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# Residues of neonicotinoids in soil, water and people's hair: A case study from three agricultural regions of the Philippines

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Synthetic pesticides such as neonicotinoids are commonly used to treat crops in tropical regions, where data on environmental and human contamination are patchy and make it difficult to assess to what extent pesticides may harm human health, especially in less developed countries.

To assess the degree of environmental and human contamination with neonicotinoids we collected soil, water and people's hair in three agricultural regions of the Philippines and analysed them by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS-MS). Five neonicotinoids, namely acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam were targeted.

Residues of neonicotinoids were found in 78% of 67 soil samples from the three provinces. Total neonicotinoid loads ranged on average between 0.017 and 0.89 µg/kg in soils of rice, banana and vegetable crops, and were 130 times higher (113.5 µg/kg) in soils of a citrus grove. Imidacloprid was the most prevalent compound at an average of 0.56 µg/kg in soil while thiacloprid was below the limit of detection. Half of the eight water samples from a rice field and nearby creek contained residues of imidacloprid (mean 1.29 ng/L) and one contained thiamethoxam (0.15 ng/L). Residues of neonicotinoids were found in 81% of 99 samples of people's hair from the surveyed regions (average total concentrations 0.14 to 1.18 ng/g, maximum 350 ng/g). Hair residue levels correlated well with the concentrations of thiamethoxam and total residues in soils from the same locality ( $r = 0.98$ ). The presence of thiacloprid in 15% of the hair samples but not in soil samples suggests an additional route of exposure among people, which is most likely to be through ingestion of agricultural food and drinks available in the market.

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## 1. Introduction

The increasing use of neonicotinoid insecticides in the last two decades, due in part to the replacement of older pesticides (e.g. organophosphates) in the agricultural sector with safer products for users (Jeschke et al., 2011), has brought about many environmental problems, some of which could not be foreseen. Among the most worrying is the widespread contamination of soil, water and agricultural produce with neonicotinoids, since these insecticides are systemic and very mobile in the environment (Hladik et al., 2018; Lu et al., 2018). Given the increasing trend in neonicotinoid usage worldwide (Douglas et al., 2020; Goulson et al., 2018), these problems will likely become more prevalent with time.

The hazardous nature of these insecticides and their negative effects on pollinators and other beneficial insects, aquatic invertebrates and ecosystems at large is well documented – see reviews (Bonmatin et al., 2015; Sánchez-Bayo et al., 2016; Wood and Goulson, 2017). Most of the evidence available comes from developed countries, where the environmental effects have been studied in detail (Mörtl et al., 2020; Pisa et al., 2017; Pisa et al., 2015). Neonicotinoids, however, are also commonly used in developing countries – most of which are in tropical regions –, and their residues are present in soil, water and bee matrices (Mitchell et al., 2017) of those countries (Al-Nasir et al., 2020; Castilhos et al., 2019; Dankyi et al., 2014; La et al., 2015), as well as in their agricultural products, such as bananas (Gomes et al., 2020), citrus and horticultural vegetables (Al-Nasir et al., 2020; Orтели et al., 2005). Moreover, environmental impacts of these insecticides in tropical and subtropical regions could be even larger than in other countries, given the greater pest pressure that leads to increasing pesticide loads, poorer agricultural practices and lack of regulation about pesticides in those regions (Grovermann et al., 2013; Khan et al., 2015; Xu et al., 2008).

A first step for managing the use of hazardous pesticides and minimizing their environmental impacts is to know the extent of contamination in a given country. To that end, surveys of soil, water, sediments and agricultural produce need to be conducted, preferably in various crops and regions so as to obtain a comprehensive picture of the problem. This is necessary, because despite having been in the market for more than 20 years, aspects of the fate and impacts of neonicotinoids such as leaching, chemical transformations and behaviour of metabolites in aquatic systems still require further investigation (Pietrzak et al., 2020; Voigt and Jaeger, 2021). Such an undertaking is expensive, as it involves chemical analysis of multiple samples, which most developing countries cannot afford. Furthermore, surveys typically use screening analytical methods which are multiresidue based (Hennion et al., 1994; Pichon et al., 1998) and less sensitive than methods targeted on a class of pesticides such as the neonicotinoids (Kammoun et al., 2019; Li et al., 2019).

This study aimed at providing a snapshot of neonicotinoid contamination in three provinces of the Philippines, so that usage patterns can be identified and remedial action taken where necessary. This class of insecticides has been ignored in previous assessments of farmers exposure to pesticides in the Philippines, which focused mainly on organophosphates, carbamates and pyrethroids (Lu, 2009; Perez et al., 2015). As environmental contamination affects the people that live in a region, we also collected hair samples from people in addition to a survey of soils and water. Similarly to feathers, which can be used to monitor residues of chemical contaminants in birds (Dauwe et al., 2005; Humann-

Guilleminot et al., 2019b), hair can be used as a matrix for the monitoring of pesticide residues in humans and animals (Smith-Baker and Saleh, 2011), providing a useful tool to explore the mid- to long-term occurrence of pesticides in the general population of a country (Yusa et al., 2015).

