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Coupling ASE, sylilation and SPME–GC/MS for the analysis of current-used pesticides in atmosphere

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ABSTRACT

An analytical methodology using Accelerated Solvent Extraction (ASE) and a sylilation procedure coupled to Solid Phase Micro-Extraction (SPME) and GC/MS was developed for the determination of 31 pesticides of different chemical classes (urea, phenoxy acids, pyrethrenoïds, etc.) commonly used in non-agricultural areas in atmospheric samples. This methodology was developed to evaluate the outdoor atmospheric contamination by non-agricultural pesticides. Pesticides were simultaneously sampled on glass fibre filters and on XAD-2 resin traps by using a low volume sampler (Partisol) for 1 week. Traps were extracted by Accelerated Solvent Extraction (ASE) with acetonitrile and concentrated to 1 mL by using a rotary evaporator. 500 μL of the extract was dissolved in 19.5 mL of 1.5% NaCl acidified water (pH=3) and SPME extracted by PA fibre for 55 min at 50 °C. Since most of the studied pesticides are polar or thermo-labile, a derivatisation step by injection of 2 μL of M*t*BSTFA just before SPME desorption was done. M*t*BSTFA was chosen since it delivers very specific ions on electronic impact (m/z=M-57).

Detection limits varied between 5 and 179 ng resin^{-1} and between 0.3 and 126 ng filter^{-1} corresponding to 2 and 750 pg m^{-3} and 30 and 1165 pg m^{-3} for 168 m^3 of air pumped through traps. Quantification limits varied between 18 and 595 ng resin^{-1} and between 1 and 420 ng filter^{-1} corresponding to 107 and 3542 pg m^{-3} and 6 and 2500 pg m^{-3} for 168 m^3 of air pumped through traps. Uncertainties varied between 7.2% and 39.6% and between 7.2% and 53.4% respectively for filter and resin.

The method was used for the analysis of atmospheric samples collected in a background urban site of Strasbourg (east of France) during spring and summer 2010.

1. Introduction

If the atmospheric behaviour of pesticides used in agriculture is relatively well documented [5,8,10,11,14–16,21], few studies are available on pesticides applied in non-agricultural areas like public and private gardens, railways, etc. Recently Scheyer et al. [15,16] have observed in rainwater that diuron, an herbicide intensively used in non-agricultural areas, presents more important concentrations in urban areas in comparison to rural areas and a non-seasonal frequency of detection. In air samples, aryloxyacids have been also detected more frequently in urban areas in relation to their use in urban public and residential areas.

The evaluation of the airborne exposure to pesticides needs the collection of representative air samples. Systems currently used are active samplers and they consist of high or low volume pumping or air on filters followed by a solid adsorbent for the simultaneous sampling of the particle and gas phase [1,3,10,15,19]. After sampling, extraction techniques and analysis methods consist generally of a solvent extraction (i.e. Soxhlet), a purification step and an injection on GC. These methods are accurate but they involve solvents and are time consuming. In addition, only a small amount of the extract, generally, 1–2 μL is injected onto the GC, resulting in many cases of problems of sensitivity. An alternative is to use Accelerated Solvent Extraction (ASE) coupled to Solid-Phase Micro-Extraction (SPME) for the extraction and pre-concentration of atmospheric pesticides. Indeed, ASE is faster than Soxhlet and this technique permits to reduce the amount of solvent drastically. SPME is an inexpensive, rapid and solvent free extraction method for the isolation of organic compounds. The main advantage of SPME technique is that it integrates extraction, concentration and purification in one step. Consequently, SPME represents a significant advance in analytical chemistry for the handling of environmental matrices containing low level of target analytes or/and high concentration of impurities [13].

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Schummer et al. [18] have used the coupling of ASE and SPME for the extraction and pre-concentration of currently used pesticides absorbed on XAD-2 passive samplers. In this study, the method developed by Schummer et al. [18] was applied to filters and XAD-2 resins, coming from low-volume sampling, together with a derivatisation step added prior to SPME injection of pesticides onto the GC following the procedure developed by Jaber et al. [7] for the analysis of phenols and nitrophenols in rainwater. The addition of the derivatisation step permits the injection in one run of pesticides from different chemical classes following the method developed by Raeppel et al. [12].

