Pyrethroid pesticide metabolite, 3-PBA, in soils: method development and application to real agricultural soils

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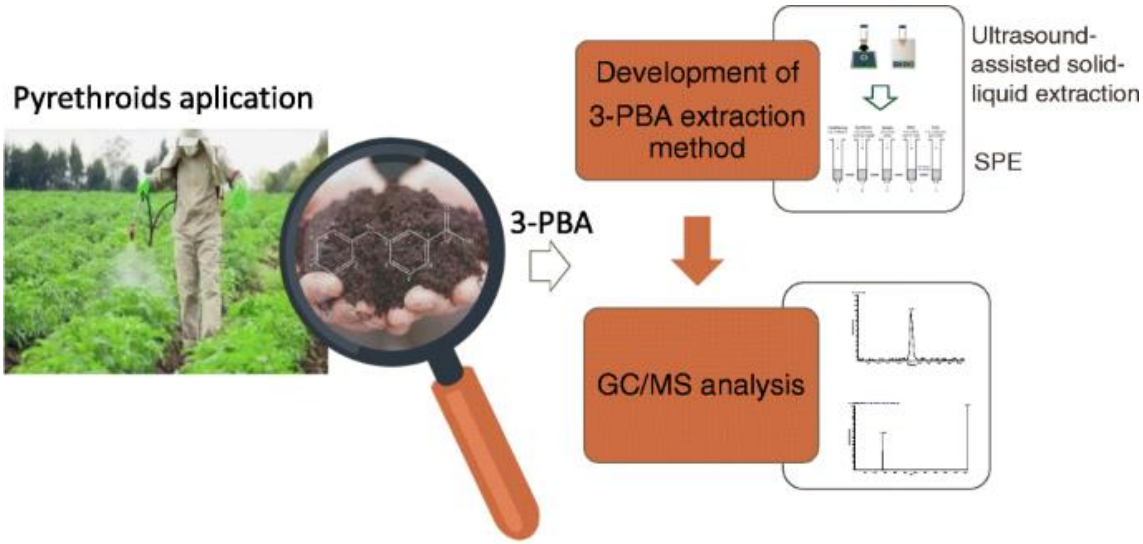
Abstract

3-Phenoxybenzoic acid (3-PBA) is a shared metabolite of several synthetic pyrethroid pesticides (SPs) resulting from environmental degradation of parent compounds and thus occurs frequently as a residue in samples. Hence, the importance of 3-PBA evaluation after pyrethroid application. There is a gap of analytical methods to determine 3-PBA in soil samples. Therefore, an analytical method that combines the solid-phase extraction (SPE) and gas chromatography–mass spectrometry (GC/MS) detection has been developed for the determination of 3-PBA in soil samples. The analytical method was validated in terms of linearity, sensitivity, intra- and inter-day batch precisions, recoveries, and quantification limits. An SPE method using a Strata X cartridge allows obtaining limits of detection and quantification equal to 4.0 and 13.3 ng g^{-1}, respectively. Under optimized conditions, the method average recovery levels ranged from 70.3 to 93.5% with a relative standard deviation below 3.4%. Method intra- and inter-day precision was under 5.0 and 4.8%, respectively. The developed method was applied to 11 agricultural soil samples in the north of Portugal. The developed methodology allowed for the determination of the pyrethroid metabolite, 3-PBA, in agricultural soil samples at levels of few ng g^{-1}.



Introduction

Synthetic pyrethroids (SPs) are a class of pesticides commonly used around the world as insecticides. These pesticides are derived from pyrethrins, which are natural insecticides produced by certain species of chrysanthemum flowers (Palmquist et al. 2012). Pyrethroids vary from many other pesticides as they have extreme hydrophobicity, rich stereochemistry (contain one to three chiral centers), and broad-spectrum high-level insecticidal activity. These pyrethroids represent a significant enhancement when compared to other insecticide classes as a result of their low non-target toxicity and high selectivity to target species (Luo and Zhang 2011). There are several registered pyrethroids molecules that are used in a myriad of products for agriculture, veterinary, domestic, and medical applications (Burns and Pastoor 2018).

