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Passive monitoring techniques to evaluate environmental pesticide exposure: Results from the Infant's Environmental Health study (ISA)

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ABSTRACT

Background: Pesticides used in agriculture may expose populations living nearby. Costa Rica is a major banana-exporting country, its production depends on extensive pesticide use.
Objectives: To evaluate environmental pesticide exposure, we measured levels of current-use pesticides in air and dust from 12 schools in Matina County, Costa Rica, with passive sampling methods.
Methods: We selected ten proximal and two non-proximal schools and placed polyurethane foam passive air samplers outdoors at each school, during four consecutive periods. At three of these schools, we also placed an active air sampler during the first 24 h of each sampling period. We collected passive dust samples by placing a glass Petri Dish at the inside of each school. We subsequently performed a chemical analysis of 18 pesticides, using gas chromatography with mass detector.
Results: With passive air samplers we detected ten different pesticides: two insecticides, two nematicides, and six fungicides, of which nine reported to be used on banana plantations. More than half of the samples contained at least five pesticides. Chlorpyrifos was detected most-frequently, in 98% of samples, followed by the nematicides etoprophos and the fungicide pyrimethanil that were both detected in 81% of samples. Chlorpyrifos concentrations were five times higher in proximal as compared to non-proximal schools: mean = 18.2 ng/m^3 (range = 6.1–36.1) and mean = 3.5 ng/m^3 (range = < 0.5–11.4) and varied more between schools than in time (intra-class correlation coefficient = 0.80). In general, results from passive and active samplers showed similar exposure patterns; yet median concentrations tended to be higher in passive samplers. In dust samples, mostly fungicides were detected; chlorothalonil was detected most frequently, in 50% of samples.
Discussion: Passive air sampling is a promising technique to characterize environmental exposure to current-use pesticides; more studies are needed to characterize the sampling rates, reproducibility and optimum sampling times for passive samplers. School environments near banana plantations are contaminated with multiple pesticides that include insecticides, nematicides, and fungicides, which is of concern.

1. Introduction

Pesticides used in agriculture may expose populations living nearby (Dalvie et al., 2014; Kawahara et al., 2005; Liu et al., 2014; van Wendel de Joode et al., 2012). For example, studies carried out in agricultural villages from the United States, Costa Rica and South-Africa have detected pesticides in outdoor and indoor air and dust (Dalvie et al., 2014; Gibbs et al., 2017; van Wendel de Joode et al., 2012). Air is a potential route of pesticide exposure, and thus important to monitor (Fenske et al., 2002, 2005; 2010; Lu et al., 2000, 2013).

To measure pesticide air concentrations, traditionally active air sampling (AAS) methods have been used (Gouin et al., 2005, 2008; Kawahara et al., 2005; Weppner et al., 2006). However, since 2002, passive air sampling (PAS) techniques using polyurethane foam (PUF) have been employed as an alternative, particularly when measuring persistent compounds (Gouin et al., 2005; Harner et al., 2004; Shoeib and Harner, 2002). PUF-PAS devices are chemical accumulators; the extent of absorption to the PUF depends on the ratio of the analyte concentration in PUF divided by the concentration in air when the two phases are in equilibrium (Shoeib and Harner, 2002). From 2008 onwards, PAS methods have been deployed as well to assess exposure to less persistent, current-use, pesticides including chlorpyrifos, azinphos-methyl, and oxygen analogs (Armstrong et al., 2014; Climent et al., 2019; Gibbs et al., 2017; Gouin et al., 2008). Whilst AAS is particularly useful for examining daily fluctuations in pesticide concentrations and identifying peak exposures (Weppner et al., 2006), PAS obtains an

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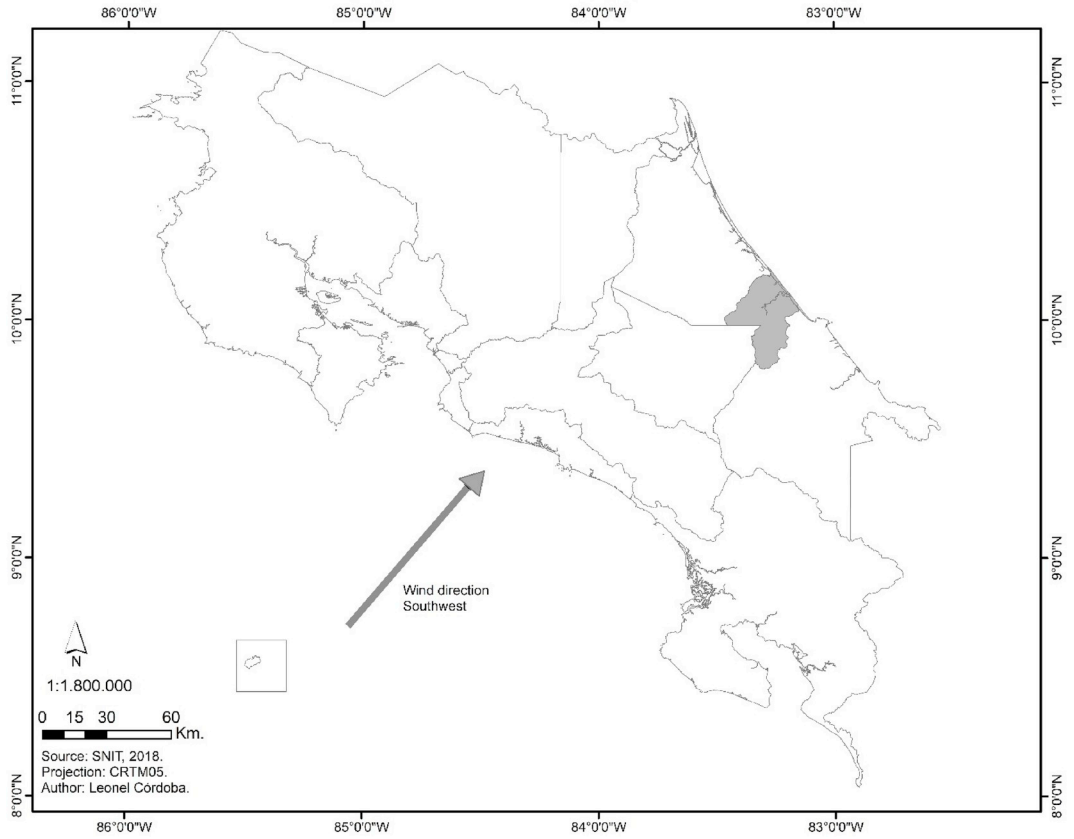

Fig. 1. Location of Matina county in Limon Province, Costa Rica.

integrated measure of pesticide concentrations over a larger period and does not require expensive equipment or electricity for sampling collection (Gibbs et al., 2017). Nevertheless, to our knowledge, studies measuring a wide range of current-use pesticides with PAS techniques are non-existing.

In addition to air, pesticides have been frequently measured in environmental dust to determine pesticide concentrations per weight of dust, or per surface area, as an indicator of environmental exposure in agricultural populations (Fenske et al., 2002; Hong et al., 2001; Obendorf et al., 2006; Starr et al., 2008). Dust sampling can be performed by means of dry or wet wiping, however, these methods generally lack information about the time-frame during which the dust contamination occurred (Boyle et al., 2015; Kim et al., 2013). Alternatively, pesticides can be measured in settled dust. For example, Weppner et al. (2006), measured methamidophos in settled dust outside, using silica gel chromatography plates, and results showed that median distance and median pesticide loading concentrations were inversely associated. Gibbs et al. (2017), used polypropylene deposition plates to collect settled indoor dust particles and found 55% of the samples had detectable chlorpyrifos concentrations; plates located in houses proximal ($\leq$250 m) to tree fruit fields had higher levels of chlorpyrifos than non-proximal houses ($>$ 250 m).

