total HFRs concentration and the distance between sampling sites and the center of the Kanyawara and Ngogo research camps (black dots). (right) Correlation between total HFRs concentration and the distance between sampling sites and the source calculated using eq (red dots). The correlation coefficient r and p values for the linear regression analysis are provided in each plot.

concentrations were 408 pg/m³ at KNP-In and 688 pg/m³ at KNP-Out, and they were indistinguishable from one another. However, significantly higher concentrations were observed for TNBP, TCEP, and TCIPP at KNP-Out, while TPEP just showed the opposite trend. The OPEs patterns were dominated by TNBP, TCEP, TCIPP, and TPEP, with the sum of these chemicals representing 58.1% and 51.5% of Σ_{19} OPEs at KNP-In and KNP-Out, respectively. To the best of our knowledge, this is the first study reporting the presence of OPEs in Uganda. These concentrations are comparable with those measured at the rural site of Sturgeon Point (207 pg/m³) in the Great Lakes region but much lower than those at the urban site of Chicago (1390 pg/m³), collected using active samplers.⁶⁸

FRs are abundant in numerous common consumer products (e.g., sofas, mattresses, curtains, and electronics).^{73,74} Previous studies showed that, in the absence of specific point sources, the atmospheric concentration of HFRs and OPEs in general is significantly correlated with the local human population.^{75,76} Given that the area around Kibale National Park is densely populated and becoming even more so,²⁴ the high atmospheric concentrations of HFRs and OPEs may not be so surprising. However, we hypothesize the presence of point sources of HFRs from research and tourist camps inside the park. To begin testing this hypothesis, regression analysis between HFRs concentration and the distance from sampling sites to the research camps (Kanyawara and Ngogo) inside KNP was conducted to help locate the potential source (Figure 3). All sampling sites were separated into two groups (Kanyawara and Ngogo) based on the distance to the adjacent research camps (see Figure S1 for the grouping).

The HFRs concentration decreased significantly with increasing distance from the research camps, with the highest

HFRs concentrations observed at sampling site #22, near the Kanyawara research camp area, and at #26, near the Ngogo research camp area, respectively (see Figure S1 for site numbers). These two sampling sites (#22 and #26) were the locations closest to the center of each of the two research camps. The correlation between the concentration of total HFRs and the distance from sampling sites to research camps was marginally significant for Kanyawara ($p = 0.061$) and significant for Ngogo ($p = 0.024$). The lower strength of the relationship for Kanyawara is probably related to the small number of samples available ($n = 8$). These findings suggest that Kanyawara and Ngogo research camps are two potential sources of HFRs inside KNP. We hypothesize that either furniture and electronic devices, which are well-known to contain HFRs, in research and tourist camps are likely point sources of HFRs⁷⁷ or that open burning of plastic inside KNP might also be the point source of HFRs, as demonstrated by previous studies.^{78,79} Future studies should explore concentrations starting at the research camps and tourist camps and route along a transect into the communities. This would be much further than our current sampling outside the park but still very near the forest edge.

Conversely, the OPEs concentration increased with the increasing distance between sampling sites and the corresponding research camps, with the highest OPEs concentration observed at sampling site #17 of the Kanyawara research camp area and at sampling site #30 of the Ngogo research camp (Figure S2). These results suggest that the potential OPEs sources are located outside of KNP, but since the majority of the samples was collected inside the park, it is not possible at the moment to speculate on possible sources for OPEs.

To test the hypothesis that the source of HFRs is inside the park, we applied a model previously used to trace the source of

DPs and PBDEs in tree barks^{80,81} to the HFRs and OPEs concentrations in the air in this study. Briefly, the concentration of a pollutant (C) as a function of distance from its source (d) is introduced by

$$C(d) = kd^{-2} \quad (1)$$

where k is a fitted constant. The distance of each sampling site from the potential source was calculated by using the spherical Euclidian distance, which is given by

$$d_i = 6373 \arccos(\sin(\text{lat}_i) \sin(\text{lat}_{\text{sor}}) + \cos(\text{lat}_i) \cos(\text{lat}_{\text{sor}}) \cos(|\text{lon}_i - \text{lon}_{\text{sor}}|)) \quad (2)$$

where d_i is the distance of the sampling site from the source location measured on a sphere; lat_i and lat_{sor} were the latitudes of the sampling sites and source locations; lon_i and lon_{sor} were the longitude of the sampling sites and source locations; and the factor of 6373 converts from radians to kilometers. To determine the location of the source, we assumed that we did not know the location of the source, and we let the values of the coordinates of sources vary in eq 2. Then, the equation was minimized

$$\epsilon_d = \sum_i [K' d_i^{-(a1+a2)} - C_i]^2 \quad (3)$$

Using the Solver feature in Excel, we calculated the fitted variables K' and $-(a1 + a2)$ and the corresponding statistics for the HFRs concentrations (see Table S6). As expected, the calculated source locations for HFRs are close to the location of research camps (see the flags and asterisks in Figure S1 and the coordinates in Table S6). The fitted location for the HFRs source around Kanyawara and Ngogo is less than 1.0 km and 4.2 km from the center of Kanyawara and Ngogo research camps, respectively (see Figure S1). Therefore, human activity inside KNP, like tourist or research activity, as well as human activity along the road and entrance to the park is the likely HFRs source inside KNP.

This study highlights the importance and need for monitoring chemical contamination data from protected areas, by providing the distributions and atmospheric concentrations of OCPs, CUPs, HFRs, and OPEs. Further monitoring efforts are needed to investigate the occurrence of anthropogenic chemicals in other environmental matrices, such as soil, water, plant, and biological samples in order to fully appreciate the potential ecological risk of anthropogenic chemicals to biodiversity and ecosystem functioning in protected areas.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00649.

Details on information and instrumental analysis of targeted chemicals; summary of recoveries of surrogates in samples at two locations; minimum, median, and maximum concentration of major target chemicals in samples at two locations; summary of land use analysis for two sites in Costa Rica; fitted variables for HFRs data sets around Kanyawara and Ngogo research areas; field blanks and lab blank levels and LOQ of target chemicals; matrix spike recoveries (%) of target chemicals in PUFs; map of sampling sites; and OPEs concentration (PDF)

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Notes

The authors declare no competing financial interest.

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