A review that summarizes the available studies (between 1986 and 2017) focused on pyrethroid residues in different media at the global scale indicated that pyrethroids have been widely detected in a range of environmental compartments (including soils (Fernandez-Alvarez et al. 2008) (Regueiro et al. 2007; Yao et al. 2010), water (Kumari et al. 2008; Li and Chen 2013), sediments (Amweg et al. 2006; Feo et al. 2010), and indoors (Leng et al. 2005; Yoshida 2009)) and in organisms (Corcellas et al. 2015; Kittusamy et al. 2014). In this review, the presence of pyrethroid metabolites was only reported for biological samples including human urine and other excretions (Tang et al. 2018).

3-Phenoxybenzoic acid (3-PBA) is a metabolite of several synthetic pyrethroid pesticides and occurs by degradation of parent compounds. 3-PBA has a pka of 3.92, is water soluble (24.7 mg L^{-1}), and its octanol-water partition coefficient (Log P) is 3.91 (Pesticide Properties DataBase n.d.). 3-PBA is not a specific biomarker of exposure to a particular pyrethroid, because it results from environmental degradation and it is a shared metabolite of a number of commonly used pyrethroid pesticides (Aylward et al. 2018), as can be seen in Fig. 1 (Chen et al. 2011a; Kaneko 2010; Liang et al. 2005; Maloney et al. 1988; Tallur et al. 2008). Research on the toxic effects of SPs metabolites is still limited; however, they could induce multiple toxic responses like parent compounds, and their toxicity should be considered for improving the understanding of environmental risks of SPs (Xu et al. 2018). A review study, regarding data from 15 published articles from observational exposure of children to pyrethroids, reported 3-PBA as the most frequently detected pyrethroids exposure biomarker (Morgan 2012). This metabolite has shown stronger reproductive toxicity, weaker hydrophobicity, and a longer half-life than the parent compounds. Consequently, this metabolite is more likely to accumulate in the environment, causing secondary pollution of agricultural products (Meyer et al. 2013; Vidal et al. 2009; White et al. 1996). There is an ongoing interest in the potential associations of 3-PBA exposure in individuals as an effective way to ensure the safety of food, the living environment, and occupational exposure levels (Ueyama et al. 2010). The 3-PBA is persistent and refractory to degradation in natural environment with half-life in soil reported to range from 120 to 180 days (Chen et al. 2011b; Halden et al. 1999). Additionally, 3-PBA can enter the aqueous phase, but it tends to be absorbed to the soil/sediment (Chen et al. 2012). The importance of developing a method for pyrethroid metabolite determination in soils is not only related to their accumulation in soils or organisms but also with the constant application of pyrethroid insecticides (Ortiz-Hernández et al. 2013) and the rule of this metabolite as pyrethroids contamination indicator.