Costa Rica, located in Central America, is one of the largest banana exporting country world-wide (FAO, 2001); its production depends on intensive pesticide use (Bravo et al., 2013; Bravo-Durán et al., 2015 ; Wesseling, 1997). In 2006, 27 active ingredients (a.i.) of pesticides were reported to be used on those plantations, with a total of 49.3 kg of a. i. per hectare per year (Bravo et al., 2013). The use of the pesticides a. i. includes, amongst others, ground applications of extremely and highly toxic organophosphate nematicides (World Health Organization Class 1a and 1 b), insecticide-treated bags, and about 16 different types of fungicides applied with light aircraft (Bravo et al., 2013). Results from studies performed in Costa Rica have evidenced environmental pesticide contamination in watersheds near agricultural areas (Arias-Andrés et al., 2018; Castillo et al., 2000); up to 32 pesticides were detected during a 4-year period in the River Madre de Dios, located downstream banana and pineapple plantations (Arias-Andrés et al., 2018). Another study showed elevated urinary 3,5,6-trichloro-2-pyridinol (TCPy) concentrations, a specific metabolite of chlorpyrifos, in children from a village adjacent to banana and plantain plantations as compared to a predominantly organic village. Outdoor soil, indoor dust, mattress dust, and outside air were contaminated with chlorpyrifos; yet only a few samples were taken from each environmental matrix (n = 2–12) (van Wendel de Joode et al., 2012). In addition, results from the Infant's Environmental Health Study (ISA), an ongoing birth-cohort study performed in Matina County, Costa Rica, with extensive banana growing, showed contamination of ethylene-thiourea (ETU), the main metabolite of the fungicide mancozeb that is sprayed with light aircrafts, in 6% of drinking water samples (N = 126) from villages nearby banana plantations (van Wendel De Joode et al., 2016). Results from the ISA cohort also showed elevated concentrations of urinary ethylene thiourea (ETU), in pregnant women living close to banana plantations (van Wendel de Joode et al., 2014).

We performed the current study within the context of the ISA study and aimed to: 1) evaluate environmental exposure to a wide range of current-use pesticides by passive sampling of air and dust in 12 schools from the ISA study area during four consecutive periods of 1–3 months; 2) compare results from passive and active air sampling techniques; 3) compare pesticide contamination in ten schools proximal to banana plantations ($<$ 100 m) with contamination in two non-proximal schools ($>$ 1.5 km); 4) understand variability in concentrations of pesticides determined with PAS between and within schools during four periods of approximately six weeks each.

2. Materials and methods

2.1. Study area

ISA is a community-based birth cohort study performed in Matina

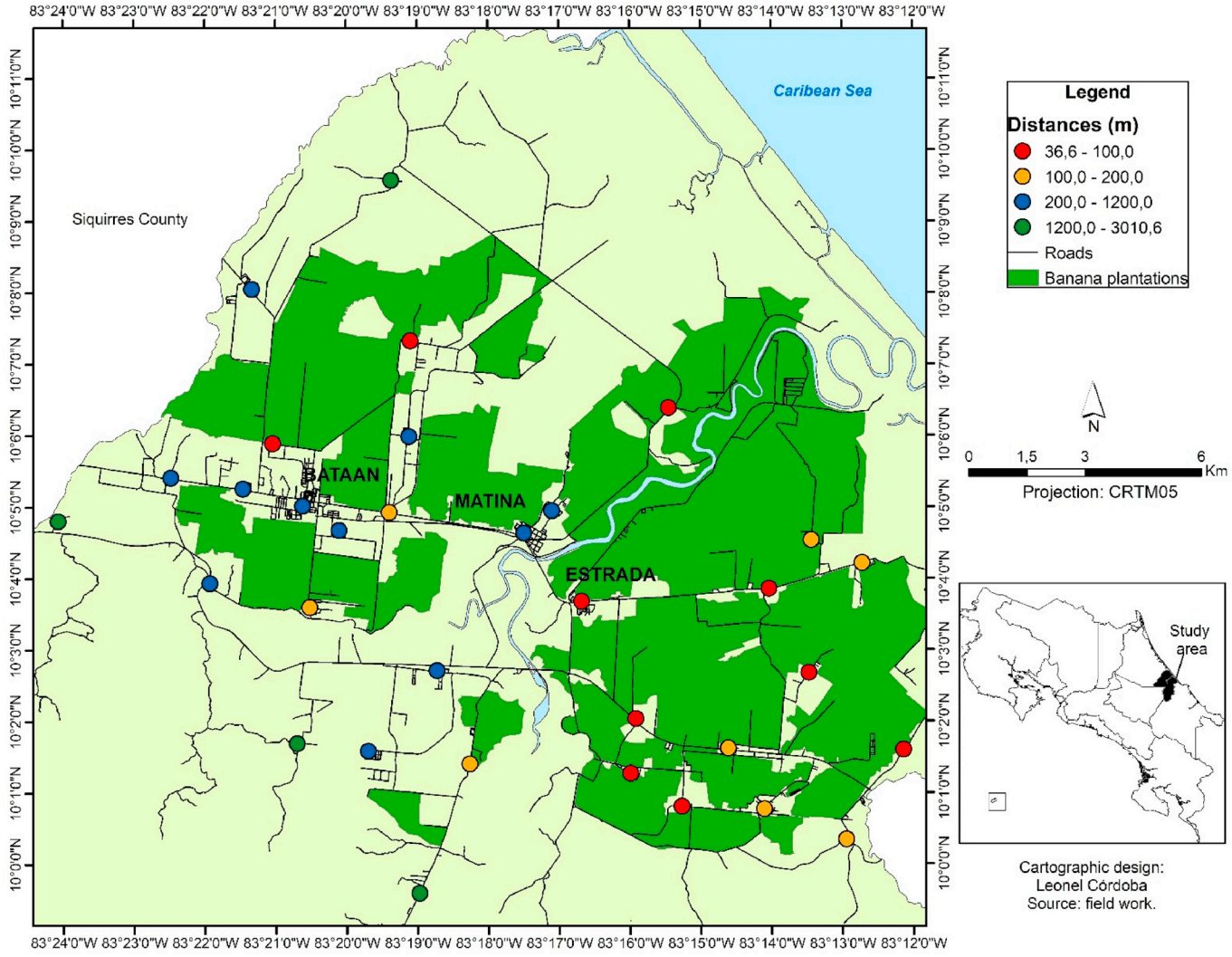

Fig. 2. Sample sites of passive air samples at ten proximate (red dots) and two non-proximate (green dots) en Matina County, Costa Rica. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

County, Limón, Costa Rica, from 2010 onwards, that examines possible effects of pesticide and manganese exposure on children's growth and neurodevelopment (Mora et al., 2018, 2015, 2014; van Wendel de Joode et al., 2014). Matina County is located on Costa Rica's North Caribbean Coast and has a humid tropical climate with 3500–4500 mm of rain a year. The North Caribbean is influenced by trade winds from the north, that change direction when hitting the Talamanca Mountains in the South (IMN, 2017) (see Fig. 1 for wind direction).

In 2010, the ISA study area had 33 primary schools, and we documented the location of these schools using a Global Positioning System (GPS) receiver (Garmin Etrex Venture HCto), a geocoded map, and Geographical Information System (GIS) ArcGIS 10.0 software, (ESRI, Redlands, CA, USA) (Fig. 2). We identified the location of banana plantations using aerial photographs [CARTA (Costa Rica Airborne Research and Technology Applications) project 2005; (Centro Nacional de Alta Tecnología, 2011)] and measured Euclidean distances from each school to the nearest border of the closest banana plantation. We observed that 50% of the schools were located at less than 180 m distance from a banana plantation (Fig. 2). We then selected ten schools that were located within 100 m of a banana plantation (proximal schools) and two schools that were at the largest distance of a banana plantation (> 1.5 km) (non-proximal schools).

2.2. Measurement strategy and sampling

Data were collected from June 2010 to October 2011 for each of the twelve schools during four periods (Table 1) using three sampling methods: 1) PAS technique with polyurethane foam (PUF) (Tisch Environmental, Cleves OH) as described by Shoeib and Harner (2002); Gouin et al. (2008); Gibbs et al. (2017); 2) High volume (600 L/min) AAS with a pre-combusted glass-fiber filter located in a metal sampling head, and a mesh cylinder containing a PUF disk and XAD-resin as described by Todd Gouin et al. (2008) and Wania et al. (2003); and 3) passive dust sampling with Petri Dishes. Outside of each school, we collocated the PUF in a stainless steel, domed chamber (22 cm diameter, Tisch Environmental) to protect the PUF from wind, precipitation and sunlight at 3–5 m height during, on average, 6.7 weeks (SD = 1.9). In addition, we collocated the AAS outside of three proximate, and one non-proximate, schools at 3 m height, at the start of each PAS-PUF measurement, during, on average 24 h. Finally, to collect dust, we collocated a Petri Dish inside of each school, at approximately at 2 m height at a place with few access and infrequent cleaning during, on average, 15.7 weeks (SD = 5.9). We left Petri dishes for a longer time than PUFs to collect enough dust. For each of the three techniques, we collected a blank sample at the first day of each of the four sampling periods.

