Occurrence of atmospheric legacy and current-use pesticides in two highly impacted areas of Brazilian southeastern coast: How much pesticides can we breathe at sub/urban areas?

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Introduction

Air pollution is perhaps the most unbiased environmental risk to human health worldwide. According to World Health Organization (WHO), 91% of the global population was exposed to air quality that does not met the standard guidelines. In 2016, outdoor air pollution was estimated to cause 4.2 million premature deaths in both rural and urban areas[1] and previous studies have shown that long-term exposure to air pollution increases mortality[2].

Even not listed by WHO guidelines, pesticides stand out as a relevant concern due to their toxic, persistent and bioaccumulative potentials as well as their long-range transport. Pesticides has been globally used for several applications, such as agricultural (in several production types and steps), domestic (insecticide), veterinary (on cattle and pets) and sanitary (lice, scabies and vectors fight) purposes. The application of current-use pesticides (CUPs) is supported by a belief that CUPs are unlikely to persist in the environment to the same extent as organochlorine pesticides (OCPs), due to their relatively more water soluble, less bioaccumulative and less persistent chacacteristics[3]. Despite that, several studies have brought opposing information about their environmental mobility and toxic potential[4,5,6]. Indeed, recently studies have highlighted their bioaccumulation[7], maternal transference in marine mammals[8], high levels in human milk[9], long-range atmospheric transport[10], behavioral and developmental toxicity[11] as well as their reproductive risks to both genders[12,13] and their potential as endocrine disruptors and cancer precursors[14].

As other tropical countries, Brazil is well known for its massive use of pesticides, not only in agriculture activities, but also in fighting vectors of endemic diseases, such as malaria, typho, dengue and more recently zika virus. Therefore, this study aimed to investigate the occurrence of legacy organochlorine pesticides and pyrethroids along spatial and seasonal gradients over environmental transects (Southeast Brazil), covering historically contaminated areas. The potential inhalation exposure of selected pesticides to local populations was also evaluated.

Materials and methods

Passive air sampling (PAS) was carried out around two highly impacted areas of Brazilian southeastern coast. Regarding different kinds of activities and occupations, 11 monitoring points were settled around Guanabara bay (Rio de Janeiro - RJ) and 9 around Santos basin (São Paulo - SP) (Table 1). PAS was based on polyurethane foam disks (PUF)[15]. Two seasonal periods (winter and summer) were covered in two deployments of ~3 months (2015-2016). Sample preparation, extraction and measurements steps were published elsewhere[16]. PUF extractions were done by automatic Soxhlet system (*Buchi, Extraction system B-811*. Labelled recovery standards (d_6 -α-HCH and d_8 - *p,p'*-DDT) were added to each sample prior to analysis. Recovery mean values of 97% and 99% were measured for d_6-α-HCH and d_8-*p,p'*-DDT, respectively, with a maximum variation coefficient at 20%. Target pesticides concentrations were not extrapolated by recovery concentrations. Measurements were made by low-resolution gas chromatography (7890A) coupled with negative chemical ionization mass spectrometry (5975C) (GC/NCI-MS) SIM mode, both Agilent Technologies (Palo Alto, CA, U.S.A.). Sampling rate was based on the Global Atmospheric Passive Sampling literature (4 m^3 d^{-1})[17]. Statistical analyses were carried out in Graphpad Prism 5.0 (GraphPad Software Inc®). Data normality was checked by Shapiro Wilk test. As only non-parametric distributions were found, Kruskall-Wallis test and posteriori Dunn's Multiple test were used to compare more than 2 groups and Mann Whitney U test was applied to compare 2 groups. Significance level was 5% for all tests.

Potential exposure (PE) from inhalation of atmospheric pesticides was calculated to six age subgroups of each studied city's population (infants: 0.5-1.5 years, toddlers: 2-3 years, children: 5-6 years, youth: 10-12 years, adult males and females: 18-65 years old) according to Li et al. (2014)[18]. Then, PE of each subgroup was divided by the acceptable daily intake (ADI) proposed by the World Health Organization[19] to access the risk quotient (RQ) for each pesticide. According to Li et al. (2014) still, RQ level of concern was set as 1.0, which means that a potential risk if the RQ is higher than the ADI[18].