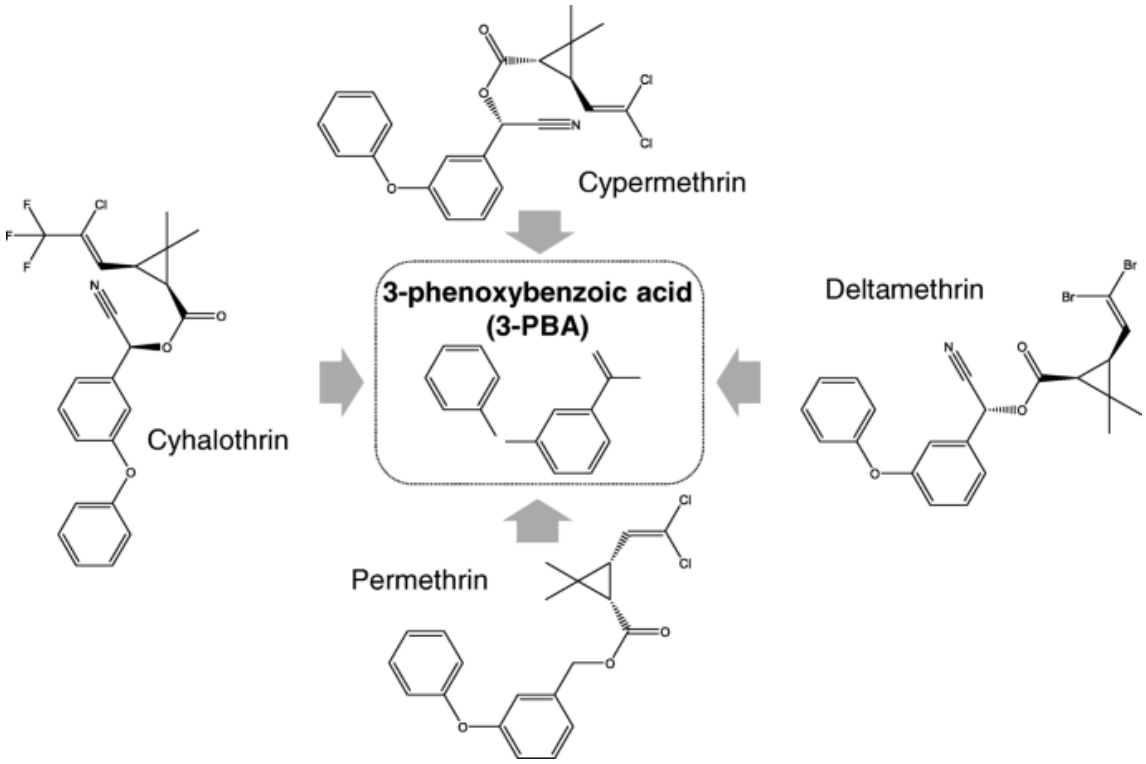


Fig. 1 The structures of some pyrethroids (cyhalothrin, cypermethrin, deltamethrin, and permethrin) and the mutual and major metabolite, 3-phenoxybenzoic acid

Currently, several analytical methods are described in the literature for the quantification of 3-PBA; however, these reports are focused on 3-PBA presence in urine samples (Fedeli et al. 2017; Jain 2016; Schettgen et al. 2016; Ye et al. 2017). Enzyme-linked immunosorbent assay (ELISA) methods can be employed for the determination of 3-PBA in urine (Ahn et al. 2011; Chuang et al. 2011; Matveeva et al. 2001; Shan et al. 2004). Within the analytical methods used, there are two mainly extraction methods applied, i.e., liquid-liquid extraction and solid-phase extraction (SPE). For this purpose, SPE is the most widely used preconcentration procedure since it is used not only to extract traces of organic compounds from environmental samples but can also remove interfering components from the matrix (Domingues et al. 2016; Rodriguez-Mozaz et al. 2007). Although SPE has a higher cost and more washing steps, this method is better than LLE in terms of higher selectivity, easier handling, and hazardous solvent reduction. QuEChERS (Quick Easy Cheap Effective Rugged and Safe) is also a reported technique for pesticide extraction as it has some advantages comparing with traditional extraction techniques such as simplicity, low cost, low solvent, and high efficiency (Vera et al. 2013). Additionally, detection methods such as liquid chromatography-tandem mass

spectrometry (LC-MS/MS) or gas chromatography/mass spectrometry (GC/MS) were the most described (Arrebola et al. 1999; Columé et al. 2001; Ueyama et al. 2010). Derivatization procedure is necessary prior to GC/MS pyrethroid metabolite detection.

There is a gap of analytical methods to determine 3-PBA in soil samples. Therefore, the aim of this work was to develop a sensitive analytical method to determine 3-PBA in soils and apply it to real samples. Preliminary studies were done testing two solid-phase extraction methods: acetonitrile (ACN) solid-liquid extraction and QuEChERS method. The developed analytical method combines an aqueous solid-liquid extraction with the SPE procedure by using a Strata X cartridge and GC/MS detection. This procedure was successfully applied to 11 agricultural soil samples in the north of Portugal, and to the best of our knowledge, it was the first time that the pyrethroid metabolite, 3-PBA, was analyzed in agricultural soil samples at levels of few ng g^{-1}. This methodology has the potential to simplify unbiased monitoring of 3-PBA in soil samples and to access contamination outcomes.

Materials and methods

Reagents, solvents, and materials

3-Phenoxybenzoic acid (98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade solvents, such as n-hexane, ACN, methanol, and ethyl acetate, were purchased from Merck (Darmstadt, Germany). HPLC-grade formic acid (99%) and ammonium acetate (> 98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA).