Table 1
Characteristics of the schools with air and dust sampling and number of samples obtained from June 2010 to October 2011, ISA study, Matina County, Costa Rica.

School	Shortest distance from school to banana plantation (m.a.s.l [a])	Community	Number of Students (n)	Number of teachers and other personnel (n)	Year of construction	Altitude (m.a.s.l.)	Number of passive air samples with PUF (n)	Active air samples PUF-XAD and Filter (n)	Number of passive dust samples (n)
Barmouth	5	Agrodisa	40	5	1984	5	4		4
La Maravilla	10	La Maravilla	57	7	1979	7	4		4
Larga Distancia	12	Larga Distancia	54	8	1961	5	4		4
Saborío	12	Saborío	63	14	1966	7	4		3
4 Millas	24	4 Millas	97	9	1960	6	4		3
Zent	30	Zent	343	17	1957	18	4	4	4
Venecia	47	Venecia	301	19	1958	13	4		4
Los Almendros	70	Los Almendros	100	8	–[b]	13	4	4	4
Santa María	74	Bananita	112	12	1964	6	4	4	4
Boston	75	Boston	169	16	1950	18	4		2
Corina	1640	Corina	132	9	1959	40	4		4
San Juan	2090	Goshen	58	5	1976	6	4	3[c]	2
Total							**48**	**15**	**42**

[a] m. a.s.l: Meters above see level.
[b] Missing information.
[c] Missing n = 1 as no electricity was available on day of sampling.

2.3. Sampling materials and preparation

Prior to collocating PUF discs (14 cm diameter, 1.35 thick, surface area = 365 cm^2, mass = 4.40 g, volume = 207 cm^3; density = 0.0213 g/cm^{-3}) (Tish Environmental) in the field, we cleaned them at our laboratory. We first submerged them in a 2% solution of phosphate free soap, and, subsequently, washed them with tap water, distilled water, and deionized water (MilliQ Millipore). Afterwards, we continued cleaning them in an ultrasonic bath, by immersing them for 1 h in Milli-Q water, 1 h in acetone and twice in petroleum ether for 1 h, respectively. All solvents were Suprasolv grade and have been purchased from Merck KGaA, Darmstadt, Germany. Once solvents were evaporated, we spiked each PUF by applying 10 mL of a mixture that contained 2 μg of PCB30, and 2 μg of PCB209 (reference materials from Dr. Ehrenstorfer, Augsburg, Germany) dissolved in petroleum ether.

For AAS, we used a high-volume sampler (600 L/min), air is sucked through a device similar to ORBO 2500 from Supelco (Supelco (North Harrison Road, Bellefonte, PA, USA) containing a glass fiber filter (VWR, 11 cm, grade 696) to capture particulate matter and then through XAD-2 (10 g de Supelpak -2SV, Supelco) stored between two PUF plugs (ORBO, 2000; Supelco) to capture gaseous compounds as described by Gouin et al. (2008). The glass fiber filter was cleaned with acetone and heated at 400 °C for 2 h. Regarding passive dust samples, we used 10 cm diameter Petri glass dishes, previously cleaned with acetone, and heated in 400 °C for 2 h. We weighted Petri dishes prior to, and after, sampling. Samples were transported at 4 °C and stored at −20 °C until extraction and chemical analysis.

2.4. Chemical analysis

We performed chemical analysis of the 18 pesticides indicated in Table 2, of which 17 reported to be used on banana plantations, and the metabolite terbufos sulfone, using gas chromatography (Agilent 7890 A) with mass detector (Agilent, 5975C), in the Selected Ion Monitoring (SIM) mode. According to Gibbs et al. (2017), compounds with Henry's Constant values $> 10^{-8}$ and log K_{OA} values 7–13 are suitable for passive sampling with PUF; these conditions were met for all the 18 pesticides from Table 2. Briefly, each sample was spiked with chlorpyrifos D10 as internal standard before extraction. For PUF from PAS, we extracted each PUF twice in an ultrasonic bath with acetone-hexane mixture (1:1) and then concentrated the sample with rotavapor, after this by nitrogen gas flow to 0.1 mL. For AAS, we extracted PUF plugs and XAD with a similar procedure as PUF from PAS. The AAS were divided in two samples, part A and B; part A is the PUF plug that becomes first into contact with the airflow, including XAD; part B is the PUF at the cartridge exit. Each part was extracted in an ultrasonic bath with acetone-hexane mixture and concentrated using rotavapor, and then with nitrogen gas flow to 0.1 mL. Both PUF-PAS and AAS extracts were reconstituted with 1–2 mL isooctane. For glass fiber air filters, dust was extracted from glass fiber filters in an ultrasonic bath with acetone-hexane mixture and concentrated with nitrogen to 0.2 mL in isooctane. Dust samples collected with Petri dishes were also extracted in an ultrasonic bath with acetone-hexane mixture and concentrated with nitrogen and reconstituted to 1 mL isooctane. For each group (PUF-PAS, PUF, and XAD-AAS, glass filter AAS and Petri dish) of extracted samples (n = 4), we used a blank reactive as quality control. The extracted samples from PUF-PAS were quantified by calibration curves prepared in PUFs. We prepared calibration curves by spiking four PUF-disks with different levels of pesticides in petroleum ether solutions, then they were extracted using same sample procedure to get four extract levels from 0.2 to 10 μg/mL, whilst extracts from PUF/XAD-2, glass fiber filters and Petri dishes were quantified with calibration curves prepared in isooctane. For each of the pesticides, we calculated its limit of detection (LODs) with WINSTAT® 3, version 2.1.0.056 (Stockholm University), using a linear regression of pesticide concentrations and MS response. Tables 3, 5 and 6 describe LODs for samples collected with PUF, PUF-XAD, glass-fiber filter, and Petri dish, respectively. For chlorothalonil, concentrations in PUF could not be quantified because it was degraded partially by acetone hexane, the solvent that we used to extract PUF samples. We determined % recovery and coefficients of variance (CV) for seven agents in five PUFs, respectively: terbufos 100%, CV = 1.2; chlorpyrifos 92%, CV = 3.5; diazinon 92%, CV = 1.4; pyrimethanil 90%, CV = 20; epoxiconazole 83%, CV = 10; difenoconazole 72%, CV = 7; terbufos sulfone 98%, CV = 1.3).

To estimate the pesticide air concentration in the PUF-PAS (ng/m^3) it is necessary to know the mass of pesticide collected (M_{PUF}, ng) and the air sampling volume (V_{air}, m^3) (see Eq. (1)).

$$C_{air}\ (ng/m^3) = M_{PUF}\ (ng) / V_{air}\ (m^3) \quad (1)$$

To determine the sampling volume (V_{air}) for each PUF (Eq. (2)), we used the equation by Shoeib and Harner (2002) and Koblizkova et al. (2012), supplied as a template by the GAPS Network (gaps.network@ec.gc.ca) (Koblizkova et al., 2012).

$$V_{air}\ (m^3) = (K'_{PUF\text{-}a}) \times (V_{PUF}) \times \{1 - \exp[\,-(t_{days}) \times (kA) / [(K'_{PUF\text{-}a})\ x\ (1/(D_{film})]]\} \quad (2)$$

Table 2
Pesticides that were analyzed in this study and their chemical properties.