Table 1: Sampling points identifyed from #1 to #20 according to the state (RJ or SP) and the major ocupation and/or activity impact (background = BG; suburban = SU; urban = UB; industrial = ID; landfill = LF and harbour = HB).

CODE	Specific place	Activity	Latitude / Longitude
#1 RJ BG	Ilhas do Rio - Cagarras	Background	23° 1' 34.16" S / 43°11' 33.11" W
#2 RJ BG	APA Guapimirim	Background	22° 40' 35.6" S / 42° 58' 29.8" W
#3 RJ BG	Subsede PNSO	Background	22° 29' 40.0" S / 43° 00' 06.3" W
#4 RJ SU	Praia de Mauá	Suburban	22° 42' 57.3" S / 43° 10' 46.2" W
#5 RJ UB	Ilha do Fundão	Urban	22° 52' 8.65" S / 43°13' 4.47" W
#6 RJ UB	INEA Jacarepaguá	Urban	22° 58' 24.8" S / 43° 23' 24.8" W
#7 RJ UB	INEA Centro	Urban	22° 54' 26.7" S / 43° 11' 42.9" W
#8 RJ UB	INEA São Gonçalo	Urban	22° 49' 55.9" S / 43° 04' 24.7" W
#9 RJ ID	Campos Elíseos	Industrial	22° 42' 03.4" S / 43° 16' 17.6" W
#10 RJ ID	Cidade dos Meninos	Industrial	23° 41' 09.6" S / 43° 19' 22.1" W
#11 RJ ID/LF	Jardim Gramacho	Industrial/Landfill	22° 45' 40.9" S / 43° 16' 43.0" W
#12 SP BG	Escola Vicente de Carvalho	Background	23° 49' 58.2" S / 46° 08' 51.3" W
#13 SP BG	Vista Linda	Background	23° 47' 58.4" S / 46° 04' 50.6" W
#14 SP SU/LF	Pilões	Suburban/Landfill	23° 53' 28.3" S / 46° 27' 15.6" W
#15 SP SU/HB	Pronto Atendim - Humaitá	Suburban/Harbor	23° 56' 59.6" S / 46° 27' 34.2" W
#16 SP SU/ID	São Vicente	Suburban/Industrial	23° 59' 02.3" S / 46° 29' 03.4" W
#17 SP SU/ID	CEAMA - Rio Branco	Suburban/Industrial	23° 58' 34.9" S / 46° 28' 39.6" W
#18 SP SU/ID	ESF - Quarentenário	Suburban/Industrial	23° 58' 47.8" S / 46° 27' 14.0" W
#19 SP UB/HB	Paecará	Urban/Harbor	23° 57' 09.5" S / 46° 18' 06.7" W
#20 SP ID	CETESB	Industrial	23° 52' 39.2" S / 46° 25' 08.7" W

Results and discussion:

To summarize data, pesticides were grouped as the sum of their respective isomers and/or metabolites. Results were briefly discussed as the average of both winter and summer periods. Pesticide concentrations in atmospheric air were mostly composed of cypermethrin (from 13 to 79%; ~52% average), permethrin (from 2 to 47%; ~18% average), HCH (from 1 to 71%; ~7% average) and DDT (from 1 to 15%; ~7% average). If grouped, CUPs concentrations were significantly higher than OCPs ($p < 0.05$) (Figure 1). However, extreme air concentrations of HCH and DDT at point #10 RJ ID and the homogeneous high air concentrations of endosulfan, methoxychlor and mirex, specially around the Guanabara bay.

