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# CONTRIBUTION TO THE ASSESSMENT OF THE EXPOSURE TO INDOOR PESTICIDES IN FRANCE

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## ABSTRACT

**Background :** Pesticides are environmental pollutants with potential health effects, but exposure of the population is badly documented.

**Objective :** Our purpose is to assess the exposure of adults living in Ile-de-France to indoor air pesticides.

**Methods :** Two greenhouses, three florist shops and three veterinarian services were investigated. Nineteen dwellings (flats and houses) with non-occupationnally exposed inhabitants were also sampled. Thirty-eight pesticides were measured in indoor air, using a MiniPartisol® air sampler (mean volume sampled : 7.1 $m^3$/24h). After extraction, samples were analysed by gas and high-performance liquid chromatographical methods (limits of quantification generally < 5 ng/$m^3$).

**Results and discussion :** Indoor air concentrations were often near the quantification limits (mean number of different pesticides detected per sample : 3.2±1.7), but maximal values reached 200-300 ng/$m^3$ (gardeners : malathion and methidathion, population : atrazine). The organophosphates dichlorvos, fenthion, malathion and parathion-methyl were detected in more than 10% of the samples. The organochlorines lindane, α-HCH (lindane-isomer), α-endosulfan and dieldrin were detected in 97, 38, 69 and 28% of the samples, whereas the herbicides atrazine, alachlor and trifluralin were found in 24, 21 and 14% of the samples, respectively.

A specific profile, consistent with occupational activity, can be observed ; on the contrary, more various pesticides were found in the dwellings, but at levels sometimes higher than in occupational places.

Our results confirm previously published levels of exposure in dwellings. However, the most frequently detected pesticides can differ : the chlorpyriphos is almost undetectable in our study, contrary to the US studies.

## INTRODUCTION

Pesticides are environmental pollutants with potential health effects, such as carcinogenicity, neurotoxicity, respiratory toxicity and reprotoxicity [1-6]. They contaminate indoor air of dwellings and of working rooms, due to indoor as well as outdoor uses for professional and residential purposes. Indeed, outdoor contaminants can be tracked in by shoes, clothes and air drift [7, 8]. Domestic uses include pet treatments, fight against household pests and lice, and garden and lawn treatments. Professional uses include crop, greenhouse, cattle and pet treatments, but also professional pest control operations.

Our purpose was to assess the exposure of adults living in Paris area to selected indoor air pesticides. We selected contrasted exposure situations, with professionals *a priori* more exposed but during a shorter period, and general population with unknown but more diffuse exposure.

The choice of the working areas was based upon their potential relation to exposure of the general population (i.e., jobs related to pet and flower treatments). Greenhouses were chosen because the pesticides are sprayed by the employees, and then the exposure is direct and well-known. On the opposite, flower sellers and veterinarian workers do not use pesticides themselves, but are indirectly exposed to unknown products used by the flower growers and by the pet owners, respectively. No published studies concerning those latter type of workers, and especially in France, have ever been conducted.

## METHODS

### *Sampling*

All the locations studied were in Paris or near suburbs. Sampling was performed during february to december 2002. Two different public greenhouses, three different flower shops and three different services of the Veterinary School of Maisons-Alfort were investigated. The other sites were composed of dwellings (flats and houses) where the inhabitants were non-occupationnally exposed to pesticides (n=19).

For the occupational places, the sampling was performed during a working day, in the main working room and during a day off in the dwellings. In the greenhouses, two air samples were made, one in the greenhouse room which was treated with insecticides 3 days before and one in a nearby room, where the gardeners used to spend most of their working time. Methidathion was sprayed in the first greenhouse, and malathion in the second. In the other sites, only one sampling was performed in the main working room or living room.