2. Materials and methods

2.1. Chemicals

Acetonitrile, n-hexane and methylene dichloride of HPLC grade were obtained from Prolabo (France). Ultrapure water was obtained from a Milli-Q water system (Millipore, St. Quentin en Yvelines, France). Standards of individual pesticides (Dichlobenil, Diuron, Carbofuran, Trifluralin, Clopyralid, Carbaryl, Flazasulfuron, Mecoprop-P, Dicamba, 2,4 MCPA, Dichlorprop, 2,4 D, Triclopyr, Cyprodinil, Bromoxynil, Fluroxypyr, Oxadiazon, Myclobutanil, Buprofezin, Picloram, Trinexapac-p-ethyl, Ioxynil, Diflufenican, Tebuconazole, Bifenthrin, Isoxaben, Oryzalin, Alphacypermethrin, Fenoxaprop, Tau-Fluvalinate and Deltamethrin) of Pestanal® quality (> 99% purity) were obtained from Riedel de Haën (Sigma Aldrich, St. Quentin Fallavier, France).

Internal standards: trifluralin d^{14} and transpermethrin d^6 were supplied from Cluzeau Info Labo (St. Croix la Grande, France) while 4-Nitrophénol-d^4 was supplied from Sigma-Aldrich (St. Quentin Fallavier, France).

M*t*BSTFA (N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide) purum ≥ 97% was purchased from Sigma Aldrich (St. Quentin Fallavier, France).

For calibration and analytical development, a stock solution of each pesticide at 1 g L^{-1} was prepared in acetonitrile. A working solution at 80 mg L^{-1} was prepared for each compound together with a mixture solution for full scan injection. For SIM injection and calibration, mixture solutions between 1 mg L^{-1} and 10 μg L^{-1} were prepared from stock solution in acetonitrile.

2.2. Cleaning of filters and XAD-2 resin

Just before sampling, filters were Soxhlet extracted for 24 h with a mixture of n-hexane/methylene dichloride (50:50) and stored in the dark in an aluminium foil. XAD-2 resin was cleaned by Accelerated Solvent Extraction by three static cycles of 15 min with n-hexane/methylene dichloride (50:50) followed by one static cycle of 15 min with acetonitrile. XAD-2 resin was then dried in an oven and stored as 10 g samples in clean hermetically capped amber glass vials.

2.3. Field sampling

Air samples were collected in Strasbourg (423,000 inhabitants) with a "Partisol 2300® Speciation Sampler" low-volume sampler. The sampler was placed in the Botanical garden of Strasbourg University, approximately 0.5 km from the town centre, 2 km from industrial zones and about 5 km from the first exploitation of high maize and cereal crops. None of the studied pesticides were used in the Botanical Garden.

Particulate and gaseous samples were collected simultaneously by using a ChemComb® cartridge equipped with a 47 mm diameter glass fibre filter (Whatman, GF/A) and 10 g of XAD-2 resin (Supelco), a copolymer of styrene/divinylbenzene and macroporous acrylic ester, for 7 day periods, at a flow rate of 1 m^3 h^{-1}, between April 9th and July 20th 2010. XAD-2 have been used as this resin is a universal sorbent very efficient for trapping pesticides and commonly used for active sampling [4,10,15,18,24].

After sampling, filters and resins were stored in the dark at -20 °C for a maximum of 4 days until extraction.

2.4. Extraction of traps and preparation of SPME solutions

After sampling, traps were separately extracted by accelerated solvent extraction (ASE). Filters were cut into small parts, mixed with "Fontainebleau sand" and introduced into a stainless steel extraction cell of 33 mL while XAD-2 resin was introduced directly in the ASE cell. Extraction was performed with acetonitrile using the procedure developed by Schummer et al. [18] for passive samplers as follows: temperature: 150 °C; pressure: 1500 psi; static: 15 min; cycles: 3; purge: 300 s; flush: 100%. After, extraction, the collected extract was concentrated to 1 mL using a rotary evaporator (40 °C; 250 mbar).

In order to reduce matrix effects and parasite peaks on the chromatograms and to increase the sensitivity, the pesticides were concentrated on a SPME-fiber (Solid Phase Micro-Extraction) prior to injection into GC/MS. For this purpose, aqueous SPME extraction solutions have been prepared in 10 mL flasks with 250 μL of the ASE extract, 50 μL of a internal standards solution (trifluralin-d^{14}, 4-nitrophenol-d^4 and transpermethrin-d^6) at 1 mg L^{-1} each and 7000 μL of ultra-pure water (pH = 3; 1.5% NaCl).