## 2. Materials and methods

### 2.1. Chemicals and solvents

Analytical standards (99.6 to 99.9% purity) of five neonicotinoids (acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam) were purchased from Sigma-Aldrich (Germany). Isotopically labelled neonicotinoids were purchased from CDN Isotopes (Canada) to be used as internal standards. Chromatography grade solvents (acetonitrile, ethyl-acetate, methanol) were purchased from Fisher Scientific (UK). Magnesium sulphate, sodium chloride, trisodium citrate and sodium hydrogen citrate sesquihydrate were purchased from Sigma-Aldrich. Isolute PSA and ZeoPrep 90 C18 bulk phases were purchased at Biotage (Sweden) and ZeoChem (Switzerland), respectively. Ultrapure water was obtained from a Milli-Q system (Millipore, France) and solvents (acetonitrile) and additives (formic acid, ammonium formate) for LC-MS were obtained from VWR (Austria).

### 2.2. Study area

Three sites located in different islands of the Philippines were selected as representatives of the main agricultural crops grown in this country: rice, bananas and horticultural fruits and vegetables (Fig. 1). Site 1 was in the municipality of Tuba, province of Benguet (Luzon). Soil samples from this site were taken on 20<sup>th</sup> January 2019 from a field of sweet peas and its surrounding area, which comprised a variety of small fields of crops such as potatoes, strawberries and cauliflower. Site 2 was in the municipality of Boac, province of Marinduque, with soil samples taken on 2<sup>nd</sup> February 2019 from a rice field and its surrounding dryland and banana plots. Site 3 was in the municipality of Malita, province of Davao Occidental (Mindanao). Soil sampling at this site was done on 23<sup>rd</sup> January 2019 within a banana plantation and its surrounding area, which had coconut palm trees and a small creek on one side and a citrus grove (pomelo) on another side. People from the same three localities were also included in the sampling of hair, as described below.

The three sites differ in their geographical location. Site 1 is located at approximately 1000 m above sea level in a mountainous region of the northern island of Luzon; the climate there is temperate and average annual temperature is around 20 °C. Site 2 is a typical rice field situated on the coastal plain of a small volcanic island in the centre of the Philippines, with monsoonal climate of 2000 mm annual rainfall and temperatures in the range 22–33 °C. Site 3 is located on a coastal plain of a thriving agricultural region in the south of Mindanao, an area of tropical rainforests with on average 219 rainy days, 1200 mm of rainfall and a temperature of 26 °C. Neonicotinoids are routinely used in the three regions as spray applications, coated seeds, granular and drench formulations, but information about the type of products and quantities used in particular crops at the selected sites is not available (Perez et al., 2015).



Fig. 1. Map of the Philippines showing the location of the three sampling sites.

### 2.3. Sampling design

A total of 67 soil samples were collected from the three sites (Table 1). Individual soil samples were a composite of five subsamples of 10 cm topsoil, taken with a bulb-planter after removing the vegetation and plant material. The five subsamples aimed to average out potential spatial heterogeneity in pesticide concentration that cannot

be inferred from visual observation. The 10 cm sampling depth corresponds to the biologically most active layer of the soil and main rooting depth of crops.

At each site, a set of 20 soil samples were collected as follows: five samples were taken within the crop field; another five samples distributed around the edges of the field; five more samples at a distance of 20 m from the field, each in a different direction; and finally, another

**Table 1**

Summary information on hair and environmental samples from the Philippines.

| Island     | Hair samples     |                 |          |            | Environmental samples |            |                  |               |               |
|------------|------------------|-----------------|----------|------------|-----------------------|------------|------------------|---------------|---------------|
|            | Date of sampling | Total (n1 + n2) | Men (n1) | Women (n2) | Age range (years)     | Crop       | Date of sampling | Soil (n = 67) | Water (n = 8) |
| Luzon      | 10-Nov-2017      | 31              | 16       | 15         | 7–83                  | Sweet peas | 20-Jan-2019      | 20            | 0             |
| Marinduque | 2-Sep-2017       | 31              | 15       | 16         | 6–50                  | Rice       | 2-Feb-2019       | 21            | 6             |
| Mindanao   | 23-Aug-2017      | 38              | 26       | 12         | 7–64                  | Banana     | 23-Jan-2019      | 17            | 2             |
|            |                  |                 |          |            |                       | Citrus     | 23-Jan-2019      | 9             | 0             |

five samples at 100 m around the field also in different directions. At site 3, extra soil samples were taken at 100 m within the citrus area, and two water samples were also taken from a creek that runs through the adjacent coconut area. In addition, six water samples were collected from the irrigated rice field at site 2. Therefore, a total of eight water samples were taken: six from the rice field in Marinduque and two from the creek in Malita.

Soil samples were kept in 250 mL PET plastic jars, and water samples in 125 mL brown HDPE plastic bottles. All samples were placed in a cooler for transportation and kept in a freezer until analysis at the Neuchâtel Platform of Analytical Chemistry, University of Neuchâtel, Switzerland.

Hair sampling was performed as a part of the study “Pesticides and their metabolites analysis in human urine and hair in Philippine three islands” conducted by Kumiko Taira. Having obtained the ethic committee approval of Tokyo Women’s Medical University (No. 4521), spot urine samples and hair samples were collected. Details of the urine results will be reported elsewhere.

Hair samples ( $n = 100$ ) were taken from randomly chosen local volunteers at the three sites, comprising 57 men and 43 women from a wide range of ages (6 to 83 years old). Samples were collected between August and November 2017, before the application of insecticides to the crops in the respective areas. The hypothesis was that since neonicotinoids are commonly applied in the three regions and are persistent in the environment, their residues would be found not only in environmental matrices but also in hair of the people who live in those regions regardless of the time of application. Although hair and soil samples were not collected at the same time, they come from the same areas and a possible correlation between them is interesting, in the assumption that application patterns of pesticides remained similar between years. Hair samples were kept in zip-locked bags and transported in a cooler to the analytical laboratory of the University of Neuchâtel. Details of the sampling are shown in Table 1.