The derivatization reagents 1,1,1,3,3,3-hexafluoro-2-propanol (HIPF, ≥ 99.8%) and N,N′-diisopropylcarbodiimide (DIC, 99%) were from Sigma-Aldrich (St. Louis, MO, USA). The QuEChERS and the dispersive solid-phase extraction (dSPE) clean-up were supplied by Agilent technologies (Bond Elut Sample preparation solutions) (Lake Forest, CA, USA). QuEChERS is a buffer-salt mixture consisting of 4 g of magnesium sulfate anhydrous grit, 1 g of sodium chloride, 0.5 g sodium hydrogenocitrate sesquihydrate, and 1 g of sodium citrate. The dSPE was composed by 150 mg magnesium sulfate, 150 mg primary secondary amine (PSA), and 50 mg C18. Ultra-pure water was prepared using a Milli-Q water purification system (Millipore, Billerica, MA, USA). SPE columns containing different sorbents were purchased from Phenomenex (Torrance, CA, USA)

(Table 1). The stock standard solution of 3-PBA (at a concentration of 242 mg L^{-1}) was prepared on a weight basis by dissolving the standard compound in ACN and was stored in a refrigerator at 4 °C.

Table 1 Comparison of the SPE cartridges based on composition, packing (sorbent amount/cartridge volume), particle and pore size, and application

Cartridge	Composition	Sorbent amount/cartridge volume	Particle size (μm)	Pore size (Å)	Application
Strata-C18-E	Octadecyl-modified silica	200 mg/6 mL	55	70	Nonpolar compounds
Strata-X	PS-DVB-VP	200 mg/3 mL	33	85	Acidic, basic, and neutral compounds
Strata-X-A	PS-DVB-modified with amine groups	30 mg/3 mL	33	85	Acids
Strata-X-C	PS-DVB-modified with sulfonic groups	200 mg/3 mL	33	85	Bases

Soil sampling and characterization

The sampling sites were located in the north of Portugal in the regional delegation of agriculture of Cávado-Vouga. Eleven different agricultural soil samples were collected during July 2016, represented in Fig. 2. At each sampling site, the upper layer (0–10 cm) was collected with a spade. Soils were sieved to a grain size of 2 mm to obtain a homogeneous sample, before being extracted and analyzed, and were stored at − 18 °C until analysis. Macro parameters, such as water content, total organic carbon content (TOC), and pH, were evaluated (Hesse 1972; Nelson 1996). For the determination of TOC in soils, a Shimadzu TOC analyzer (model VCSN, Shimadzu, Japan) with a solid sample module (SSM-5000A) was used. Water content was determined using a moisture analyzer (Kern MLS 50-3IR160, Germany). For measuring the pH, a mixture (suspension) of soil and water (1:1) was read with an electronic pH meter (Crison 2002, Spain). Triplicate of all the determinations was made.