Pesticide type	Application method on banana[a]	Substance group	Active ingredient	Mol. weight[b]	$LogK_{OW}$[b]	$LogK_{OA}$[c]	Solubility (mg/L)[b]	Henry's Constant ($Pa.m^3/mol$)[d]	Vapor pressure (25°) (mPa)[d]	Volatility[d]
Insecticides	Treated bag	Organophosphate	Chlorpyrifos	350.58	4.96	8.40	0.39	0.478	1.43	Moderate volatile
		Thiadiazine	Buprofezin[e]	305.44	4.93	8.97	0.90	2.8×10^{-02}	0.04	Non-volatile
	Not reported to be used on banana	Organophosphate	Diazinon[f]	304.34	3.69	8.89	60	6.09×10^{-02}	11.97	Non-volatile
Nematicides	Manual dispenser	Carbamate	Carbofuran	221.25	2.32	8.11	351	5.0×10^{-05}	0.08	Non-volatile
		Organophosphate	Cadusafos	270.38	3.90	8.18	245	0.13	119.60	Moderatelyvolatile
			Ethoprophos[g]	242.33	3.59	8.77	750	1.35×10^{-02}	78.00	Non-volatile
			Fenamiphos	303.35	3.23	9.72	329	9.90×10^{-05}	0.12	Non-volatile
			Terbufos[h]	288.41	2.77	7.49	5.07	2.70	34.60	Moderately volatile
Fungicides	Aerial spraying	Anilinopyrimidine	Pyrimethanil	199.25	2.84	8.67	121	3.60×10^{-03}	1.10	Non-volatile
		Chloronitrile	Chlorothalonil[i]	265.90	2.94	8.11	0.81	2.50×10^{-02}	0.07	Non-volatile
		Morpholine	Fenpropimorph[j]	303.49	4.50[j]	8.93	4.32	2.74×10^{-04}	3.90	Non-volatile
			Spiroxamine	297.48	2.89	10.87	405	3.80×10^{-03}	3.50	Non-volatile
		Strobilurin	Azoxystrobin	403.39	2.50	14.03	6.00	7.40×10^{-09}	1.10×10^{-07}	Non-volatile
		Triazole	Bitertanol	337.42	4.10	12.17	3.80	2.60×10^{-07}	1.36×10^{-06}	Non-volatile
			Difenoconazole	406.26	4.40	11.93	15.0	9.00×10^{-07}	3.33×10^{-05}	Non-volatile
			Epoxiconazole	329.75	3.30	9.11	7.1	4.71×10^{-04}	1.00×10^{-02}	Non-volatile
			Propiconazole	342.22	3.72	9.24	100	9.20×10^{-05}	0.05	Non-volatile
			Tebuconazole	307.82	3.70	10.19	36	1.00×10^{-05}	1.30×10^{-03}	Non-volatile

[a] Reported to be used on banana by Bravo et al. (2013), the following pesticides were also reported but were not analyzed: bifenthrin, mancozeb, tridemorph, pyraclostrobin, trifloxystrobin, diquat, paraquat, glufosinate, glyphosate.
[b] Data on chemical properties are from PubChem https://pubchem.ncbi.nlm.nih.gov, solubility in water at 20 °C, pH 7 (mg/L).
[c] Log K_{OA} (octanol air partition coefficient) is calculated from the log K_{OW} (octanol water partition coefficient) using the ideal gas constant and Henry's Constant value (Meylan and Howard, 2005).
[d] Data on chemical properties are from IUPAC Pesticides Properties Database (PPDB) https://sitem.herts.ac.uk/aeru/ppdb/en/; According to Gibbs et al. (2017), Henry's Constant values $> 10^{-8}$ and $logK_{OA}$ values 7–13 indicate that the compound is ideal for passive sampling with PUF; volatility interpretation according to Henry's Constant.
[e] Reported to be used together with bifenthrin in bags to protect banana fruit (Ruepert, personal communication).
[f] Not reported to be used on banana.
[g] Also reported to be used on pine-apple.
[h] The metabolite terbufos sulfone was also analyzed.
[i] Was not quantified for Passive Air Sampling (PAS).
[j] Data on chemical properties are from EPA https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_PC-121402_01-Mar-06.pdf.

Where:

- V_{air} is the sampled volume of air (m^3);
- $K'_{PUF\text{-}a}$ is a partition coefficient between the passive air sampling media and air, calculated from octanol–air partition coefficient K_{oa} according to Shoeib and Harner (2002) (see Eq. (3));
- V_{PUF} = the volume of the passive sampling medium (m^3);
- t is sampling time in days;
- kA is the air-side mass transfer coefficient (mass/day). Like Shoeib and Harner (2002) and Koblizkova et al. (2012), we calculated site-specific kA values from the loss of depuration compounds (PCB 30 and PCB 209), spiked on each PUF prior to deployment;
- D_{film} is the effective film thickness (m).

$$\log K_{PUF\text{-}a} = 0.6366 \times \log K_{oa} - 3.1774 \quad (3)$$

$$K'_{PUF\text{-}a} = 10(\log K_{PUF\text{-}a} \times PUF_{density}) \quad (4)$$

In Eq. (3), K_{oa} is the octanol/air partition coefficient at 25 °C. For chlorpyrifos and diazinon, Koa was calculated using a template "PUF/SIP Disk Effective Air Volume Calculation for Target Chemicals" 2014 provided by Tom Harner. For the other pesticides, the octanol-air partition coefficient (Koa) used for each pesticide was calculated by Epi Suite™ (US-EPA, 2012). In Eq. (4), $PUF_{density}$ is denisity of PUF (g/m^3).

For the calculation of the air concentration of PUF/XAD-2 and the glass fiber filter from AAS, the air flow was obtained from the air sampling pump.

2.5. Statistical analysis

We used descriptive statistics to analyses pesticide concentrations of proximal and non-proximal schools. We calculated 50th, 75th and 90th percentiles for pesticides detected in more than 50% of the samples. We also tested whether concentrations followed a normal (Shapiro-Wilk W test) or log-normal distribution (Shapiro-Wilk W test after natural log-transforming the pesticide concentrations). To evaluate whether pesticide concentrations were different for proximal and non-proximal schools, we used Student's T-test for chlorpyrifos concentrations from PAS and Wilcoxon/Kruskal–Wallis rank sum test for continuous measures for the other pesticide concentrations as they did not follow a normal distribution. We compared the percentage of samples above LOD of proximal and non-proximal schools with Pearson's Chi-Square Test. To verify whether pesticides concentrations of passive (PUF) and active air samples (XAD-PUF) were correlated, we calculated Spearman's r correlation coefficients for concentrations that were detected in more than 50% of samples of both PUF and XAD-PUF.

For pesticide concentrations that were detected in more than 80% of the samples and followed a normal or log-normal distribution (chlorpyrifos, ethoprophos, and pyrimethanil), we estimated temporal variability of pesticides concentrations between and within schools by calculating Intraclass correlation (ICC) using variance components models with random effects (Rosner and Bernard, 2000). For these pesticides, we also used Decision Tree Method of recursive partition modeling (Cook and Goldman, 1984) to explore the clustering of pesticide concentrations with respect to schools, and subsequently

Table 3
Description of pesticide concentrations measured in PUF from passive air sampling (PAS) for proximal (n = 40, schools = 10) and non-proximal schools (n = 8, schools = 2) during four periods of, on average, 6.7 weeks (SD = 1.9, range: 3.9–12.1), from June 2010 to October 2011, ISA study, Matina County, Costa Rica.