2.5. SPME-GC/MS analysis of pesticides extracted from filter and XAD-2 resin.

Analyses were carried out by using an autosystem XL GC coupled to a turbomass gold detector (Perkin-Elmer Corp., Norwalk, CT, USA).

Separation has been performed on a Varian Factor-Four V5-MS (equivalent to 5% phenyl, 95% polydimethylsiloxane) capillary column (60 m × 0.25 mm i.d., 250 μm film thickness) as follows: 50 °C (5 min) to 150 °C at 25 °C/min, to 250 °C at 3 °C/min and to 300 °C (15 min) at 15 °C/min. Helium was used as gas vector at 1.0 mL min^{-1} (regulated constant flow). Temperatures of the MS source and transfer line were maintained at 280 °C and 320 °C respectively. Spectra of pesticides were obtained by electron impact ionisation (EI) at 70 eV. Depending of pesticides, two of three ions were selected from the spectrum of each pesticide to quantify the response in the selected ion monitoring mode (SIM).

For SPME, a polyacrylate (PA) 85 μm fibre was used. An aliquot of 4 mL of the aqueous ASE extract was introduced in SPME amber vials of 4 mL. In the case of two injections of one sample, a new fresh 4 mL solution was used. A stirrer was added and vials were sealed with silicon cap furnished with a PTFE-faced septum and placed in the SPME device maintained at 50 °C.

Upon injection of the SPME syringe through the septum vial, the fibre was exposed to aqueous solution for 55 min magnetically stirred at 400 rpm.

After retraction of the fibre back into the syringe and before introduction of the SPME needle into the injection port of the GC maintained at 250 °C, 2 μL of M*t*BSTFA was injected directly into the injector (derivatisation on the injector). With this procedure, no degradation of the column was observed.

Desorption time was set at 5 min (splitless time). Possible carryover was prevented by keeping the fibre in the injector for an additional time (15 min) with the injector in the split mode (20 mL min^{-1}). Blanks were periodically run during the analysis to confirm the absence of contamination.

SPME fibres were conditioned before first used at 280 °C for 2–3 h. For next experiments the conditioning time was reduced to 15 min.

Calibration curves were obtained by spiking filters and XAD-2 resin from 1 ng to 2000 ng of each pesticide. All calibration points were done in triplicate. The entire analytical procedure was applied for each filter and resin and calibration was determined by the internal standard method.

Quantification limits (QLs) varied between 5 pg m^{-3} and 2 ng m^{-3} and between 79 pg m^{-3} and 3 ng m^{-3} and detection limits (DLs) varied between 1 pg m^{-3} and 667 ng m^{-3} and between 26 pg m^{-3} and 947 ng m^{-3} for filter and resin respectively for 189 m^3 of air. Uncertainties varied between 7.2% and 39.6% and between 7.2% and 53.4% respectively for filter and resin.

3. Results and discussion

3.1. Chromatographic separation

In a previous work [12], a gas chromatographic method for the analysis of 31 pesticides from different chemical classes was developed. This method was used for the SPME pre-concentration of ASE extracts. Retention times and m/z ions chosen for the SIM procedure are presented in Table 1.

Internal standards used were trifluralin d^{14} for non-derivatised pesticides, nitrophenol d^4 for derivatised pesticides and transpermethrin d^6 for pyrethrenoids pesticides. Some pesticides were difficult to analyse (diuron, trinexapac-ethyl and oryzalin). The addition of SPME pre-concentration on the method developed by [12] did not increase the capacity of analysis for these compounds.

Table 1
Retention time and SIM m/z chosen for the 31 pesticides analysed in air samples.