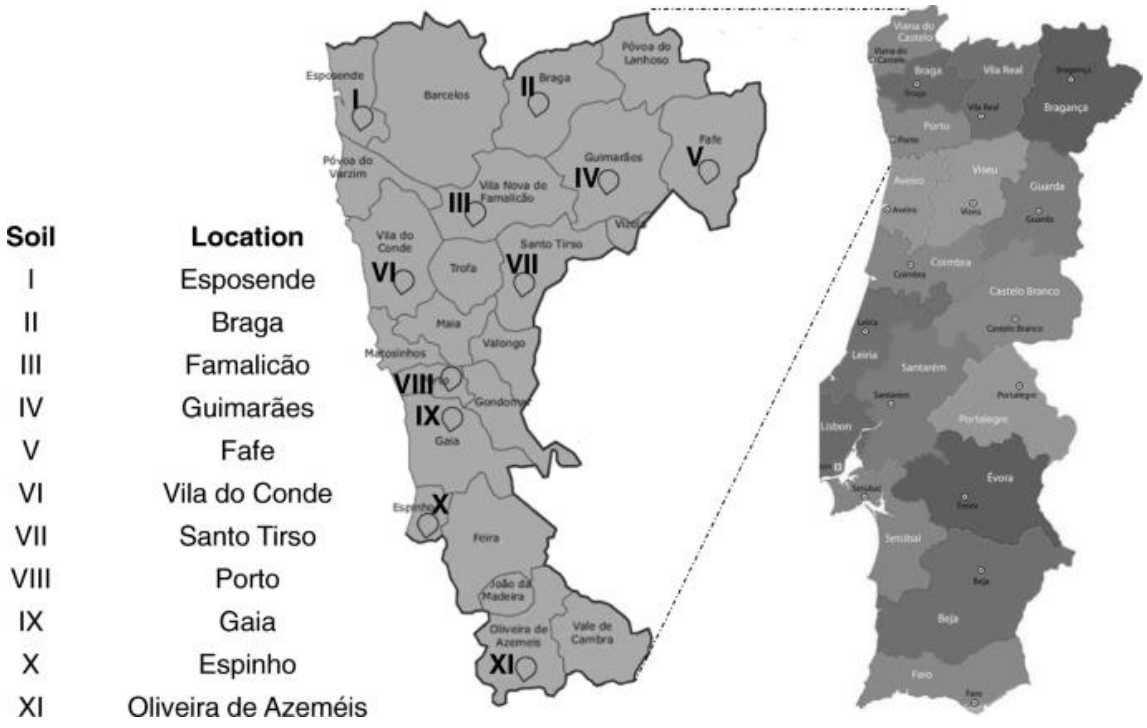


Fig. 2 Geographical location of the soil samples

Sample preparation

Several procedures of sample preparation were tested to evaluate 3-PBA and all the tests were spiked with an intermediate 3-PBA standard solution of 20,000 μg L^{-1} in ACN. The spiking amounts added were calculated to have in the final extract a 100 μg L^{-1} of 3-PBA concentration, and the spiking solvent was evaporated with a gentle stream of nitrogen.

QuEChERS method

Soil samples, spiked with 3-PBA, were extracted using a QuEChERS method adapted from Yang et al. (2010). The amounts of this method were reduced to half, which was described as follows: each sample (5 g) was weighed into a 50-mL centrifuge tube, then 10 mL of ACN was added to the tube. After capping, the tube was vortexed shaken vigorously for 1 min, and after that, the tubes were placed for 10 min in an ultrasonic bath. A QuEChERS buffer-salt mixture was added to the suspension derived from the first extraction to induce phase separation and pesticide partitioning. The closed tube was shaken vigorously by vortex for 1 min; then, the tubes were sonicated for 10 min in an ultrasonic bath and were centrifuged for 5 min at 4500 rpm. The ultrasonic bath was used as a homogenization technique as it was described before to improve the obtained results, as soil is a complex and heterogeneous matrix (Braganca et al. 2012; Vera et al. 2013).

After centrifugation, the extracts were subjected to a clean-up step. So, an aliquot of 1.5 mL was sampled from the upper layer and transferred into a 2-mL dSPE clean-up tube and vortexed for 1 min and then centrifuged for 5 min at 8000 rpm. An aliquot of 0.5 mL from the upper layer was transferred into a vial and evaporated to dryness with a gentle stream of nitrogen. These dry residues were then subjected to derivatization process.

Optimization of an extraction process combining aqueous solid-liquid extraction followed by SPE

To select the most appropriate SPE extraction process, 15 mL of 3-PBA water solution was processed via solid-phase extraction using four different copolymer sorbents in Phenomenex^{R} cartridge format: Strata-C18-E, Strata™-X-A, Strata™-X-C, and Strata™-X. Table 1 presents a summary of the characteristics of each SPE cartridge. Methods adapted from those suggested by SPE cartridge suppliers (Table 2) were used to evaluate the cartridge performance to 3-PBA extraction.

Table 2 Solid-phase extraction procedures tested for the different cartridges

Procedure	Cartridge	Conditioning	Equilibrate	Load	Wash	Dry	Elute
I	Strata-C18-E	Methanol	Water	3-PBA in water	30% methanol in water		5% methanol in ethyl acetate
II	Strata-X	ACN	Water		30% methanol in water		acetonitrile
III		Methanol	Water		30% methanol in water		2% formic acid in methanol
IV	Strata-X-A	ACN	Water		Ammonium acetate 100 mM	1 h	5% formic acid in methanol
					Methanol	(full vacuum)	
V		Methanol	Water		Ammonium acetate 100 mM		5% formic acid in ACN
					Methanol		
VI	Strata-X-C	Ethyl acetate	Water	3-PBA in water	HCl 0.1 N		5% methanol in ethyl acetate
		Methanol	HCl 0.1 N	(pH adjusted to 2.5)	NH_4OH		

For aqueous soil extraction, a 10 g of soil sample was added to a 50-mL Teflon centrifuge tube, and extraction with 30 mL of different aqueous solvents (water or the buffer ammonium acetate 100 mM) was evaluated. The mixture was vortexed for 1 min, ultrasonicated for 10 min in a 195 W ultrasonic bath from J.P. Selecta (Spain) at room temperature, and centrifuged at 4500 rpm for 5 min. Then, 15 mL of the upper layer of the soil extract was passed through SPE cartridges.