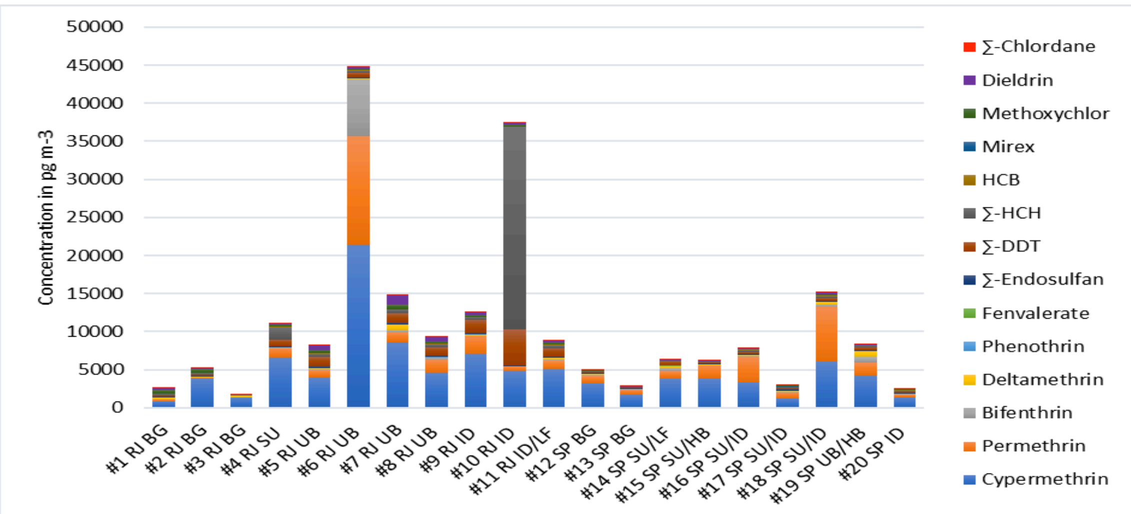

Figure 1: Bar graphic comparing atmospheric concentrations of measured pesticides at each sampling point.

CUPs and OCPs concentrations did not significantly differ in most cases, if compounds are separated (Figure 2). Although atmospheric concentrations of pesticides were slightly higher in summer, there was no significantly difference between winter and summer periods regarding all pesticides or even when CUPs and OCPs were separated ($p > 0.05$). Air concentrations were also slightly higher in urban areas than other sampling points, however, there was no significantly difference between activities and occupations or among sampling points ($p > 0.05$).

Therefore, despite of the identified hotspots, pesticides concentrations in atmospheric air seemed to be homogenously spread among sampled areas, with some particular variations between pesticide profile and sampling points. Extremely high concentrations (#6 RJ UB and #10 RJ ID) can be explained by local emissions. #6 RJ UB, where the highest air concentrations of pyrethroids were measured, is a sampling point surrounded by private condominiums, with relatively high income, which are known to make use of insecticide spraying services. It is also noteworthy that while this study was carried out, Brazil was facing an outbreak of zika virus infection. Moreover, with the 2016 Summer Olympics in Rio de Janeiro forthcoming (most of the games were settled at this same region), it is reasonable to assume an increase on CUPs surrounded spraying. On the other hand, # 10 RJ ID, where the highest concentrations of OCPs were measured (specially HCH and DDT) is well known to be one of the worst cases of environmental contamination in Brazil. In this place an HCH and DDT factory from the Brazilian Ministry of Health was deactivated in the 1960s leaving ~300 t of chemical residue behind[20]. Until present time the impacts of pesticides organochlorines on human health are unclear[21]. The most impacted area in Santos (#18 SP SU/ID) is the case of an irregular settlement in a place where approximately 12 kt of organochlorine residues were irregularly dumped by the multinational Rhodia, which became known as the "Rhodia case" in Brazil[22].