Pesticides	LOD (ng/m^3)	Overall % > LOD	Overall ICC	Proximal schools (ng/m^3) (n = 40, schools = 10)									Non-proximal schools (ng/m^3) (n = 8, schools = 2)							
				% > LOD	Mean (SD)	Min	p10	p25	p50	p75	p90	Max	% > LOD	Mean (SD)	Min	p10	p25	p50	p75	p90	max
Insecticides																						
Chlorpyrifos[a]	0.5	98%	0.80	100%	18.2 (6.3)	6.1	10.7	13.4	18.4	22.0	25.9	36.1	88%	3.5 (3.8)	< 0.5	< 0.5	0.6	2.1	5.4	11.4	11.4
Diazinon	0.3	31%		28%	0.6 (1.0)	< 0.3	< 0.3	< 0.3	< 0.3	0.7	2.8	4.0	50%	1.2 (1.3)	< 0.3	< 0.3	< 0.3	0.9	2.0	3.8	3.8
Nematicides																						
Etoprophos	0.5	81%	0.00	85%	5.5 (10.9)	< 0.5	< 0.5	0.6	1.6	4.8	18.7	60.9	63%	2.2 (3.0)	< 0.5	< 0.5	< 0.5	0.7	4.5	8.2	8.2
Terbufos	3.0	17%		20%	6.2 (13.7)	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	16.0	61.7	0%								
Terbufos sulfone	0.5	56%		60%	6.3 (8.0)	< 0.5	< 0.5	< 0.5	2.6	10.7	21.3	28.7	38%	1.2 (1.9)	< 0.5	< 0.5	< 0.5	< 0.5	1.5	6.1	6.1
Fungicides																						
Pyrimethanil[b]	0.5	81%	0.80	90%	5.4 (6.9)	< 0.5	< 0.5	1.0	1.7	8.3	19.1	22.2	38%	0.4 (0.2)	< 0.5	< 0.5	< 0.5	< 0.5	0.5	0.7	0.7
Chlorothalonil[c]	—[c]	48%		48%	–	–	–	–	–	–	–	–	50%	–	–	–	–	–	–	–	–
Fenpropimorph[d]	1.5	31%		38%	2.3 (3.5)	< 1.5	< 1.5	< 1.5	< 1.5	2.2	5.1	21.0	0%								
Spiroxamine	3.0	10%		13%	5.5 (12.1)	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	21.4	61.9	0%								
Difenoconazole	1.0	6%		8%	1.3 (3.4)	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	0.5	21.3	0%								
Epoxiconazole	1.0	27%		33%	3.1 (4.5)	2.5	< 1.0	< 1.0	< 1.0	4.3	10.6	15.9	0%								

[a] Concentrations of proximal schools were higher and more frequently detected than non-proximal schools: Student's t-test $p < 0.0001$, Pearson Chi-Square $p < 0.05$.
[b] Concentrations of proximal schools higher and more frequently detected than non-proximal schools: Wilcoxon/Kruskal Wallis $p < 0.0001$, Pearson Chi-Square $p < 0.0001$.
[c] Chlorothalonil concentrations could not be quantified because it was degraded partially by acetone hexane used to extract the sample.
[d] Concentrations of proximal schools more frequently detected than non-proximal schools: Pearson Chi-Square $p < 0.05$.

compared differences in exposure between groups with One-way Analysis of Variance (ANOVA), Tukey's HSD (honestly significant difference) test.

We considered findings statistically significant if $p < 0.05$. Data were analyzed in JMP version 8 (SAS Institute, Cary, NC).

3. Results

3.1. Description of schools with environmental sampling

Data from Table 1 show the schools had relatively small populations of students, with on average 127 students (range 40–343). The schools provided preschool and elementary lessons, meal services and several schools had permanent cleaning service. The schools were created from 1950 to 1984 to assure banana workers' children access to education. Ten out of the 12 schools were situated at less than 100 m, of which four at less than 50 m from banana plantations.

3.2. Passive air samples with PUF

3.2.1. General

Table 3 shows we overall detected ten different pesticides (two insecticides, two nematicides, and six fungicides), of which nine have been reported for use on banana (chlorpyrifos, ethoprophos, terbufos, pyrimethanil, chlorothalonil, fenpropimorph, spiroxamine, difenoconazole, epoxiconazole), and one pesticide metabolite (terbufos sulfone). Ethoprophos has reported to be used as well on pineapple plantations, whereas diazinon has been reported to be used on pineapple and pasture, but not on banana (Bravo et al., 2013) (Table 2). Four of the detected pesticides were organophosphate pesticides (chlorpyrifos, diazinon, ethoprophos, and terbufos). In 28 out of the 48 samples (58%) we detected five or more pesticides (excluding terbufos sulfone) at the same time.

Results from Table 3 shows chlorpyrifos was detected most frequently, in 98% of the samples, followed by ethoprophos and pyrimethanil (both detected in 81% of the samples), and terbufos sulfone (detected in 56% of the samples). The additional seven pesticides were detected in less than 50% of the samples. Only chlorpyrifos concentrations followed a normal distribution (Shapiro Wilks W = 0.98) whilst ethoprophos and pyrimethanil concentrations followed an approximately log-normal distribution (Shapiro Wilks W = 0.95 and 0.93, respectively, for log-transformed concentrations). The additional pesticide concentrations did not follow a specific distribution ($W < 0.83$) (data not shown). Chlorpyrifos concentrations was moderately correlated with pyrimethanil concentrations (Spearman's $r = 0.53$, $p < 0.0001$) but not with etoprophos ($r = 0.21$, $p = 0.14$) or terbufos sulfone ($r = 0.15$, $p = 0.32$) concentrations. Ethoprophos and terbufos sulfone concentrations were negatively correlated ($r = -0.58$, $p < 0.0001$), and did not correlate with pyrimethanil concentrations ($r = 0.12$ and $r = 0.00$, respectively) (data not shown). Finally, chlorpyrifos and ethoprophos negatively correlated with the number of days the PAS-PUF was collocated in the field, $r = -0.3$ $p = 0.03$ and $r = -0.7$ $p < 0.0001$, respectively, whilst terbufos sulfone showed a positive correlation ($r = 0.6$, $p < 0.0001$). The other pesticide concentrations that were detected in more than 50% of samples did not correlate with days of sampling.

3.2.2. Insecticides

Table 3 shows chlorpyrifos was detected in 100% of the samples obtained from proximal schools (range 6.1–36.1 ng/m^3) and in 88% of the samples from non-proximal schools (< 0.5–11.4 ng/m^3). Chlorpyrifos mean concentrations were five times higher in proximal schools as compared to non-proximal schools, 18.2 ng/m^3 and 3.5 ng/m^3, respectively (mean difference = 14.7, 95%CI 10.03–19.37) (Table 3). Strikingly, the two non-proximal schools still differed, with 'Goshen' having higher concentrations (mean = 6.3 ± 3.6) than 'Corina'

Table 4
Results from partitioning modeling of chlorpyrifos concentrations, explaining 79% of total variability, measured from June 2010 to October 2011, ISA study, Matina County, Costa.

Group	Schools	Mean (95% CI)	Mean difference compared with low group
Low	Corina, San Juan	3.5 (0.7–6.2)	..
Moderate	Boston, Larga Distancia, Almendros	11.8 (9.6–14.1)	8.3 (3.6–13.1)
High	4-Millas, la Maravilla, Saborio, Zent, Santa María	18.8 (17.1–20.6)	15.4 (11.0–19.7)
Very high	Barmouth, Venecia	26.0 (23.2–28.8)	22.5 (17.3–27.7)

(mean = 0.7 ± 0.4). Eighty percent of the variability in chlorpyrifos concentrations was explained by differences between schools and only 20% by differences within schools (ICC = 0.80, $\sigma^2_{\text{between-schools}}$ = 55.1 and $\sigma^2_{\text{within-schools}}$ = 14.1). In addition, results from recursive partition modeling showed four groups of exposure explained 79% of the variability; the moderate, high and very high chlorpyrifos exposure groups had significantly higher chlorpyrifos concentrations as compared to group with low concentrations (=non-proximal schools), mean differences in chlorpyrifos concentrations were 8.3, 15.4, and 22.5 ng/m^3, respectively (Table 4).

Table 3 also shows the insecticide diazinon was detected in 16 out of 52 samples (31%) (Range < 0.3–4.0) and was detected somewhat less frequent in proximal schools (28% > LOD, 11 out of 40) as compared to non-proximal schools (50% > LOD, 4 out of 8).

3.2.3. Nematicides

We detected ethoprophos in 81% of samples (range < 0.5–60.9), somewhat more frequent in proximal schools (85% of samples, n = 34) as compared to non-proximal schools (63%, n = 5), with slightly higher concentrations in proximal schools (median = 1.6 and 0.7 ng/m3, respectively) (Wilcoxon-Kruskal Wallis p = 0.23). Overall, for ethoprophos differences within schools (between sampling periods) explained 100% of the variability in exposure (ICC = 0.00, $\sigma^2_{\text{between-schools}}$ = 0.0, and $\sigma^2_{\text{within-schools}}$ = 2.0 for ln-transformed concentrations).