Pesticides	t_R (min)	m/z SIM (Da)
Diuron	–	187–189–124
Dichlobenil	16.17	171–173–136
Carbofuran	22.03	205–278
Trifluralin d^{14}	22.80	315–267–349
Trifluralin	23.06	264–306
4-Nitrophenol d^4	26.10	200–257–199
Clopyralid	27.15	248–250–146
Carbaryl	27.34	258–185
Flazasulfuron	27.55	231–188
Mecoprop-P	28.92	271–199–225
Dicamba	29.50	277–203–262
2.4 MCPA	30.51	257–211–229
Dichlorprop	31.07	219–291
2.4 D	32.76	277–249
Triclopyr	34.35	314–256–254
Cyprodinil	35.26	224–225
Bromoxynil	35.94	334–336–173
Fluroxypyr	38.83	253–311–255
Oxadiazon	39.10	258–302
Myclobutanil	39.91	150–179 -181
Buprofezin	39.67	105
Picloram	42.13	297–299–195
Ioxynil	45.27	301–428
Trinexapac-ethyl	–	235–309–310
Diflufenican (derivatized)	45.72	377–451
Diflufenican (non-derivatized)	46.56	394–246
Tebuconazole	46.65	125–250
Bifenthrin	48.67	181–165–166
Isoxaben	50.22	165–389–305
Transpermethrine d^6	56.43	183–165–169
Oryzalin	–	403–431
Alphacypermethrin	59.42+60.02	181–163–165
Fenoxaprop	62.15	318–390
Tau-Fluvalinate	63.02+63.27	250–181
Deltamethrin	64.69+65.42	181–253

Concerning diflufenican, the addition of M*t*BSTFA induces a non-complete derivatisation of this pesticide. As the non-derivatised form was the more intense one (about 80%), it was decided to use it for quantification and calibration.

3.2. Optimisation of SPME procedure

SPME extraction needs the optimisation of some parameters like the type of fibre, the temperature and duration of extraction. As pesticides under study are aryloxyacids, it was decidedthat a solution of pH 3 be used in order to have these pesticides in their protonated form [17]. The percentage of NaCl was also fixed to 1.5% as previously determined by Schummer et al. [18] as the better percentage for the extraction of pesticides where some of them are included in the present study.

Analysis of pesticides in several matrices (water, air, hair, etc.) by SPME is generally done by using 100 μm PDMS, 65 μm PDMS-DVB of PA fibres [2,6,13,16–18,20,22]. In consequence, each of these fibres was evaluated for the pesticides under study and results are presented in Fig. 1. It appears that the experimented fibres give good extraction efficiencies but PDMS-DVB and PA seems slightly better for most of the compounds analysed. This result is in agreement with previous studies already mentioned. However, for derivatised pesticides, it can be seen that PA was the better fibre, except for ioxynil, in terms of extraction efficiency. Then, PA fibre was selected for the extraction of pesticides from air samples.

Among the parameters which need to be optimised, only the temperature of extraction and its duration were tested. pH and salinity were considered as valid since acidic herbicides required an acidic pH for the extraction from water [17,23] while salinity was already validated in a previous work [18].

Optimal extraction temperature was found to be different depending of pesticides as shown in Fig. 2. Indeed, pyrethroids pesticides were more efficiently extracted over 70 °C. In order to not work with high temperature, which can cause the deformation of the septum of the SPME vial, it was decided to perform extraction at 50 °C since this temperature permits to extract all pesticides under study with enough sensitivity including pyrethroids. This temperature is in the range of those used previously [17,18]. Concerning the extraction time, different times were tested (between 25 and 60 min) and the optimal duration was obtained for 55 min.

3.3. SPME-GC/MS repeatability and calibration range

The calibration and the validation of the method have been done by spiking of clean filter and resin between 2 and 2000 ng of each pesticide. Each calibration point was done three times.

Spiked filter and resin were treated following the same procedure as the one used for real samples and previously described in Section 2.

All calibration curves were plotted following the internal standard method and linearity for each pesticide is function of its quantification limits. Linear regression coefficient varied between 0.905 and 0.992 and between 0.903 and 0.999 for the filter and resin matrix respectively (Tables 2 and 3).

These values were considered sufficient as they integrate the all analytical chain. However, the calibration was not possible for 8 pesticides (diuron, clopyralid, flazasulfuron, carbofuran, trinexapac-ethyl, picloram, oryzalin and isoxaben) since these pesticides were not detected in the concentration range used for calibration of detected only in high concentrations.

Coefficient of variation (CV%) was calculated from five independent samples spiked at 2000 ng analysed the same day (intra-day variability) or on five different days (inter-day variability).