Indoor air was sampled by using a MiniPartisol® air sampler 2100 (Ruppert&Pataschnik, USA) and a cartridge containing a polyurethan foam (ref. 226-92, SKC) and a quartz fiber filter (ref. QM-A 1851, Whatman) maintained by a teflon ring and a metal screen. The MiniPartisol® was placed on a table or working furniture at a height of approximately 1.60 meter. The sampling lasted approximately 24 hours without interruption at a flow rate of 5L/min ; the mean volume sampled was 7.1 $m^3$/24h. Immediately after the end of sampling, cartridges were frozen (-20°C) and rapidly brought on ice to the INERIS laboratory to be analysed.

### *Sample analysis*

All reagents and solvents used were Pestanal® (Fluka) or Pestipur® (SDS) grade.

The polyurethan foams and the quartz fiber filters were then extracted with dichloromethan in a soxhlet during 16h, concentrated with a turbovap at 0.1 ml in isopropanol and then recovered in 2 ml acetone.

After extraction, samples were analysed by gas chromatography followed by electron capture detection (ECD) for the organochlorine (OC) pesticides, chlorpyriphos, permethrin and the herbicides alachlor, metolachlor and oxadiazon or by thermo-ionic detection (TSD) for the organophosphates (OPs) and the herbicides atrazine, terbuthylazine and trifluralin or by high-performance liquid chromatography (HPLC) with UV diode-array detection (UV/DAD) or with post-column derivatization and fluorimetric detection for non-volatile pesticides (carbamates, pyrethroids, urea herbicides and fungicides). The limits of quantification were generally < 5 ng/m$^3$ for most of the compounds analysed (and 0.1 to 3 ng/m$^3$ for OCs), except for the HPLC-UV/DAD method, for which limits of quantification ranged from 15 to more than 100 ng/m$^3$.

Thirty-eight different pesticides were measured ; methidathion was analysed only in the first greenhouse, where it had been sprayed, and was replaced by the fenthion in the other sample analyses.

*Statistical analysis*

Due to the low number of samples in each group, we performed non-parametric tests by using the BMDP® statistical software (University of California, Berkeley). For statistical purpose, three groups were made depending on the type of occupation : the group of plant and flower places (greenhouses and florist shops), the group of veterinarian places and the group of the dwellings. Concerning OP pesticides, sums of molar dimethyl-OPs (dichlorvos, fenthion, malathion, parathion-methyl) and of diethyl-OPs (chlorpyriphos, diazinon, parathion) were calculated. Kruskal-Wallis test was performed to analyse differences in mean levels of pesticides found in the air according to the type of location. Comparisons of the frequencies of detection between the different types of locations were performed with the determination of the Pearson's chi-square.

## RESULTS

Seventeen pesticides were detected in at least one air sample. Frequencies of detection, median levels and ranges are presented in tables 1, 2 and 3 for OP insecticides, OC and carbamate insecticides, and herbicides, respectively. The mean number of different pesticides detected per sample was 3.2±1.7 and was not different between the locations. However, maximal number of compounds detected was 7, in a dwelling. Overall, indoor air concentrations were often near the quantification limits, but maximal values reached 200-300 ng/m$^3$ in the greenhouses (malathion and methidathion), and in the dwellings (atrazine and propoxur).

The OPs were detected in 10% (diazinon, malathion and parathion-methyl) or more than 20% (dichlorvos, fenthion) of the samples, at concentrations between 1.5 and 371.6 ng/m$^3$. Chlorpyriphos was detected only once, in a dwelling and at a very low concentration (table 1). Propoxur was the only carbamate detected, in 34% of the samples, at levels ranging from 2.3 to 256 ng/m$^3$ (table 2) The OCs lindane, α-endosulfan, α-HCH (lindane-isomer) and dieldrin were detected in 97% (not detected in only one dwelling), 69%, 38% and 28% of the samples respectively, at levels between 0.2 and 75 ng/m$^3$ for the lindane, and at lower levels for the others (table 2). The herbicides atrazine, alachlor and trifluralin were present in 24, 21 and 14% of the samples, respectively, at levels lower than 30 ng/m$^3$, except for atrazine which reached 268 ng/m$^3$ in dwellings (table 3).