We detected terbufos in 17% of samples from proximal (range < 3.0–61.7), and in none of the samples from non-proximal schools. We detected terbufos sulfone, a metabolite from terbufos, more frequently in proximal schools (60%, n = 24) than non-proximal schools (38%, n = 3). Concentrations in proximal schools tended to be higher than non-proximal schools, median 2.6 ng/m3 versus < 0.5 ng/m3, respectively (Wilcoxon/Kruskal-Wallis test p = 0.06).

3.2.4. Fungicides

We detected pyrimethanil more frequently, and median concentrations were higher, in proximal (90% > LOD, n = 36; median = 1.7) as compared to non-proximal schools (38% > LOD, n = 3; median < 0.5 ng/m^3) (Wilcoxon/Kruskal-Wallis test p < 0.0001). Differences between schools explained 80% of the variability in exposure (ICC = 0.80, $\sigma^2_{\text{between-schools}}$ = 2.0, and $\sigma^2_{\text{within-schools}}$ = 0.3 for ln-transformed concentrations). We detected the fungicides fenpropimorph, spiroxamine, epoxiconazole and difenoconazole only in samples

Table 5
Description of pesticide concentrations detected in passive and active air samples in three proximal schools (Zent, Santa María, Los Almendros) on four occasions (n = 12), and one non-proximal school (San Juan) on three occasions (n = 3), from June 2010 to October 2011, ISA study, Matina County, Costa.

	Passive air samples PUF (ng/m^3) Mean (SD) sampling time = 7.1 (2.2) weeks					Active air samples PUF-XAD (ng/m^3) Mean (SD) sampling time = 24.6 (0.5) hours					Spearman's r for PUF and XAD-PUF[a]	Active air samples glass-fiber filter (ng/m^3) Mean (SD) sampling time = 24.6 (0.5) hours				
	LOD (ng/m3)	% > LOD	p50	p75	max	LOD (ng/m^3)	% > LOD	p50	p75	max		LOD (ng/m^3)	% > LOD	p50	p75	max
Insecticides																
Chlorpyrifos[b]	0.5	100%	15.4	12.0	22.3	0.3	100%	5.0	10.3	16.0	0.69	0.02	0%			
Buprofezin	0.2	0%				0.1	7%	< 0.1	< 0.1	0.2		0.01	7%	< 0.01	< 0.01	0.29
Diazinon	0.3	53%	0.7	2.9	4.0	0.1	27%	< 0.1	0.7	6.4		0.01	13%	< 0.01	< 0.01	0.04
Nematicides																
Carbofuran	N.A.					1	0%					0.01	7%	< 0.01	< 0.01	0.26
Cadusafos[c]	N.A.					0.3	73%	2.1	16.7	100.9		0.01	53%	0.03	0.16	0.57
Ethoprophos	0.5	93%	2.2	4.5	23.2	0.4	73%	1.2	4.0	57.4	0.61	0.01	33%	< 0.01	0.05	0.35
Terbufos[d]	3.0	7%	< 0.3	< 0.3	61.2	0.1	80%	1.7	5.7	242.9		0.01	13%	< 0.01	< 0.01	0.06
Terbufos sulfone	0.5	60%	1.6	6.3	25.2	0.2	20%	< 0.2	< 0.2	1.6		0.02	33%	< 0.02	0.03	0.24
Fungicides																
Pyrimethanil[e]	0.5	93%	4.9	19.3	22.2	0.1	73%	1.0	2.3	3.7	0.47	0.01	7%	< 0.01	< 0.01	0.03
Chlorothalonil[f]	–	33%				0.1	60%	0.9	5.0	43.2		0.01	27%	< 0.01	0.08	0.17
Fenpropimorph	1.5	40%	< 1.5	2.1	21.0	N.A.						N.A.				
Spiroxamine	3.0	27%	< 3.0	22.0	61.9	0.1	20%[e]	< 0.1	< 0.1	4.4		0.01	80%	0.09	0.30	0.57
Difenoconazole	1.0	7%	< 1.0	< 1.0	4.4	1	0%					0.05	47%	< 0.05	0.44	6.92
Epoxiconazole	1.0	20%	< 1.0	< 1.0	9.3	0.5	0%					0.05	20%	< 0.05	< 0.05	0.12

Abbreviations: LOD = Limit of detection; N.A. not analyzed.

[a] Only presented for concentrations that were detected in more than 50% of samples of both PUF and XAD-PUF.

[b] Chlorpyrifos concentrations were higher in samples from proximal schools as compared to non-proximal schools: 1) PUF median = 17.2 and 4.9 ng/m3, respectively, p < 0.01; 2) PUF-XAD median = 5.3 and 0.8 ng/m3, p = 0.01.

[c] Spearman's r for concentrations from XAD-PUF and glass-fiber filter were r = 0.64, p < 0.001.

[d] Terbufos concentrations tended to be higher in samples from proximal schools as compared to non-proximal schools: XAD-PUF median = 2.3 and 0.3 ng/m^3, respectively, p = 0.07.

[e] Pyrimethanil concentrations were higher in samples from proximal schools as compared to non-proximal schools: 1) PUF median = 12.7 and 0.5 ng/m3, respectively, p < 0.01; 2) PUF-XAD median = 1.3 and 0.1 ng/m3, p = 0.02.

[f] Chlorothalonil concentrations could not be quantified in PUF due to a partial degradation by acetone-hexane used to extract the sample.

Table 6
Description of pesticides concentrations detected in dust samples (n = 42) in twelve schools during four periods of 1–3 months, from June 2010 to October 2011, ISA study, Matina County, Costa Rica.

Pesticides	LOD (ug/g)	Overall % > LOD	Dust samples (ug/g) (n = 42, schools = 10)				
			Mean (SD)	p50	p75	p90	Max
Insecticides							
Cypermethrin	1.5	4%	0.77 (0.36)	< 1.5	< 1.5	< 1.5	2.6
Nematicides							
Terbufos sulfone	1	2%	–	< 1.0	< 1.0	< 1.0	1.9
Fungicides							
Pyrimethanil	0.4	4%	0.33 (0.65)	< 0.2	< 0.2	< 0.2	4.01
Chlorothalonil[a]	0.5	50%[a]	16.69 (39.02)	0.9	12.7	58.7	209.3
Spiroxamine	0.9	11%	2.23 (9.85)	< 0.9	< 0.9	3.0	64.1
Difenoconazole	5.5	16%	7.14 (13.45)	< 5.5	< 5.5	20.6	77.7
Epoxiconazole	3.1	21%	10.91 (38.14)	< 3.1	< 3.1	18.1	242.0
Tebuconazole	3.6	7%	2.75 (5.19)	< 3.6	< 3.6	< 3.6	35.3
Propiconazole	1.6	0%	–	< 1.6	< 1.6	< 1.6	< 1.6
Bitertanol	4.7	2%	–	< 4.7	< 4.7	< 4.7	32.3

[a] Concentrations tended to be higher in samples from proximal schools as compared to non-proximal schools, median 2.79 and 0.30 μg/g respectively, Wilcoxon/Kruskal-Wallis test, p = 0.13.

from proximal schools, in 31%, 10%, 27%, and 6%, respectively, ranging from < 1.0 to 61.9 ng/m^3. Chlorothalonil was detected in 48% of samples but could not be quantified due to chemical-analytical limitations.

3.3. Active air samples

3.3.1. PUF-XAD

In Table 5, we present results from samples obtained simultaneously with PAS and AAS in three proximal and one non-proximal school, the AAS were obtained on the first day of the measurement period of the PAS using a high-volume air sampler. Like PUF from PAS, we detected 10 pesticides and one metabolite (terbufos sulfone) in the PUF-XAD from AAS. We detected the same pesticides in PUF from PAS and PUF-XAD from AAS, except from difenoconazole and epoxiconazole (only detected with PAS in 7%, and 20% of samples, respectively), and buprofezin (only detected with AAS in 7% of samples). For the most-frequent detected pesticides, concentrations moderately correlated for PUF and PUF-XAD samples obtained with PAS and AAS, respectively: Spearman's r for chlorpyrifos r = 0.69, p < 0.01; ethoprophos r = 0.61 p < 0.05, and pyrimethanil r = 0.47 p = 0.08. Terbufos and terbufos sulfone concentrations for PUF and PUF-XAD did not correlate, as detection frequencies differed: Terbufos = 7% (PUF) and 80% (PUF-XAD); and Terbufos sulfone = 60% (PUF) and 20% (PUF-XAD) respectively. For chlorpyrifos, ethoprophos, and pyrimethanil median concentrations in PUF from PAS tended to be two to five-times higher than concentrations in PUF-XAD from AAS. Yet, maximum concentrations of ethoprophos and terbufos were two and four-times higher in PUF-XAD from AAS as compared to PUF from PAS.