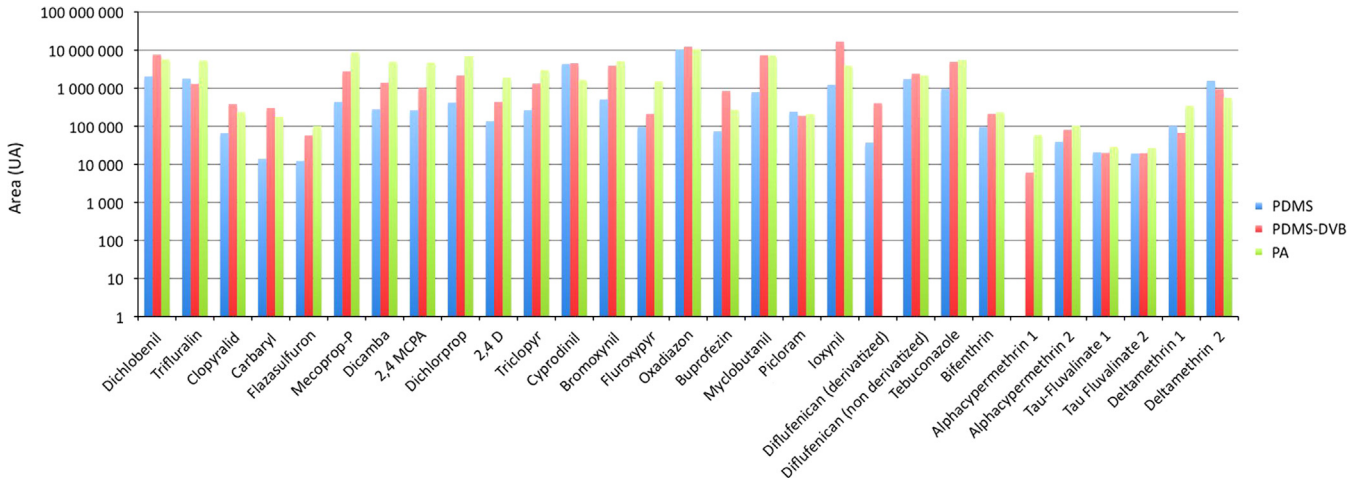

Fig. 1. Comparison of extraction efficiencies for the three tested fibres.

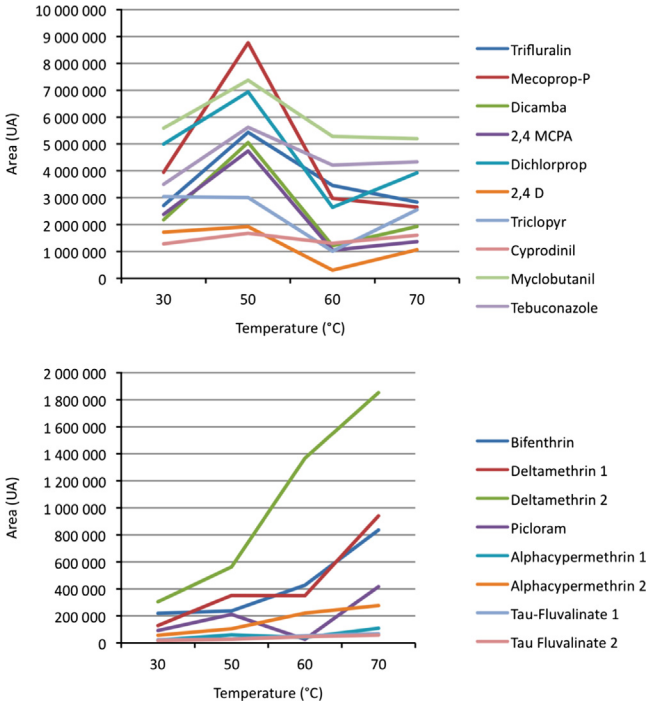

Fig. 2. Influence of the temperature on the extraction efficiency.

For resin samples, CV inter- and intra-days varied between 7.1% (bifenthrin) and 53.4% (trifluralin) and between 9.9% (bifenthrin) and 53.1% (trifluralin) respectively. For filters, CV inter- and intra-days varied between 7.2% (bromoxynil) and 39.6% (dicamba) and between 9.6% (bifenthrin) and 87% (tau-fluvalinate) respectively.

Coefficients of variations are comparable but slightly lower in some cases for filter samples. This can be explained by the lower matrix effect caused by filter in comparison to resin. Generally higher CV is obtained for compounds which are eluted at the end of the temperature ramp of for pesticides with higher quantification and detection limits.

Detection and quantification limits were obtained with the Turbomass software as 3 times the background noise multiplied by the response factor of the compound and as 10 times the background noise multiplied by the response factor of the compound respectively.