#### 2.4. Sample extraction and analysis

The extraction of soil and water samples was performed according to Bonmatin et al. (2019). Hair samples were prepared using an adapted protocol. Specifically, hair samples were ground to a fine powder in a tissue lyser (Retsch MM 400, Germany) for 2 min at 30 Hz using a 20 mm stainless steel bead. Twenty-five milligrams of hair powder were transferred to a 2.0 mL microcentrifuge tube, and 1.5 mL of acetonitrile as well as 10  $\mu$ L of internal standard solution containing the five isotopically labelled neonicotinoids (125 ng/mL in acetonitrile) were added to the tube. The mixture was shaken in the tissue lyser for 3 min at 30 Hz, centrifuged and the supernatant was reserved. The centrifuged tube containing the hair pellet was reextracted in 1.5 mL of acetonitrile and the second extract combined with the first one. A QuEChERS (Quick, Efficient, Cheap, Easy, Rugged and Safe) procedure was then applied to the acetonitrile extracts by adding 2 mL of acetonitrile, 5 mL water, and 3.25 g of a mixture of salts composed of anhydrous  $MgSO_4$  (2.0 g), NaCl (0.5 g), sodium citrate dehydrate (0.5 g) and sodium citrate sesquihydrate (0.25 g). The tube was vigorously shaken by hand, centrifuged, and the epiphase recovered and transferred to another tube containing 0.15 g  $MgSO_4$ , 0.1 g C18 bulk phase, and 0.1 g

primary-secondary amine bulk phase for dispersive SPE. After another round of shaking and centrifugation, the supernatant was evaporated, reconstituted in 0.25 mL of methanol 25%, filtered and transferred to an HPLC vial for analysis.

All samples were analysed by ultra-high performance liquid chromatography-tandem mass spectrometry using an Acquity UPLC™ (Waters) coupled to a TQ-S triple quadrupole mass spectrometer (Waters) using a well-established method (Bonmatin et al., 2019; Humann-Guillemot et al., 2019a; Kammoun et al., 2019). Blank water samples (2–3 per batch of 50–80 samples) were included in the runs to ascertain the quality of the analysis obtained. Limits of detection (LOD) and quantitation (LOQ) for water samples ranged between 0.03–0.3 ng/L and 0.1–1 ng/L, respectively, depending on the molecules. For soil samples, LODs ranged 0.3–2 ng/kg and LOQs were at 1–5 ng/kg for the five neonicotinoids. For hair samples, LODs ranged 3–10 pg/g and LOQs were 8–30 pg/g depending on each molecule.

#### 2.5. Data analysis

Residue data for soil and water were log-transformed for statistical analysis, as they followed a gamma distribution. Average concentrations are, therefore, represented by the geometric mean.

Soil residue levels among the four crops and three sites were compared by one-way ANOVA, using Tukey-Kramer post hoc test for individual comparisons between crops or sites (explanatory variables). Residue levels were also compared between inside and various distances outside the treated fields using the same statistical procedure.

One-way ANOVA was also used to compare hair residue levels among people from the islands. Comparisons between sexes, dyed hair and occupations were done by Tukey-Kramer post hoc test or Fisher’s exact test. Correlations between the hair and soil datasets from the three sites were calculated for total neonicotinoids as well as the individual compounds. All statistical analyses were performed in StatPlus version 7.1.30 (AnalystSoft Inc. 2019).

### 3. Results

#### 3.1. Soil and water

A high proportion of soil samples (80%) were found to contain at least one neonicotinoid, and 64% of samples contained three compounds. Imidacloprid was detected in all samples that tested positive, having a geometric mean concentration of 0.4  $\mu$ g/kg (ppb) and a maximum concentration of 903  $\mu$ g/kg at the citrus grove adjacent to the banana plantation in Mindanao (Table 2). Thiamethoxam and clothianidin were the second most common compounds detected in 73% and 69% of soil samples, respectively. However, as some clothianidin residues result from the degradation of thiamethoxam, the concentrations of clothianidin (0.156  $\mu$ g/kg) were on average six times higher than those of thiamethoxam (0.027  $\mu$ g/kg). Nevertheless, thiamethoxam reached higher levels of contamination: maximum 268  $\mu$ g/kg compared to 126  $\mu$ g/kg for clothianidin (Fig. 2), both again in the citrus grove in Mindanao. In contrast, acetamiprid was only found in two soil samples from Luzon at concentrations close to the limit of quantitation. Thiocloprid was not detected in any of the soil and water samples

**Table 2**

Summary of residues of neonicotinoids in soil ( $\mu\text{g}/\text{kg}$ ), water ( $\text{ng}/\text{L}$ ) and hair ( $\text{ng}/\text{g}$ ) from three locations in the Philippines. The number and percentage of positive detections is also indicated.