Like chlorpyrifos measured in PUF from PAS, chlorpyrifos concentrations were detected in all the 15 samples, and median concentrations were more than five times higher in PUF-XAD from proximal schools as compared to non-proximal schools, 5.3 and 0.6 ng/m^3, respectively (Wilcoxon/Kruskal-Wallis test p < 0.01). Also, median concentrations of terbufos and pyrimethanil in PUF-XAD from AAS seemed to be higher in proximal schools (median terbufos = 2.3 ng/m^3; median pyrimethanil = 1.3 ng/m^3) as compared with non-proximal schools (median terbufos = 0.3 mg/m^3; median pyrimethanil = 0.1 ng/m^3) (Table 5, table note (d) and (e)). Terbufos was the second-most-detected in PUF-XAD from AAS (80% of samples). For PUF-XAD from AAS, cadusafos, ethoprophos, and pyrimethanil were the third-most detected pesticides (73% of samples). Pyrimethanil was only detected in proximal schools, in 11 out of 12 samples. Cadusafos was detected in ten of 12 samples from proximal schools and in one out of three samples from non-proximal schools, whilst ethoprophos was detected in nine out of 12 samples from proximal, and two out of three from non-proximal schools.

3.3.2. Glass fiber filters

Table 5 shows results from dust collected with the glass fiber filters in three proximal and one non-proximal school (n = 15). Like PUF and PUF-XAD, we detected 11 pesticides and one metabolite (terbufos sulfone). Yet, the pattern of the detected pesticides was different from results from PUF and XAD-PUF; for example, chlorpyrifos was not detected in any of the dust collected, whereas spiroxamine and difenoconazole were detected more frequently in dust from glass fiber filters (80% and 47%, respectively) as compared to PUFs (27% and 7%, respectively) and PUF-XAD (20% and 0%, respectively). Apart from spiroxamine, only cadusafos was detected in more than 50% of dust samples (Table 5). No clear differences between proximal and non-proximal schools were observed (results not reported).

3.3.3. Settled dust from petri-dishes

We collected 42 samples in 12 schools, 36 in proximal schools and six in non-proximal schools. We detected nine pesticides and one environmental metabolite (terbufos sulfone, Table 6). Eight of these pesticides were fungicides aerially applied on bananas (chlorothalonil, epoxiconazole, difenoconazole, spiroxamine, tebuconazole, propiconazole, pyrimethanil, bitertanol), and one was the insecticide cypermethrin reported to be used on rice plantations, as well as vector control and domestic use. In general, frequencies of detection were low; only chlorothalonil was detected in 50% of samples. Detection frequencies of chlorothalonil were similar for proximal (56%, n = 20) and non-proximal (50%, n = 21) schools, concentrations tended to be higher in proximal schools than non-proximal schools (median 2.79 and 0.30 μg/g respectively) (p = 0.13).

4. Discussion

In this study we evidence PAS-PUF sample devices can be used to characterize air concentrations to a broad range of current-use pesticides; the method is a promising technique to monitor current pesticide concentrations in multiple regions obtaining an integrated estimate of exposure during several weeks. The results of this study evidence external air in schools situated nearby banana plantations are contaminated with multiple pesticides; we detected 13 different pesticides with PAS and AAS, of which 12 reported to be used on banana, and one pesticide metabolite. We detected the insecticide chlorpyrifos in almost all air samples; concentrations were about five times higher in proximal schools as compared to non-proximal schools. In addition, nematicides

and fungicides were detected frequently in air samples, and generally more often in proximal schools. Our results indicate pesticide drift from aerial spraying, insecticide-treated bags and ground applications, which coincides with previous studies (i.e. Ramaprasad et al., 2004). Pesticide drift not only occurred to proximal schools situated at less than a hundred meters, some pesticides, like chlorpyrifos contaminated schools situated at more than 1.5 km distance from application fields.

On banana plantations, bags treated with chlorpyrifos (1% w/w) are used to protect bananas from birds and insects (Matlock & De La Cruz, 2002). Its constant detection in external air is noteworthy, as exposure to chlorpyrifos has been associated with impaired fetal growth and neurodevelopment, as well as behavioral problems (Fortenberry et al., 2014; Rauh et al., 2011, 2006; 2012; van Wendel De Joode et al., 2016; Whyatt et al., 2004). Bananas are grown whole year round, and each bag covers a banana bunch during its ripening. At the time of study, it was reported that at some plantations chlorpyrifos-treated bags were rotated with bags treated with both bifenthrin (pyrethroid) and buprofezin (thiadiazine). Nonetheless, the results of this study showed a constant drift of chlorpyrifos concentrations to schools, that even reached schools located at 1.5 km; concentrations were about five times higher in proximal schools (< 100 m) than non-proximal schools (> 1.5 km). The ICC of 0.80 indicates differences between schools were larger than differences in time (within schools). Results from partitioning modeling resulted in the grouping of schools into four groups, that explained 79% of total variability; mean concentrations in highest exposed schools were seven-times higher than schools with lowest exposure. Differences may be explained by some schools being more immersed in banana plantations than others, wind direction, and presence, or absence, of barriers between schools and banana plantations.

In an agricultural area in Washington State where apple and cherries were grown, Gibbs et al. (2017) analyzed indoor and outdoor air using PUF-PAS; like our study, they detected chlorpyrifos in all the outdoor samples at proximal farmworker and non-farmworkers households within 100 m from crops fields. In spring season, concentrations inside farmworkers' houses exceeded about four times our chlorpyrifos levels (mean 72 ng/m^3 vs 18.2 ng/m^3) whereas concentrations inside non-farmworkers households were similar to the levels in our study (mean 23 ng/m^3 vs 18.2 ng/m^3). In contrast, in winter season chlorpyrifos concentrations in the study in farmworker households were five times lower than our levels (mean 3.5 ng/m^3 vs 18.2 ng/m^3). More recently, in Chile (Climent et al., 2019), PUF-PAS were used to measure pesticides in air from an agricultural area; chlorpyrifos concentrations were higher in summer as compared to spring (3.47 ng/m^3 and 1.18 ng/m^3, respectively); in both sampling periods chlorpyrifos concentrations in Chile were lower than mean chlorpyrifos concentration measured in this study (18.2 ng/m^3 in PUF-PAS). Finally, median chlorpyrifos concentrations in proximal schools in this study (PAS = 18.4 ng/m^3 (n = 40), AAS = 5.3 ng/m^3 (n = 12)) were also higher than measured in a school proximal to banana plantations in Talamanca, Costa Rica (PAS = 8.3 ng/m^3, AAS = 3.1 ng/m^3) (van Wendel de Joode et al., 2012), but only two passive and three active samples were obtained in this previous study. Furthermore, Morgan et al. (2005) analyzed internal and external air with AAS in nursery schools and detected chlorpyrifos in internal air samples (median = 3 ng/m^3, n = 20) and in external air samples (median = 0.3 ng/m^3, n = 13). The differences between internal and external were explained by chlorpyrifos use for vector control inside the nursery schools, as data were collected before US-EPA forbid residential use in 2001 (US-EPA, 2002). In the current study, air concentrations were measured outside; yet, as classrooms are well ventilated and often windows do not have glass because of the tropical climate, we expect outdoor and indoor concentrations to be similar. Also, sometimes students receive lectures outside because of the hot climate (see Fig. 3). Median concentrations measured by active air sampling in proximal schools from our study (5 ng/m^3) were slightly higher than internal air concentrations reported by Morgan et al. (2005), and about five times higher than concentrations reported in external air by Morgan et al. (2005). In contrast, median concentrations in non-proximal schools were about three times lower than the concentrations for internal air and slightly higher than the concentrations reported for external air, respectively, reported by Morgan et al. (2005). These differences can be explained by distinct use of chlorpyrifos, which in our study was external, outside schools on banana plantations, whereas in the study by Morgan et al. (2005), use was inside schools to control insects.