Detection limits varied between 5 and 179 ng resin^{-1} and between 0.3 and 126 ng filter^{-1} corresponding to 2 and 750 pg m^{-3} and 30 and 1165 pg m^{-3} for 168 m^3 of air pumped through traps. Quantification limits between 18 and 595 ng resin^{-1} and between 1 and 420 ng filter^{-1} corresponding to 107 and 3542 pg m^{-3} and 6 and 2500 pg m^{-3} for 168 m^3 of air pumped through traps.

Detection and quantification limits obtained for filter and resin are in the same order of magnitude but lower for filter samples. This is the consequence of the higher matrix effect produced by the extraction of resin as previously mentioned for coefficients of variation. Values obtained for resin are comparable to those obtained by Schummer et al. [18] after ASE extraction and SPME pre-concentration of XAD-2 passive samplers.

3.4. Application to atmospheric samples

A sampling campaign using Partisol low-volume samplers have been done between 09 April and 10 July 2010 on a weekly basis corresponding to 12 samples. Each week, filter and XAD-2 resin were changed and analysed separately using the developed method. On the 31 pesticides, 13 have been detected but among these 13 pesticides, carbofuran, carbaryl, flazasulfuron and picloram were below quantification limits. The concentration range of the detected pesticides are summarised in Table 4 and compared with previous data obtained in France and Strasbourg.

Some pesticides were already measured by previous studies performed in the same area since Scheyer et al. [15] and Mothiron et al. [10] have detected alphacypermethrin, bifenthrin, myclobutanil and trifluralin concentrations obtained in this study are in the same order of magnitude (Table 4) except for bifenthrin which presents higher levels which can only be explained by application during the sampling campaign.

Concentrations of 2,4 D, dichlobenil and oxadiazon can be compared with those obtained by French Atmospheric Pollution Networks (AASQA) data obtained between 2001 and 2007 [9]. Concentration of dichlobenil and oxadiazon obtained in the present study is comparable from those obtained by AASQA. However, concentrations of 2,4-D is about 50 times higher but no interpretation can be advanced regarding the lack of informations concerning data obtained by AASQA.

Highest concentrations obtained for oxadiazon and bifenthrin are coherent with values obtained for other pesticides by Mothiron et al. [10] in the same sampling site and these authors explained this result by application of pesticides during sampling. The same hypothesis can be advanced for the present study.

As the sampling campaign have been done during application periods the non-detection of some pesticides could be explained by their non-use during the sampling period or their presence in

Table 2
Linearity, uncertainties and quantification and detection limits of resin samples.

Pesticides	Coefficient of determination R^2	Coefficient of variation (%) Intraday	Coefficient of variation (%) Interday	LQ (ng resin^{-1})	LQ (pg.m^{-3})	LD (ng.resin^{-1})	LD (pg.m^{-3})
Dichlobenil	0.982	12.5	46.0	45	268	13	77
Trifluralin	0.977	53.4	53.1	56	333	17	101
Carbaryl	0.983	11.9	11.7	73	435	22	131
Mecoprop-p	0.992	11.0	23.7	178	1060	54	321
Dicamba	0.987	16.0	25.8	178	1060	53	315
2,4 MCPA	0.990	13.9	25.7	327	1946	98	583
Dichlorprop	0.982	8.4	26.7	217	1292	65	387
2,4 D	0.987	22.2	28.8	268	1595	80	476
Triclopyr	0.988	10.6	25.6	114	679	34	202
Cyprodinil	0.975	11.6	45.5	45	268	14	83
Bromoxynil	0.992	8.4	21.0	26	155	8	48
Fluroxypyr	0.987	13.0	24.0	277	1649	83	494
Oxadiazon	0.975	10.6	25.9	18	107	5	30
Myclobutanil	0.946	14.1	48.5	165	982	49	292
Buprofezin	0.916	12.5	43.5	432	2571	130	774
Ioxynil	0.905	23.8	29.0	123	732	37	220
Diflufenican	0.974	11.5	21.8	40	238	12	71
Tebuconazole	0.987	12.1	53.0	68	405	20	119
Bifenthrin	0.991	7.1	9.9	130	774	39	232
Alphacypermethrin	0.976	8.9	27.2	295	1756	89	530
Fenoxaprop	0.988	23.9	28.1	94	560	28	167
Tau Fluvalinate	0.923	29.0	34.8	595	3542	179	1065
Deltamethrin	0.947	17.3	37.9	426	2536	128	762

Table 3
Linearity, uncertainties and quantification and detection limits of filter samples.