|                      | Luzon (sweet peas) |                   |       | Marinduque (rice) |                   |       | Mindanao (banana, citrus) |                   |         |
|----------------------|--------------------|-------------------|-------|-------------------|-------------------|-------|---------------------------|-------------------|---------|
|                      | Positives          | Mean <sup>a</sup> | Max   | Positives         | Mean <sup>a</sup> | Max   | Positives                 | Mean <sup>a</sup> | Max     |
| <b>A) Soil</b>       |                    |                   |       |                   |                   |       |                           |                   |         |
| Acetamiprid          | 2 (10%)            | 0.002             | 0.002 | 0                 | –                 | –     | 0                         | –                 | –       |
| Clothianidin         | 20 (100%)          | 0.022             | 0.236 | 0                 | –                 | –     | 26 (100%)                 | 1.430             | 126.31  |
| Imidacloprid         | 20 (100%)          | 0.758             | 39.56 | 6 (29%)           | 0.013             | 0.028 | 26 (100%)                 | 1.048             | 903.31  |
| Thiamethoxam         | 18 (90%)           | 0.005             | 0.050 | 5 (24%)           | 0.005             | 0.011 | 26 (100%)                 | 0.278             | 267.87  |
| Total neonicotinoids | 20 (100%)          | 0.888             | 39.57 | 6 (29%)           | 0.017             | 0.036 | 26 (100%)                 | 3.819             | 1187.61 |
| <b>B) Water</b>      |                    |                   |       |                   |                   |       |                           |                   |         |
| Acetamiprid          | –                  | –                 | –     | 0                 | –                 | –     | 0                         | –                 | –       |
| Clothianidin         | –                  | –                 | –     | 0                 | –                 | –     | 0                         | –                 | –       |
| Imidacloprid         | –                  | –                 | –     | 3 (50%)           | 1.29              | 3.03  | 1 (50%)                   | 5.22              | 5.22    |
| Thiamethoxam         | –                  | –                 | –     | 1 (17%)           | 0.15              | 0.15  | 1 (50%)                   | 0.20              | 0.20    |
| Total neonicotinoids | –                  | –                 | –     | 3 (50%)           | 1.31              | 3.18  | 1 (50%)                   | 5.41              | 5.41    |
| <b>C) Hair</b>       |                    |                   |       |                   |                   |       |                           |                   |         |
| Acetamiprid          | 4 (13%)            | 0.025             | 0.069 | 4 (13%)           | 0.019             | 0.055 | 5 (14%)                   | 0.023             | 0.07    |
| Clothianidin         | 7 (23%)            | 0.102             | 0.333 | 15 (48%)          | 0.088             | 0.532 | 24 (65%)                  | 0.261             | 6.72    |
| Imidacloprid         | 20 (65%)           | 0.155             | 0.630 | 8 (26%)           | 0.134             | 0.242 | 33 (89%)                  | 0.388             | 341.40  |
| Thiacloprid          | 2 (7%)             | 0.011             | 0.011 | 1 (3%)            | 0.009             | 0.009 | 12 (32%)                  | 0.011             | 0.02    |
| Thiamethoxam         | 4 (13%)            | 0.102             | 0.247 | 1 (3%)            | 0.080             | 0.080 | 26 (70%)                  | 0.705             | 129.28  |
| Total neonicotinoids | 25 (81%)           | 0.137             | 0.658 | 20 (65%)          | 0.103             | 0.532 | 35 (95%)                  | 1.175             | 350.52  |

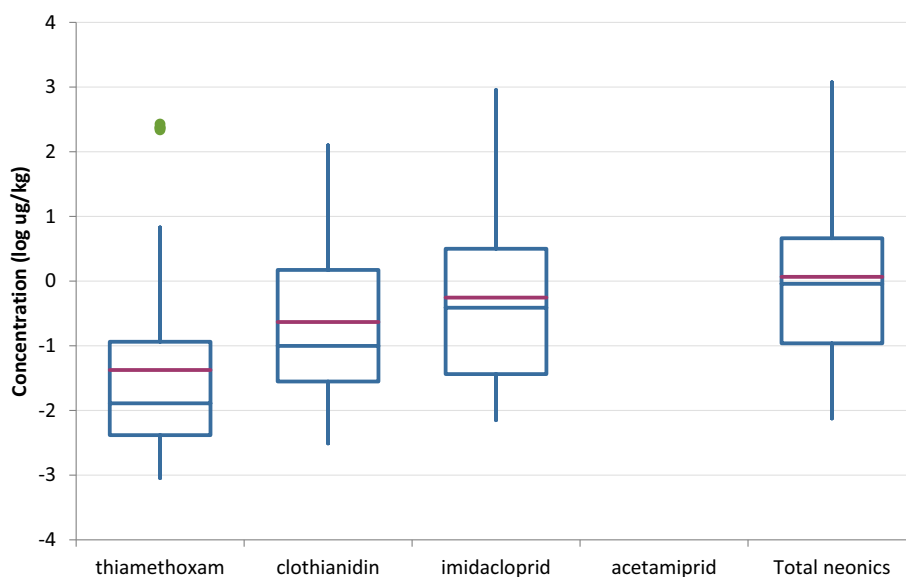
<sup>a</sup> Geometric mean.

from the three islands, suggesting it is not used in the crops of those regions, or may be rapidly degraded under local conditions (half-life in soil is 1–27 days, (Bonmatin et al., 2015)).