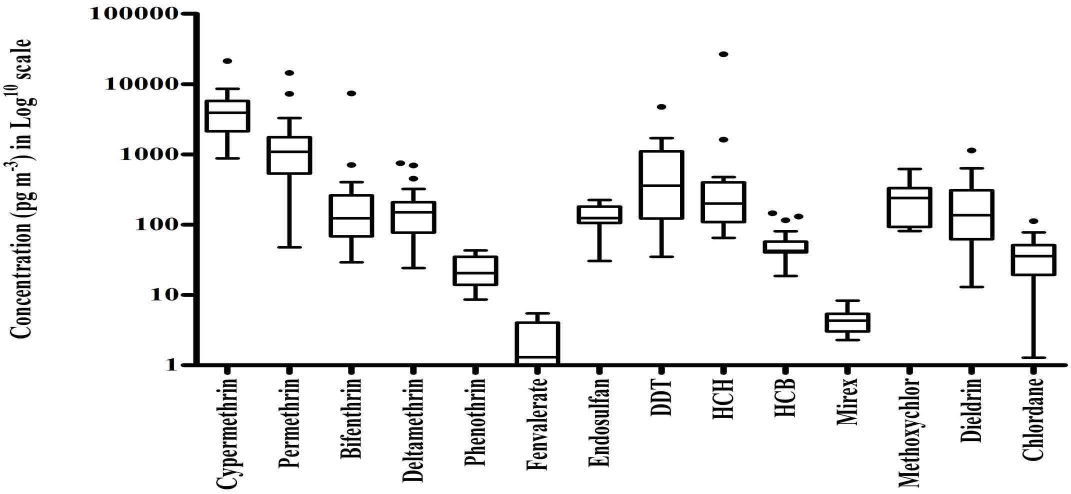

Figure 2: Box plot representing (-) median; ([]) 25% - 75%; (I) minimum and maximum of mean pesticide concentrations of the two studied cities (Rio de Janeiro and Santos).

Inhalation PE and RQ were calculated considering the average concentrations measured at all sampling points for each pesticide. Present air concentrations were up to one order of importance higher than those measured in outdoor urban areas in China[18]. Actually, high air concentrations were more consistent with indoor air levels in China, during steady application of mosquitos repellents[20]. Although inhalation PE values can be considered quite high, RQ values did not exceed the ADI in any case (Table 2), neither if considered the maximum pesticide concentrations or an exposure period of 24 hours.

This study brought the knowledge about outdoor atmospheric contamination by OCPs and CUPs in highly impacted areas and the reflex of the abusive use of insecticides to fight endemic diseases vectors, such as mosquitos, in Brazil. Although RQ values dismissed health risks directly from inhalation of atmospheric pesticides, a more extensive study must be done to evaluate total human exposure to pesticides, since additional routes, such as ingestion and dermic uptake should not be neglected.

Table 2: Potencial Exposure (PE in pg kg^{-1} d^{-1}) and the respective Risk Quotient (RQ) calculated for each pesticide, considering their respective acceptable daily intakes and an outdoor exposion time of 154 min.

PE and RQ	Cyper	Perm	Bifen	Delta	Phen	Fenv	Endo	DDT	HCH	HCB	Mirex	Metho	Diel	Chlord
PE Adult M	3070	1332	438	141	15	1	84	482	1054	36	3	179	152	25
PE Adult F	2908	1262	415	133	14	1	80	457	999	34	3	170	144	24
PE Youth	4309	1870	615	198	21	2	118	677	1479	51	4	252	214	35
PE Children	5424	2353	775	249	26	2	149	852	1862	64	5	317	269	44
PE Toddlers	5221	2265	746	239	25	2	143	820	1792	61	5	305	259	42
PE Infant	5643	2448	806	259	27	2	155	887	1937	66	5	330	280	46
RQ Adult M	2E-04	3E-05	4E-05	1E-05	2E-07	7E-08	1E-05	5E-05	2E-04	6E-05	3E-07	2E-05	2E-03	5E-05
RQ Adult F	1E-04	3E-05	4E-05	1E-05	2E-07	6E-08	1E-05	5E-05	2E-04	6E-05	3E-07	2E-05	1E-03	5E-05
RQ Youth	2E-04	4E-05	6E-05	2E-05	3E-07	9E-08	2E-05	7E-05	3E-04	8E-05	4E-07	3E-05	2E-03	7E-05
RQ Children	3E-04	5E-05	8E-05	2E-05	4E-07	1E-07	2E-05	9E-05	4E-04	1E-04	5E-07	3E-05	3E-03	9E-05
RQ Toddlers	3E-04	5E-05	7E-05	2E-05	4E-07	1E-07	2E-05	8E-05	4E-04	1E-04	5E-07	3E-05	3E-03	8E-05
RQ Infant	3E-04	5E-05	8E-05	3E-05	4E-07	1E-07	3E-05	9E-05	4E-04	1E-04	5E-07	3E-05	3E-03	9E-05

Compounds are listed as the sum of their respective isomer and/or metabolite: cypermethrin, permethrin, bifenthrin, deltamethrin, phenothrin, fenvalerate, endosulfan, dichlorodiphenyltrichloroethane, hexaclorociclohexane , hexaclorobenzene, mirex, methoxychlor, dieldrin and chlordane. (infants: 0.5-1.5 years, toddlers: 2-3 years, children: 5-6 years, youth: 10-12 years, adult males and females: 18-65 years old).

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