Pesticides	Coefficient of determination R^2	Coefficient of variation (%) Intraday	Coefficient of variation (%) Interday	LQ (ng filter^{-1})	LQ (pg m^{-3})	LD (ng filter^{-1})	LD (pg m^{-3})
Dichlobenil	0.993	18.5	34.8	90	536	27	161
Trifluralin	0.994	7.7	20.9	1	6	0.3	2
Carbaryl	0.989	8.3	12.9	46	274	14	83
Mecoprop-p	0.996	9.6	30.9	72	429	22	131
Dicamba	0.999	39.6	52.9	83	494	25	149
2,4 MCPA	0.979	11.3	32.5	173	1030	52	310
Dichlorprop	0.982	7.3	17.7	139	827	42	250
2,4 D	0.998	9.5	31.0	202	1202	61	363
Triclopyr	0.994	9.8	33.3	60	357	18	107
Cyprodinil	0.977	22.0	41.8	9	54	3	18
Bromoxynil	0.997	7.2	22.6	3	18	1	6
Fluroxypyr	0.991	8.8	23.5	6	36	2	12
Oxadiazon	0.992	21.0	28.0	2	12	1	6
Myclobutanil	0.974	21.5	29.7	14	83	4	24
Buprofezin	0.956	22.3	43.1	392	2333	118	702
Ioxynil	0.974	9.3	27.4	9	54	3	18
Diflufenican	0.990	30.9	31.6	17	101	5	30
Tebuconazole	0.984	24.5	24.5	21	125	6	36
Bifenthrin	0.998	9.9	9.6	6	36	2	12
Alphacypermethrin	0.994	29.4	43.3	100	595	30	179
Fenoxaprop	0.980	30.0	47.0	50	298	15	89
Tau Fluvalinate	0.903	37.9	87.0	418	2488	125	744
Deltamethrin	0.968	32.7	64.8	420	2500	126	750

Table 4
Range of concentrations of pesticides detected in atmospheric samples and comparison with other studies.

Pesticide	Concentration range (ng m^{-3})			
	This study	AASQA data [9]	Strasbourg [10]	Strasbourg [17]
2,4 D	1.1–31–3.1	0.06	–	
Alphacypermethrin	0.3–33–3.8	–	0.11–111–1.02	
Bifenthrin	0.2–202–20.7	0	0.06–006–0.31	
Dichlobenil	0–10–1.7	0.01–401–4.7	–	
Dichlorprop	0–10–1.5	–	–	
Mecoprop-P	0.4–04–0.8	–	–	
Myclobutanil	1.1–81–8.7	–	0.04–304–3.09	
Oxadiazon	0–850–85.8	0.01–7501–75	–	
Trifluralin	0.7–17–1.6	0.01–4101–41	0.06–006–0.22	< LQ – 0.2

air but at very low concentrations which do not permit their quantification.

However, some pesticides whose application is now forbidden in France have been detected. This is the case for dichlorprop, trifluralin and dichlobenil where the use was restricted to December 2003, December 2008 and March 2010 respectively. The detection of dichlobenil and trifluralin in air can be explained by their potential persistence or by transport from area where their uses are allowed. For dichloprop, the peak observed in the chromatogram could correspond to dichlorprop-p. Indeed, diclorprop was replaced by its R-isomer as an active substance authorised for application. The analytical method developed use a racemic mixture of dichlorprop where isomers cannot be separated. Then, the detection of this herbicide in atmospheric samples could be the diclorpprop-p and in this case, the quantification was not correct as calibration was done the racemic mixture. Then, data for dichlorprop can be considered as qualitative.

4. Conclusions

An analytical method coupling ASE extraction, SPME preconcentration and GC–MS analysis was developed for the quantification of some pesticides in atmospheric samples. The method permits the quantification of pesticides in the aerosol and gaseous phase with accuracy and sensitivity. Among the pesticides analysed most of them required a derivatisation step before GC–MS analysis. This step was added after SPME extraction by on-injector derivatisation. Other pesticides were not influenced by the derivatising agent used (M*t*BSTFA).

This method permits to decrease detection limits in comparison to classic liquid injection after extraction and also to decrease the matrix effect in particular for filter samples. Resin samples presents a more important background but SPME preconcentration permits the quantification of pesticides which cannot be detected in liquid injection.

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