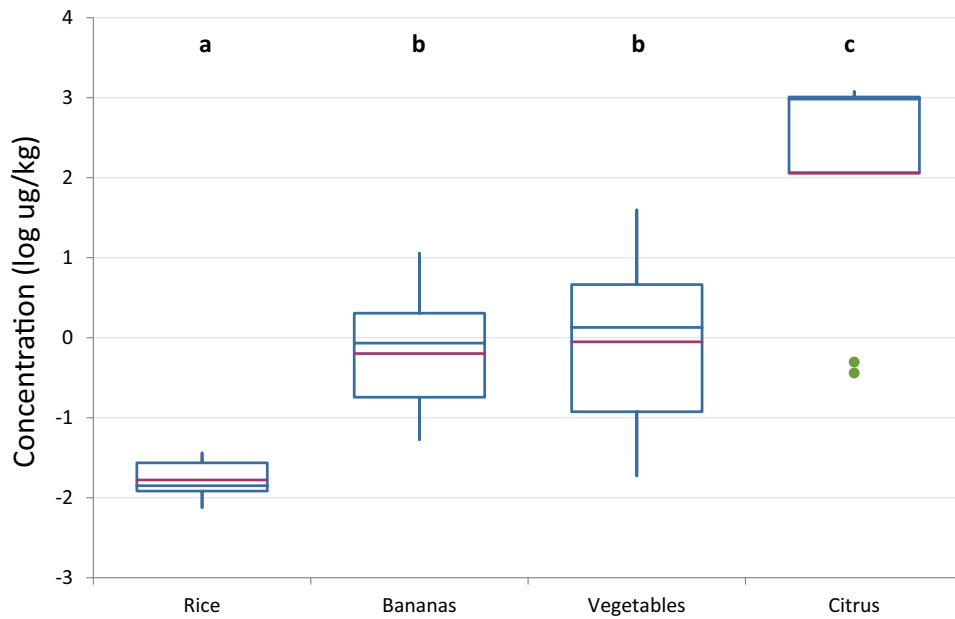
Soil residues of total neonicotinoids varied significantly among crops ( $p < 0.001$  ANOVA). The lowest residue loads (mean  $\pm$  standard deviation) were found in the rice crop at  $0.022 \pm 0.004 \mu\text{g}/\text{kg}$  dry soil, and the highest in the citrus grove at  $576 \pm 463 \mu\text{g}/\text{kg}$ . The banana and sweet pea crops had average residues of  $2.33 \pm 2.59$  and  $4.30 \pm 5.86 \mu\text{g}/\text{kg}$ , respectively. The rice field and surrounding area in Marinduque had the lowest proportion (29%) of soil samples contaminated with neonicotinoids, and also the lowest concentrations of the only two compounds found there:  $0.013 \mu\text{g}/\text{kg}$  imidacloprid and  $0.005 \mu\text{g}/\text{kg}$  thiamethoxam (Table 2). This residue level was significantly lower than in other crops (Fig. 3), while the citrus grove adjacent to the

banana plantation of Mindanao had total neonicotinoid loads in soil that were 130–250 times higher than in the banana and sweet pea crops.

The spatial distribution of soil residues showed a similar pattern for the vegetable fields and the banana plantation, with residue concentrations in soil decreasing with distance from the treated field (Fig. 4). At the sweet pea crop in Luzon, total neonicotinoid loads were highest in the treated field ( $3.84 \mu\text{g}/\text{kg}$  in-field,  $4.77 \mu\text{g}/\text{kg}$  at the edge of field) and decreased towards the periphery ( $0.38 \mu\text{g}/\text{kg}$ ); the peak at 20 m distance from the field is due to an outlier of imidacloprid. Equally, total neonicotinoid loads in the banana plantation decreased from  $3.85 \mu\text{g}/\text{kg}$  at the edge of the field to  $0.50 \mu\text{g}/\text{kg}$  at 100 m. In Marinduque, total residue levels of neonicotinoids did not differ between the treated rice field and the surrounding areas at 100 m, even though none of the



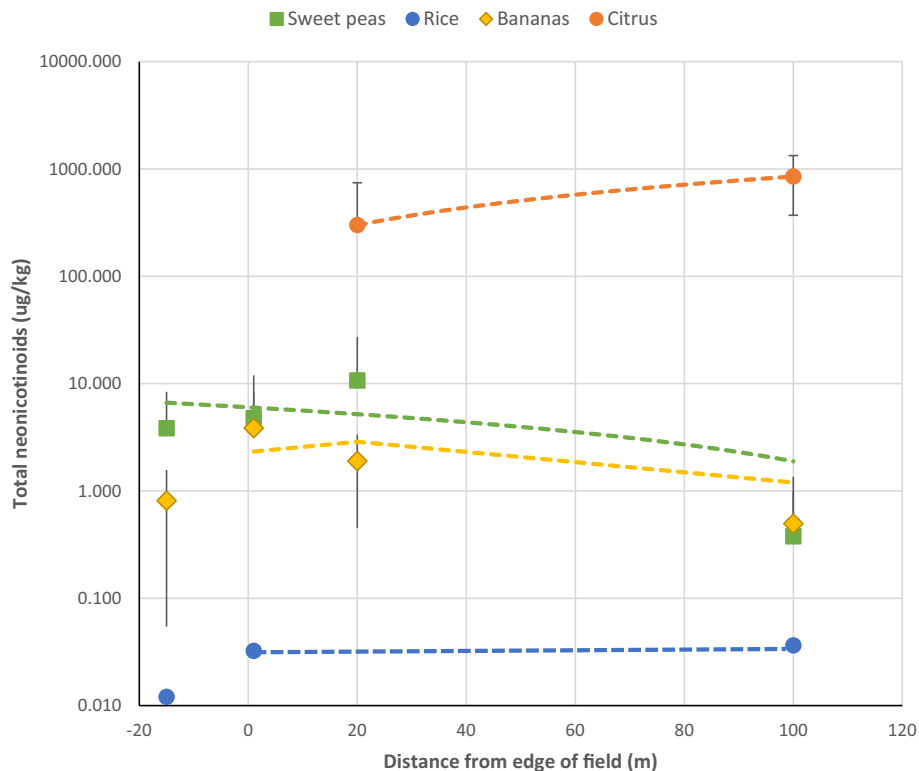
**Fig. 2.** Neonicotinoid residues ( $\mu\text{g}/\text{kg}$  dry soil) in agricultural soils of the Philippines. The plot shows the inter-quartile-ranges (box), median (blue line in box), geometric mean (red line in box) and outliers (green dots). Acetamiprid is not plotted as only 2 samples were positive (mean  $0.002 \mu\text{g}/\text{kg}$  dry soil).