Considering the greenhouses, air levels of sprayed insecticides were much higher in the treated rooms (more than 200 ng/m$^3$ for methidathion and malathion) than in the working rooms (10 to 50 fold lower). In the first greenhouse, parathion-methyl, sprayed in another room of the greenhouse, was also found in the main working room and in the studied room, but at low levels (6.5 and 17 ng/m$^3$, respectively).

In the florist shops, dichlorvos and fenthion were detected in the air samples of two shops, malathion, parathion-methyl, alachlor and atrazine in one out of three ; however, concentrations were below 15 ng/m$^3$, except for dichlorvos that reached 130 ng/m$^3$.

In the veterinarian places, diazinon and propoxur were found everywhere, with a median air concentration of 31.5 ng/m$^3$ and 3.5 ng/m$^3$, respectively. The α-endosulfan was also detected in the 3 places, although at levels below 1 $ng/m^3$. Dichlorvos was found in one service at 28.9 $ng/m^3$.

In dwellings, propoxur and atrazine were found in one third of the air samples, reaching concentrations of more than 200 $ng/m^3$. OP insecticides were much less detected (mainly fenthion and dichlorvos) and at low levels. Concerning the OCs, $\alpha$-HCH, dieldrin and $\alpha$-endosulfan were frequently found, at levels reaching 1.8, 0.3 and 13.5 $ng/m^3$, respectively. Alachlor and trifluralin were detected in approximately 20% of the dwellings, with maximal concentrations of 10.2 and 30.9 $ng/m^3$, respectively.

When comparing frequencies of detection in the different types of location, $\alpha$-endosulfan and propoxur frequencies were found to be significantly different between the three groups (Pearson's chi-square = 9.842, p=0.0073 for $\alpha$-endosulfan ; Pearson's chi-square = 18.585, p=0.0001 for propoxur).

When comparing mean levels of pesticides found in the three groups, propoxur levels in the air of veterinarian places were significantly different from those of the other places (Kruskal-Wallis test, p = 0.0023 ; Zstat = 3.48 (versus plant group) and 2.24 (versus dwellings)). Dieldrin levels in the air of dwellings were also significantly different from levels found in the other locations (Kruskal-Wallis test, p=0.0067 ; Zstat= 2.46 (versus plant group) and 2.71 (versus veterinarian group)).

The apparently different pattern of exposure, according to the occupation, was confirmed by comparing dimethyl-OP and diethyl-OP levels between the different groups. Dimethyl-OP levels in the plant group were significantly different from those found in the veterinarian placces and in the dwellings (Kruskal-Wallis test, p=0.0001 ; Zstat = 2.97 (versus veterinarian group), Zstat = 4.25 (versus dwelling group)). On the opposite, diethyl-OP air levels in veterinarian places significantly differed from levels found in other places (Kruskal-Wallis test, $p<10^{-4}$, Zstat=5.28 (versus plant group), Zstat = 5.58 (versus dwelling group)).

No other significant difference of pesticide levels depending on the type of location was observed. However, the variety of pesticides found was greater in dwellings than in occupational locations ; indeed, 14 different compounds were detected, as compared to 7, 8 and 6 in the greenhouses, the florist shops and the veterinarian places, respectively.

Using the CG-ECD, the following pesticides were never detected : aldrin, *cis* and *trans* chlordane, heptachlor and its two epoxides, metolachlor, oxadiazon, *cis* and *trans* permethrin (LOQ between 0.10-0.44 $ng/m^3$ for OCs ; LOQ = 11.3 and 19.3 $ng/m^3$ for *cis* and *trans* permethrin). Carbaryl was not detected by HPLC with post-column derivatization and fluorimetric detection (LOQ = 1.9 $ng/m^3$). Parathion and terbuthylazine were not detected by the CG-TSD method, with LOQ of 0.77 and 6.3 $ng/m^3$, respectively. The other not detected pesticides - chlorothalonil, deltamethrin, diflufenican, diuron, fenoxaprop-p-ethyl, folpet, isoproturon, tau-fluvalinate – had been analysed by HPLC-UV/DAD, with LOQ between 15 $ng/m^3$ (diflufenican) to 560 $ng/m^3$ (chlorothalonil).