Fig. 3. Students receiving lectures outside classrooms because the hot climate, Matina County, Costa Rica.

In addition to chlorpyrifos, ethoprophos, and pyrimethanil were detected in 81% of PAS-PUF samples. Ethoprophos concentrations varied more in time than between schools (ICC = 0,00) which is consistent with the application frequency of nematicides of about three times a year (Wesseling, 1997). For PAS-PUF, the negative correlation between ethoprophos and terbufos-sulfone nematicides (r = −0.58) is also consistent with application patterns, as the distinct nematicides are applied alternately. Pyrimethanil is a fungicide applied by aircraft alternate with other fungicides. It possesses low acute toxicity but is possibly carcinogenic (US-EPA, 2018). In some school pyrimethanil concentrations were higher than others, as reflected by the ICC = 0.80, indicating a rather constant exposure to pyrimethanil in part of the schools. Median pyrimethanil concentrations measured in this study in proximate schools (5.4 ng/m3) were about a hundredfold higher than maximum concentrations measured with PAS-PUF from a rural area in Chile (0.05 ng/m^3) (Climent et al., 2019).

When comparing results from PAS-PUF with AAS-PUF-XAD, except terbufos, we observed similar exposure patterns as reflected by the moderate correlations (r = 0.5 to 0.7) between the most-detected pesticides with PAS and AAS (chlorpyrifos, ethoprophos, and pyrimethanil). The latter is striking as sampling time of PAS was much longer (mean = 6.7 weeks) than AAS (mean = 25 h). Yet, absolute concentrations between PAS-PUF and AAS-PUF-XAD differed. Median pesticide concentrations tended to be two (i.e. chlorpyrifos, etoprophos) to five (pyrimethanil) times higher in PAS compared to AAS. This finding coincides with Gouin et al. (2008) who also detected higher concentrations with PAS-PUF as compared with AAS-PUF-XAD. Nevertheless, maximum concentrations with PAS were not always higher than concentrations measured with AAS: for example, maximum ethoprophos concentrations were a two-fold lower in PAS-PUF compared to PAS-PUF-XAD from AAS. The differences in pesticide concentrations between PAS-PUF and AAS-PUF-XAD may be explained by several reasons. First, by differences in sampling periods; pesticides are more likely to be detected with PAS-PUF as the sampler was collocated for a longer time in the field, therefore the chance that pesticides were used during the sampling period increased. Second, air volume with PAS is measured indirectly, and therefore less precise than AAS. Third, in time PAS-PUF may become saturated leading in decreased absorption of pesticide by PAS-PUF, and, fourth, or pesticides may degrade in PAS-PUF which would result in an underestimation of pesticide air concentrations. For example, in PAS-PUF chlorpyrifos and ethoprophos, both inversely correlated with the number of days the sampler was collocated in the field (r = −0.3 and r = −0.7, respectively)

indicating part of the substance may have degraded. Also, in PAS-PUF, terbufos sulfone, degradation production of terbufos, was detected more frequently than terbufos, in 56% and 17% of samples, respectively, suggesting part of terbufos degraded into terbufos sulfone during measurement period. This coincides with the positive correlation between terbufos sulfone and number of days the PAS-PUF was collocated in the field ($r = 0.7$). In contrast, for PUF-XAD with AAS, terbufos was detected more frequently than terbufos sulfone, in 80% and 20% of the samples, respectively. The maximum nematicide concentrations detected with AAS were considerable, for example, maximum concentration of terbufos was 242.9 ng/m3. More studies are needed to characterize the sampling rates and optimal sampling times of PAS-PUF and to better understand how results from PAS-PUF relate to AAS.

With respect to concentrations measured with AAS-PUF-XAD and AAS glass fiber filter, it is striking that chlorpyrifos was detected in all PUF-XAD samples and in none of the dust samples, indicating chlorpyrifos was mainly present in the gaseous/vapor phase. Also, diazinon, cadusafos, ethoprophos, terbufos, pyrimethanil, and chlorothalonil were detected more frequently in PUF-XAD than in inhalable dust, suggesting their presence was mainly in gaseous/vapor phase, but they also adhered to some extend to dust particles. In contrast, difenoconazole, and epoxiconazole were mainly present in dust measured with glass fiber filters which corresponds to volatility and other physical-chemical properties of the pesticides. With respect to dust deposited in petri dishes, inside schools, almost exclusively fungicides applied with light aircraft were detected, chlorothalonil was detected most frequently.

This study has several limitations. First, due to logistical constraints, we were unable to standardize the sampling period of PAS-PUF. In this study we aimed to sample for six weeks; yet mean (SD) sampling period was 6.7 (1.9) weeks (range 3.9–12.1 weeks). Although length of sampling period explained pesticide concentrations to some extent, it is unlikely that this variation in sampling periods contributed to differences in pesticide concentrations between schools as sampling periods were not systematically different between schools. Second, we were unable to collocate PAS-PUF simultaneously at all 12 schools. However, we do not expect this to have influenced our findings because: (i) Bananas are grown whole year round; (ii) Climatological conditions at the Caribbean slope are similar throughout the year with temperatures varying between 31 and 21 °C and rainfall throughout the year with only a relatively drier period from February to April and September and October; (iii) Schools were sampled during both relatively drier and wetter months; iv) Pesticides are being applied throughout the year. A third limitation was that we did not have access to pesticide spraying records from banana plantations and lacked information about specific pesticide use during sampling periods; this information would have given more insight into the extent of pesticide drift from banana plantations, and drift from other pesticides not reported for use on banana but detected in the course of this study. A fourth limitation was the number of sampling sites for active air sampling, that was only performed on three out of 12 schools. In contrast, the number of PAS was a strength. To our knowledge this is the first study to measure air contamination using PAS-PUF at 12 locations during four periods for a broad range current-use pesticides. A fifth limitation was for part of the petri dishes only a little amount of dust was deposited, resulting in many samples had pesticide concentrations below the limit of detection. In a future study, we therefore recommend leaving the dishes during a longer time in the field. A final limitation of PAS-PUF is that only a few researches has been performed measuring non-persistent pesticides, and even less information is available in tropical climates. We, therefore, recommend, for future studies, measure temperature and relative humidity inside PAS during sampling, collocate simultaneously two PAS at one sampling site to study variability in concentrations, change PUF after periods of two, four and six weeks to better understand degradation, losses of pesticides from PUF, sampling rates and optimal sampling times. We also recommend extending simultaneous sampling with PAS-PUF and AAS to understand for what pesticides ranking of concentrations is similar.

Despite the limitations, in this study we were able to repeatedly measure a broad range of current-use pesticide using passive sampling techniques in a tropical country. Our results evidence PAS-PUF is a promising technique to monitor and evaluate environmental pesticide exposure to a broad range of pesticides that allows ranking and grouping of exposures that can be used in epidemiological studies. Furthermore, our results indicate pesticides used at banana plantations drift to schools situated nearby, showing a need for measures to reduce this drift, not only for aerially sprayed pesticides but as well for pesticides applied with ground applications. In Costa Rica, aerially spraying of pesticides may only be performed at more than 100 m from residential areas in absence of a natural vegetative barrier, such as trees, and 30 m in presence of a natural vegetative barrier (La Gaceta, 2008), for ground applications no buffer zones are defined. The results from this study demonstrate that current legislation insufficiently prevent drift of pesticides used in agriculture to adjacent schools.

Credit author statement

Leonel Córdoba: Conceptualization, Methodology, Investigation, Data Curation, Formal Analysis, Writing-Original draft preparation. **Karla Solano:** Methodology, Writing-Reviewing and Editing. Methodology, Investigation, Writing-Reviewing and Editing. **Clemens Ruepert:** Methodology, Writing-Reviewing and Editing. Methodology, Investigation, Writing-Reviewing and Editing. **Berna van Wendel de Joode:** Conceptualization, Methodology, Investigation, Writing-Reviewing and Editing, Funding Acquisition, Supervision, Project Administration.

Declaration of competing interest

The authors declare they have no actual or potential competing financial interests.

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