**Fig. 3.** Residues of total neonicotinoids ( $\mu\text{g}/\text{kg}$  dry soil) in soils of four different crops. The plot shows the inter-quartile-ranges (box), median (blue line in box), geometric mean (red line in box) and outliers (green dots). Letters above the boxes (a, b, c) indicate significant differences ( $p < 0.005$ ) between treatments (Tukey-Kramer post hoc test).

five samples taken at 20 m from the field resulted in positive detections (Fig. 4). The apparent reverse pattern with distance found in soils of the citrus grove can be explained if one considers that the grove was located on one side of the banana plantation and citrus trees were treated

separately from the neighbouring bananas, either by vertical boom sprayers or by soil drenching. Assuming that the application rates in citrus are higher than those in bananas, soils closer to the banana plantation (i.e. 20 m) are expected to have lower concentrations of



**Fig. 4.** Total neonicotinoid residues in soils with distance to the treated fields. Error bars are standard deviations, and stippled lines indicate the trends with distance.

neonicotinoids than those near or within the citrus grove (i.e. 100 m from the bananas), as it is actually the case: 300 µg/kg at 20 m from the banana plot and 851 µg/kg at 100 m, within the citrus grove.

Water from a creek that runs along the bottom side of the banana plantation contained imidacloprid and thiamethoxam residues at 5.2 and 0.2 ng/L, respectively, suggesting the neonicotinoids were transported into the creek via surface runoff from the treated fields above, since our sampling took place long after the insecticide treatment. Such residue levels were higher than those of the same compounds in waters of the rice field at Marinduque (Table 2).

### 3.2. Hair

The five neonicotinoids targeted for analysis were found in people's hair. Out of the 99 hair samples analysed (one sample was lost), 81% had residues of at least one neonicotinoid, with two compounds being most common (29% samples). Residues in hair followed a typical gamma distribution, with a geometric mean concentration of 0.33 ng/g for all compounds. Imidacloprid was the neonicotinoid most frequently found (62% samples), with a mean concentration of 0.25 ng/g and the highest variation in residue levels among individuals (Fig. 5). Clothianidin was found in 47% of hair samples, thiamethoxam in 31%, thiacloprid in 15% and acetamiprid in 13% of samples. The lowest average concentrations were for thiacloprid at 0.01 ng/g, and the highest for thiamethoxam at 0.51 ng/g. The source of thiacloprid is unknown, as this compound was not found in any of the soil and water samples from the three sites; it is most likely used in other crops. However, it cannot be ruled out that fast degradation of thiacloprid under the local conditions could have prevented the detection of this insecticide in soils.

There was no statistical difference in residue levels between sexes ( $p = 0.056$ , Fisher's exact test) or among the three age groups defined as children (6 to 16 years old,  $n = 28$ ), adults (17 to 40 years old,  $n = 45$ ) and seniors (40 years old and over,  $n = 27$ ) ( $p = 1.0$ , ANOVA). However, there was a significant difference among people from various occupations, with farmers having significantly lower residues (0.16 ng/g,  $n = 25$ ,  $p = 0.04$ , ANOVA) than the rest of the community. Interestingly, neonicotinoid residues in dyed hair (0.08 ng/g,  $n = 7$ ) seemed lower than in not-dyed hair, although the difference was not statistically significant ( $p = 0.12$ , Fisher's exact test). The most notable difference was that people from Mindanao had higher residues

of neonicotinoids in their hair (mean 1.17 ng/g,  $n = 35$ ) than people from the other two islands (mean 0.14 ng/g in Luzon and 0.10 ng/g in Marinduque), and that difference was significant ( $p < 0.001$ , ANOVA) despite the large variation in residues among individuals (Fig. 6). This significant difference in contamination of hair depending on the location is certainly due to agricultural practices.

Even if the samples were taken during two different time frames for hair (2017) and soil (2019), we performed a tentative correlation analysis for the total residues as well as for the individual compounds between hair and soil samples from the three islands. The correlation appeared to be strongest and significant for thiamethoxam ( $r = 0.98$ ,  $p = 0.02$ ) and total residues ( $r = 0.99$ ,  $p = 0.009$ ) and was also high but not significant for clothianidin ( $r = 0.81$ ,  $p = 0.19$ ).

## 4. Discussion

Information about residues of neonicotinoids in soils of tropical countries is scarce (Bonmatin et al., 2019; Dankyi et al., 2014), as the majority of data available are from temperate countries. Even more scarce are data on soil residues, since most of the surveys about neonicotinoids refer to water and sediments (Hano et al., 2019; Hladik and Kolpin, 2016; Mahai et al., 2019). In the case of the Philippines, residue data on neonicotinoids is non-existent (Perez et al., 2015), so this research aimed at measuring the environmental and human contamination with these ubiquitous pesticides in the Philippines, a densely populated tropical country of South East Asia, and assessing the patterns of contamination in three regions and contrasted agricultural crops.