| | | dichlorvos | fenthion | malathion | methidathion | parathion methyl | chlorpyriphos | diazinon |
|---|---|---|---|---|---|---|---|---|
| greenhouses (n=4) | percent detect | nd* | nd (n=2) | 50 | 100 (n=2) | 50 | nd | nd |
| | median | | | 38.6 | 110.3 | 3.3 | | |
| | range | | | nd-371.6 | 0.4-220.2 | nd-17 | | |
| flower shops (n=3) | percent detect | 67 | 67 | 34 | na* | 34 | nd | nd |
| | median | 22.9 | 0.7 | nd | | nd | | |
| | range | nd-130.1 | nd-1.5 | nd-3.1 | | nd-14.3 | | |
| veterinarian services (n=3) | percent detect | 34 | nd | nd | na | nd | nd | 100 |
| | median | nd | | | | | | 31.5 |
| | range | nd-28.9 | | | | | | 14.8-52.9 |
| dwellings (n=19) | percent detect | 16 | 23.5 | nd | na | nd | 5 | 5 |
| | median | nd | nd | | | | nd | nd |
| | range | nd-13.6 | nd-6.4 | | | | nd-0.7 | nd-12 |

Table 1.Indoor air concentrations of OP insecticides

| | | α-HCH | lindane | α-endosulfan | β-endosulfan | dieldrin | DDT | propoxur |
|---|---|---|---|---|---|---|---|---|
| greenhouses (n=4) | percent detect | 50 | 100 | 25 | 25 | nd | nd | nd (n=2) |
| | median | 0.1 | 11 | nd | nd | | | |
| | range | nd-0.5 | 1.0-75.0 | nd-0.7 | nd-0.4 | | | |
| flower shops (n=3) | percent detect | nd | 100 | 34 | nd | nd | nd | nd |
| | median | | 0.6 | nd | | | | |
| | range | | 0.2-28.6 | nd-1.1 | | | | |
| veterinarian services (n=3) | percent detect | 34 | 100 | 100 | nd | nd | nd | 100 |
| | median | nd | 2.7 | 0.3 | | | | 3.5 |
| | range | nd-0.3 | 1.4-11.8 | 0.3-0.8 | | | | 2.3-3.5 |
| dwellings (n=19) | percent detect | 42 | 95 | 79 | 5 | 42 | 5 | 37 |
| | median | nd | 3.6 | 0.3 | nd | nd | nd | nd |
| | range | nd-1.8 | nd-72.2 | nd-13.5 | nd-1.1 | nd-0.3 | nd-0.9 | nd-256.0 |

Table 2. Indoor air concentrations of OC and carbamate insecticides

| | | atrazine | trifluralin | alachlor |
|---|---|---|---|---|
| greenhouses (n=4) | percent detect | nd | nd | nd |
| | median | | | |
| | range | | | |
| flower shops (n=3) | percent detect | 34 | nd | 34 |
| | median | nd | | nd |
| | range | nd-2.8 | | nd-6.0 |
| veterinarian services (n=3) | percent detect | nd | nd | nd |
| | median | | | |
| | range | | | |
| dwellings (n=19) | percent detect | 32 | 21 | 26 |
| | median | nd | nd | nd |
| | range | nd-268.0 | nd-30.9 | nd-10.2 |

Table 3. Indoor air concentrations of herbicides

**nd : not detected*
**na : not analysed*

## DISCUSSION

This study was performed in order to assess levels of indoor air pesticides to which professionals and general population are exposed in Paris.

Pesticides sprayed in greenhouses, and almost only these pesticides, were detected in the rooms treated but also in the main working rooms. Levels found were lower than threshold exposure levels (TEL) of 10 $mg/m^3$ for malathion and 0.2 $mg/m^3$ for parathion-methyl during a working day [9] ; there is no TEL for methidathion. No herbicide was detected, but no such use was reported by the greenhouse workers ; therefore, exposure of the gardeners seems to be specific to the used pesticides. Moreover, greenhouses differ considerably from the other buildings : they have a glass and metallic structure and communicate directly with the outside, without stages and basement. This can explain the low number of non-used pesticides detected, except lindane and $\alpha$-HCH.

