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# Exposure of an urban population to pesticides assessed by wastewater-based epidemiology in a Caribbean island

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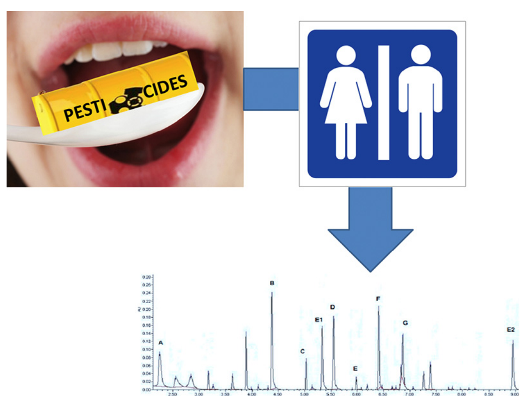
## HIGHLIGHTS

- A wastewater-based epidemiology approach was used to examine pesticide exposure.
- The Martinique population was exposed to organophosphates and pyrethroids.
- Mass loads indicated higher exposure to pyrethroids than in Europe, close to the ADI.
- This study illustrates the high human exposure with indoor pesticide use.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Wastewater-based epidemiology is an innovative approach to estimate the consumption of chemicals and their exposure patterns in a population, on the basis of measurements of biomarkers in wastewater. This method can provide objective real-time information on xenobiotics directly or indirectly ingested by a population. This approach was used to examine the exposure of the Martinique population to the three classes of pesticides: triazines, organophosphates and pyrethroids. Martinique island (French West Indies) is a closed market and has been closely monitored since the early 2000's when contamination with chlordecone, an organochlorine insecticide widely applied between 1972 and 1993 in banana plantations, became a critical political issue.

The aim of this study was to identify and quantify the patterns of human exposure and compare the results to those from other countries. Wastewater was collected as 24-h composite samples and analysed for selected urinary pesticide metabolites by liquid chromatography-tandem mass spectrometry. Organophosphate and pyrethroid metabolites were found in all the samples up to 330 ng/L, while triazines were found only at trace levels. Mass loads indicated higher exposure to pyrethroids than in some cities in Europe, but lower exposure to triazines and organophosphates. The estimated human intake for pyrethroids was close to the Acceptable Daily Intake, but importation of these pesticides to Martinique was low. This study illustrates the high human exposure with indoor pesticide use in comparison to its use in agriculture.



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## 1. Introduction

Global pesticide uses cause the discharge of residues in the environment; these are partially adsorbed on solid matrices and often pollute the food chain. Ecosystem contamination resulting from agricultural and non-agricultural uses of pesticides and biocides has been the subject of many studies (Schulz, 2004; Hussain et al., 2015). Metrological development, leading to lower quantification and detection limits for pesticides, provides abundant information about environmental contamination and increases the need to establish priorities for these molecules, considering their impact for human and environmental health.

The health impact of pesticides on a local population is currently assessed by analysing food samples taken at shops or stalls, but pesticide exposure estimates also take account of food preparation. These investigations are often integrated by toxico-kinetic studies and blood and/or urine sampling campaigns on the population scale. However, these techniques are time-consuming, need the human subject's agreement following ethical guidelines, are expensive and the results are marred by uncertainty relating to the fate of the pesticide during food preparation and to the representativeness of the population sampled.

Wastewater-based epidemiology (WBE) is a novel tool that can provide information on population exposure to contaminants in a short time, at reasonable cost. This method was first proposed by Daughton (2018) and was implemented by Zuccato et al. (2005, 2008) to investigate the use of illicit drugs in a population. It is based on the measurement of drug metabolic residues (biomarkers) in urban wastewater and subsequent back-calculation, using metabolism data (Zuccato et al., 2008). WBE is now applied worldwide to estimate illicit drug use and several studies have reported significant differences between countries in the consumption of illicit drugs (Thomas et al., 2012). This approach has also been applied to compare illicit drug consumption in a Caribbean island and in mainland France (Devault et al., 2014, 2017).

New WBE applications include the assessment of population consumption of pharmaceuticals, nicotine, alcohol, caffeine, and exposure to plasticizers, mycotoxins (Daughton, 2018) and pesticides by analysing a selected panel of human excretion products (Rousis et al., 2016, then applied by Rousis et al., 2017a,b,c). In the case of illicit drug consumption, users consciously consume the substances and WBE can depict a clandestine market, while pesticide consumption is unconscious and WBE can provide data to assess the real ingestion rates.

Populations are exposed to pesticides by many routes: in farming or in food (Zettler and Arthur, 2000), contamination of a neighborhood by agricultural application and dispersion, or for prophylactic strategies (Ahmed et al., 2011; Davies et al., 2000), in treated building materials (Gerecke et al., 2002) and household articles (Whitmore et al., 1992; Weschler and Nazaroff, 2008).