Soil residues of neonicotinoids in the Philippines ranged widely among crops. Banana and vegetable (sweet pea) crops had average residues of 2.33 and 4.30 µg/kg, respectively, which are comparable to residues of the same compounds in tropical crops of Belize (Bonmatin et al., 2019), arable crops of the United Kingdom (Jones et al., 2014), and corn fields of New Zealand, Canada and the United States (de Perre et al., 2015; Pook and Gritcan, 2019; Schaafsma et al., 2015). However, the residue loads in the citrus grove were higher than in any other crop of any country; a maximum imidacloprid concentration of 251 µg/kg measured in soils of a cocoa plantation of Ghana (Dankyi et al., 2014) is still half the average concentration found in the citrus crop of Mindanao.

As previously found in Belize (Bonmatin et al., 2019), neonicotinoid concentrations in soil decreased with distance from the treated fields,

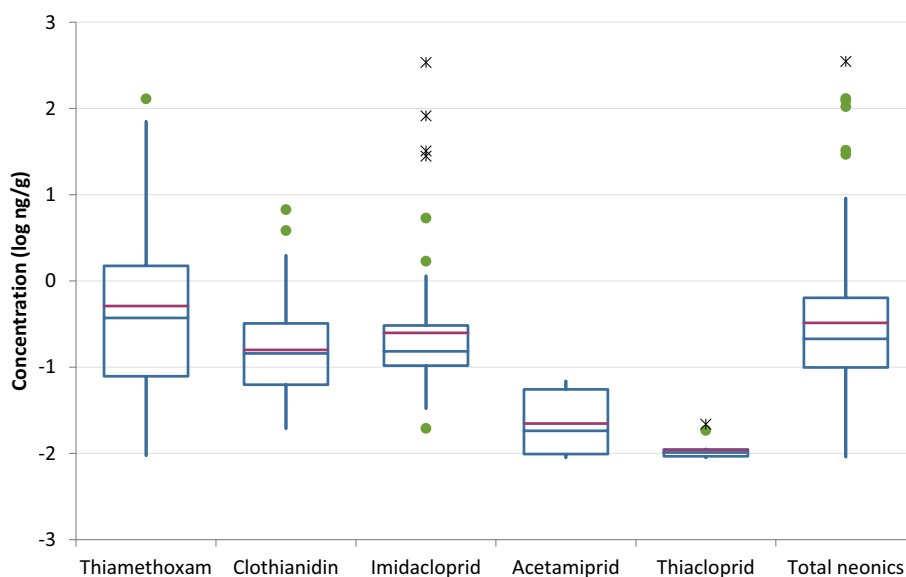
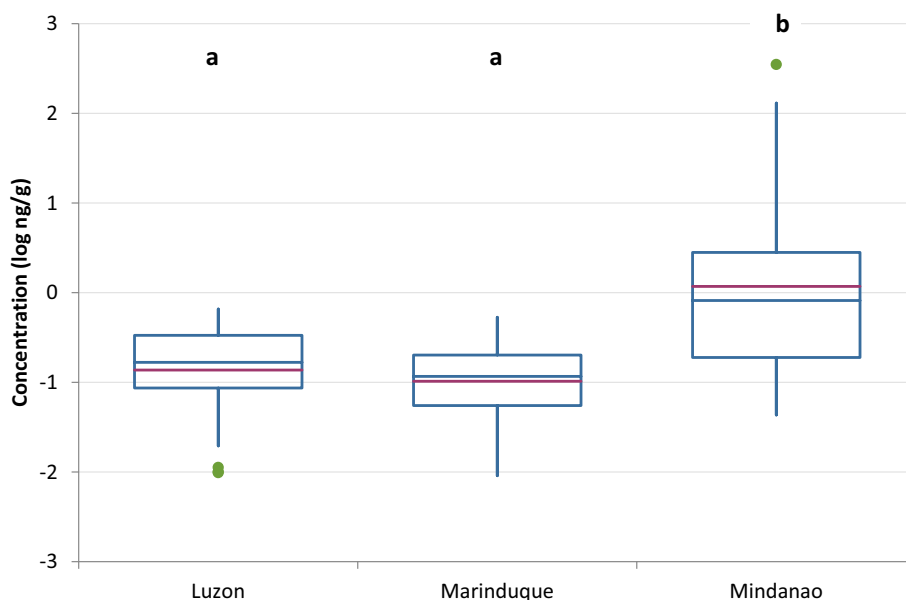


Fig. 5. Neonicotinoid residues (ng/g) in hair samples from the Philippines. The plot shows the inter-quartile-ranges (box), median (blue line in box), geometric mean (red line in box), mild outliers (green dots) and extreme outliers (black crosses).





**Fig. 6.** Total neonicotinoids in hair samples (ng/g) from different regions in the Philippines. Neonicotinoids: thiamethoxam, clothianidin, imidacloprid, acetamiprid and thiacloprid. The plot shows the inter-quartile-ranges (box), median (blue line in box), geometric mean (red line in box) and mild outliers (green dots). Letters above the boxes (a, b) indicate significant differences ( $p < 0.001$ ) among the islands (Tukey-Kramer post hoc test).

except in the case of rice which are constantly in water, although the limited number of samples in soils around the rice field prevents us from making any conclusive statement in this regard. In general, total neonicotinoid loads in soils at 100 m were one order of magnitude lower than in the treated fields (Fig. 4). Spray drift may be responsible for such levels in the surrounding areas, but contamination by lateral movement through water runoff may be more important, particularly if the insecticides were applied in granular form, as seed-coatings or soil drenches. Also, wind-blown dust (Limay-Rios et al., 2016; Schaafsma et al., 2015) cannot be discarded as an additional route of transport. Although in this study we only took two samples of water from a creek at 100 m from the banana plantation, the presence of neonicotinoids in the creek many days after the insecticides were applied to the crop adds to the evidence of such lateral movement occurring.