In florist shops, where pesticides likely to be found were unknown, we detected fenthion, dichlorvos and methyl-parathion as insecticides, and alachlor and atrazine as herbicides. These results probably reflect pesticides used by flower and plant growers, especially for insecticides, and treatment habits related to the different countries where the flowers and plants come from.

Propoxur, diazinon and fenthion are known to be used for pet treatments against ectoparasites ; as expected, diazinon and propoxur were detected in all veterinarian places, but fenthion was not detected. Fenthion seems to be more related to flower and plant treatment than to pet treatment. Dichlorvos was detected once, but no pet treatment indication is known for this compound.

The wider range of different pesticides found in dwellings reflects the great variety of pesticides to which the population can be exposed in indoor air, even if for some the levels and the frequencies are low. However, for some pesticides and in some habitation samples, pesticides levels found were higher than those found in occupational places ; this was the case for atrazine, propoxur, lindane and $\alpha$-endosulfan. When considering the difference between time spent in working areas (max. 8 hours a day) and time spent at home (approx. 12-14 hours a day or more), exposure due to contamination of indoor air in the dwellings cannot be neglected.

When we compare our results with indoor air concentrations found in other studies, we found lower levels than in other occupational studies which took place in greenhouses [10-12] but we did not find any study concerning florist shops nor veterinarian rooms. In indoor air of dwellings, levels found for atrazine, dichlorvos and diazinon are of the same order from those found by several studies performed in the United States [13-15]. However, the most detected pesticides are not the same : for instance, chlorpyriphos was almost undetectable in our study, contrary to the results of the US studies [13, 16, 17]. On the opposite, propoxur and fenthion which were not always emphasized in the US studies, were frequently detected in our study.

The only OP never detected, parathion, was banned since 2002 from all use in France. Chlorpyriphos and malathion, probably among the most used OPs in agriculture, were almost never detected in our air samples.

The OC lindane, which was banned since 1998 from agricultural use, has been used against human lice and scabies and pet fleas until 2003 in France. But the fact that we found it everywhere indicates that, due to its remanency in the environment, levels found reflect ancient uses, probably as termiticide or for other indications. The $\alpha$-HCH, which is an isomer of lindane (which is the $\gamma$-HCH isomer), is a contaminant of commercial formulas and is more carcinogenic than lindane [18]. We found it relatively less frequently, and at much lower levels, than lindane. The $\alpha$-endosulfan is still authorized in France, but its uses are very restricted to a few crops ; the ubiquitous contamination observed seems to be related with outdoor air drift. Among other OCs, banned because of their great persistence in the environment, dieldrin was found only in some dwellings and at very low levels, DDT was detected only once in the air of a dwelling and aldrin, chlordane and heptachlor were not detected in our sample of locations.

The three pyrethroids tested were not detected, but there is a wide variety of pyrethroids available in France for domestic uses, and moreover, these insecticides are not very volatile.

Concerning atrazine and terbuthylazine, their use was restricted to some agricultural uses since 1996 and they were completely banned since the end of 2003. Moreover, triazines were not approved for domestic use ; occupational and dwelling air contaminations observed here seem to be due to persistant contamination of outdoor air. The herbicides diuron, isoproturon, fenoxaprop-p-ethyl, diflufenican, metolachlor and oxadiazon were not detected too ; except oxadiazon, the others are not approved for domestic use in France.

The two fongicides studied, chlorothalonil and folpet, were not detected in our sample; however, they are not approved for domestic use and they are not very volatile.

## CONCLUSION

Our present study is the first focusing on the analysis of 38 different pesticides in indoor air of specific locations in France.

A specific profile of pesticides, consistent with occupational activity, can be observed in working areas ; on the contrary, more various pesticides are found in the population.

Our results in greenhouses are far lower than the TLVs, but those found in habitations confirm previously published levels, which can be important in certain cases. However, the most frequently detected pesticides can differ according to the country.

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