The French island of Martinique in the Caribbean was selected to monitor pesticide human exposure for several reasons: (1) as an island it is a closed market; (2) pesticide imports are strictly recorded because of its special customs status outside the Schengen area; (3) local tropical crops are mainly sugar cane and banana for which these pesticides are not applied; (4) local dietary habits are based on massive food imports.

One of the main requirements for a WBE biomarker is that it must be a specific product of human excretion (Rousis et al., 2017b), so to assess population exposure to pesticides one must ensure that the biomarkers do not come from environmental sources such as run-off and lixiviation of contaminated soils. For this reason, an urban catchment area was selected for investigation (Baran and Arnaud, 2013), where there were no banana plantations or animal husbandry and slaughter, which can be sources of pesticide contamination (Vymazal, 2009). The groundwater of this area too was free from the pesticides studied (Baran and Arnaud, 2013). Additionally, as also mentioned in previous publications, the selected biomarkers were preferably human excretion products, which are analysed in biomonitoring studies as markers of exposure (Rousis et al., 2016), to ensure the sole source was human metabolism.

The aim of this study was to assess population exposure to pesticides and compare the findings with sales and use data. A WBE approach was employed, following the procedure reported by Rousis et al. (2017b). This study included 18 biomarkers from the *s*-triazine, pyrethroid, and organophosphate families. They were measured in urban wastewater samples and their loads were compared with results from other countries and local figures for pesticides use.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Analytical standards for diethylphosphate (DEP, purity 97.6%), chlorpyrifos (CPF, purity 99.9%), chlorpyrifos methyl (CPF-MET, purity 99.5%) and 3,5,6-trichloro-2-pyridinol (TCPY, purity 99.5%) were purchased from Chemical Research 2000 (Rome, Italy). Atrazine (ATZ, purity 97.5%), atrazine desethyl (DEA, purity 99.9%), terbutylazine desethyl (DES, purity 97.4%), atrazine desisopropyl (DIA, purity 95.4%), dimethyl chlorophosphate (DMCIP, purity 96%), dimethyl chlorothiophosphate (DMCITP, purity 97%), and *O*,*O*-diethyl thiophosphate (DETP, purity 98%) potassium salt were supplied by Sigma-Aldrich (Schnelldorf, Germany). Atrazine mercapturate (AM, purity 95.0%), 3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane) carboxylic acid (DCCA, purity 99.0%), 3-phenoxybenzoic acid (3-PBA, purity 99.0%), 2-isopropyl-6-methyl-4-pyrimidinol (IMPY, purity 99.5%), and malathion monocarboxylic acid (MMA, purity 97.0%) were purchased from Lab Service Analytica (Bologna, Italy). Isotopically labeled compounds (deuterated or 13C-enriched) were used as internal standards. 3-Phenoxybenzoic acid-C6 (3-PBA-13C6, phenoxy-13C6, 99%; purity 98%) and 3,5,6-trichloro-2-pyridinol-C3 (TCPY-C3, 4,5,6-13C3, 99%; purity 97%) were obtained from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA); atrazine-D5 (ATZ-D5, 99.5%) from Sigma-Aldrich (Schnelldorf, Germany); and chlorpyrifos-D10 (CPF-D10, 97.0%) from Lab Service Analytica (Bologna, Italy). Dimethyl phosphate (DMP) and dimethyl thiophosphate (DMTP) were synthesized by simple hydrolysis of DMCIP and DMCITP (Rousis et al., 2016).

Hydrochloric acid (HCl, 37%) and acetonitrile for liquid chromatography-mass spectrometry (LC-MS) were purchased from Riedel de Haen (Seelze, Germany); methanol (MeOH) for pesticide analysis from Carlo Erba Reagents (Italy); triethylamine and acetic acid from Fluka (Buchs, Switzerland). HPLC grade Milli-Q water was obtained with a Milli-RO Plus 90 apparatus (Millipore, Molsheim, France).

### 2.2. Target biomarkers

The selected target biomarkers are reported in Table 1. The list includes the urinary metabolites of the three classes of pesticides (triazines, organophosphates and pyrethroids) and some parent substances, selected as described elsewhere (Rousis et al., 2016).

### 2.3. Local use of the chemicals studied

Data about the local use of pesticides were collected from public departments dealing with the monitoring of environment (DEAL 972), water (ODE 972 and CG 972) and agriculture (DAAF 972), and from Rateau (2014).

In the present study *s*-triazines were selected among herbicides that have been banned in the European Union since 30 September 2003. The only herbicide used in Martinique banana plantations was atrazine. *s*-Triazines are persistent in the environment and atrazine's main metabolite, atrazine desethyl (DEA), was quantified at the ng/L level in 5% of the 101 samples from rivers in Martinique (2% for atrazine) in 2012 (most recent data). However, DEA is not a specific human or vertebrate metabolite and, in comparison to DIA, it could be used to distinguish aerobic or anaerobic degradation due to microflora (Devault et al., 2015). In the wastewater treatment plant (WWTP) catchment, the last