The concentrations of neonicotinoids in soils of the Philippines are correlated with the residues of the same compounds in hair of people from the same areas. Thus, the highest average residues in hair among the people from Malita in Mindanao (1.17 ng/g) match the exceedingly high concentrations measured in soils of that locality, whereas the lowest average hair residues among the people of Marinduque (0.10 ng/g) correspond to the lowest neonicotinoid loads in soils in and around the rice fields of that island (Table 2). This is consistent with the intensity of agricultural practices in the various regions studied here.

Our study could not determine the route of people's hair contamination with these insecticides, which could be multiple. However, since farmers had the lowest level of contamination in the community the direct exposure to spray drift and dust in the field may not be the main route of exposure to these insecticides – most likely neonicotinoids were applied as seed-coatings or granular formulations that result in no drift. House wives, school children and laborers who do not work in the fields had higher residues in their hair than the farm workers. Also, the presence of thiacloprid in hair only suggests there was another route of contamination, since this compound was not found in soils. It is most likely, therefore, that residues of neonicotinoids in hair result from ingestion of both food and water contaminated with these insecticides, given the prevalence of neonicotinoids residues in a large variety of food items in the market (Chen et al., 2014; Craddock et al., 2019) and in drinking water (Chau et al., 2015; Klarich et al., 2017; Wan et al.,

2019), whereas direct exposure in the field may contribute to a lesser extent. This could be further substantiated when taking into account that many farmers in the Philippines produce food by intensive cultivation for the global market (e.g., mangoes, bananas) and do not necessarily consume the food produced locally.

Our findings demonstrate that people's exposure to systemic insecticides is not restricted to farmers and pesticide applicators but affects the community at large. Contamination by neonicotinoids is thus more widespread and ubiquitous than originally thought and goes beyond the boundaries of the treated agricultural fields. Contamination of soils is in direct correlation with the intensity of agricultural practices. More indirectly, this study also shows that such residues in hair reflect the pattern of utilization of these insecticides in the local area, with the highest residue levels in people's hair correlating with the highest loads applied to the crops in the same locality.

A limitation of our study is that the hair samples were collected 14–17 months before the environmental samples. However, it should be noted that agricultural practices in the three provinces of the Philippines were mostly unchanged during the last decade. The analysed hair integrates the contamination of people over the preceding months, although this depends on how long the hair was at the time of sampling. Neonicotinoids in soil can accumulate from year to year owing to the long-term persistence of these compounds, with their half-lives ranging from 1–27 days (thiacloprid) to 148–6900 days (clothianidin) (Bonmatin et al., 2015). Thus, although it would have been preferable to collect all samples simultaneously or better, having several time points for both sample matrices in the study, the clear correlation we observed between environmental and human contamination suggests that neonicotinoid concentrations measured in human hair reflect the general contamination of the region where the people live. The fact that farmers' hair was less contaminated than other people's hair may suggest that exposure to neonicotinoids by spray drift in the field is minor compared to other routes such as the regular ingestion of contaminated food and water. This is consistent with probable major uses of neonicotinoids by seed-coating.

Hair sampling offers an easy way to gauge the mid-term level of contamination among people, as it integrates all routes of exposure into one single measure. However, the relatively low levels of neonicotinoids found in people's hair cannot be used to assess the health risks that

these chemicals may pose to the individuals, because residues found in hair are only a proportion of the actual exposure of people to the same compounds, while another unknown proportion would be metabolized and eliminated in the urine (Marfo et al., 2015; Taira et al., 2013; Tao et al., 2019). For assessing the risks to people, a direct measure of neonicotinoid residues in agricultural produce is necessary and more appropriate. For example, such an assessment should include consumption of residues in fruits, vegetables, cereals, honey (Mitchell et al., 2017), tea (Taira, 2014), as well as drinking water and soft drinks (Lu et al., 2018; Ying et al., 2016; Zhang et al., 2019). Another complementary exposure assessment is to measure short term exposure of people by analysing their urine (Ichikawa et al., 2019).

## 5. Conclusions

We documented the contamination of the environment and people with neonicotinoids in three selected regions of the Philippines characterised by distinct cultivation patterns. Residues of four neonicotinoids were found in 80% of soils from three provinces, with imidacloprid being the most common compound. Total neonicotinoid loads in soils of a citrus grove were about 130 times higher than in soils of vegetable and banana crops, whereas rice fields had much lower residue levels in both soil and water. Residues of five neonicotinoids were found in 81% of people's hair from the surveyed regions, and their residue levels correlated well with the concentrations of the individual compounds in soils from the same locality. However, the presence of thiacloprid in 15% of the hair samples – a compound not applied to the crops in the selected regions – suggests a further route of contamination among people, which is most likely to be through ingestion of agricultural products available in the market.

## CRedit authorship contribution statement

FC, FSB, J-MB and MBvL designed the study. GG carried out the chemical analysis. FC and ELH carried out the field sampling. FSB and KT analysed the data. EM, J-MB and FSB wrote the first draft, and all authors contributed to the writing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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