For the SPE cartridge that allowed for the best recoveries, a study was performed by optimizing different ratios (1:6, 1:3, and 1:2) of mass of soil sample (g) per volume (mL) of extraction solvent, using 5, 10, and 15 g of soil for 30 mL of extraction solvent. The SPE was preconditioned with 5 mL of methanol and 5 mL of water, for obtaining the best conditions in extraction of the analyte from the soil sample. The precondition step of

equilibration of the cartridge described in Table 2 was also done with ammonium acetate instead of water, followed by methanol conditioning. The cartridge was washed with 5 mL of mixed solvent (methanol/water, 30/50, *v*/*v*) and finally eluted by 5 mL of 2% formic acid in methanol. An aliquot of 0.5 mL was taken and dried in a gentle stream of nitrogen. This dry residue was then subjected to the derivatization process.

Derivatization

Derivatization procedure was necessary prior to gas GC/MS analysis. 3-PBA derivatization of the dry residues from the extraction methods tested above was performed by the addition of 30 μL HFIP and 20 μL of DIC to the previously described dry residues prevenient from the extraction procedures and slightly shaken (vortex, 1600 rpm) for 10 min, at room temperature. In the final phase of the procedure, a liquid-liquid extraction (LLE) was performed with 1 mL of a 5% aqueous potassium carbonate solution (to neutralize the excess derivatizing agent) and 500 μL of n-hexane in the vial with 5 min vortex (1600 rpm) shake. An aliquot of the organic layer (200 μL) was transferred to the autosampler vials for GC/MS analysis.

Gas chromatography analysis

A volume of 1 μL was injected onto a Thermo Trace-Ultra gas chromatograph, coupled to an ion trap mass detector Thermo Polaris, operated in the electron impact ionization at 70 eV. The ion source temperature and the MS transfer temperature were at 250 °C. Operating in the splitless mode, the helium was used as carrier gas at a constant flow rate of 1.3 mL min^{-1}. The injector was maintained at 240 °C. The column, a 30 m ZB-5MSi (0.25 mm i.d., 0.25 μm film thickness Zebron-Phenomenex), oven temperature was programmed as follows: initial temperature 40 °C (held for 1 min), increased by 15 °C/min to 160 °C (held for 0.5 min), increased by 15 °C/min to 180 °C (held for 1 min), and finally increased by 20 °C/min to 250 °C. A program was developed in the SIM mode, based on the detection of selected ions for 3-PBA (141, 196, and 364).

Method validation

For 3-PBA analysis, the experimental method validation was performed according to the European Union SANCO guidelines on pesticide residue analytical methods (European

2010; European 2013). The influence of the soil matrix in the GC/MS signal was evaluated by preparing a n-hexane and a match-matrix 3-PBA calibration curves. To assess the matrix effect (ME), the slope of the match matrix calibration curve was compared with the slope of the calibration curve prepared in hexane. The calibration curves and linear ranges of the detector response for 3-PBA were evaluated by analyzing the working standard solutions (15–180 μg L^{-1}, 8 concentrations) in triplicate. In this study, the LOD and LOQ were calculated as the minimum amount of analyte detectable with a signal-to-noise ratio (S/N) of 3 and 10, respectively. The linearity of the method was established by setting calibration curves using linear regression analysis over the concentration range. Selectivity was verified by comparing the chromatograms of the standards dissolved in n-hexane, the standards extracted from the spiked soil and the matrix blanks (non-spiked soil). The accuracy of the analytical optimized method was evaluated through recovery studies at three concentration fortification levels (low: 90, medium: 600, and high: 1080 ng g^{-1}), using three replicates. The intraday precision and the inter-day precision of the method were evaluated at 600 ng g^{-1}, the intermediate concentration of the spiking level. The intraday precision of the assay was estimated by calculating the relative standard deviation (RSD) for the analysis of soil samples in six replicates on 1 day ($n = 6$). Inter-day precision was determined by the analysis of three replicates of soil samples on three consecutive days ($n = 9$).

Results and discussion

QuEChERS extraction

The extraction of 3-PBA with ACN ultrasound-assisted solid-liquid extraction even with QuEChERS extraction procedure showed to be inefficient, as the results obtained were below the n-hexane calibration curve limit of detection (LOD = 0.69 μg/L). It was found that the extraction with acetonitrile for this compound is not a good choice as it was not even possible to calculate recoveries. Therefore, considering the solubility of 3-PBA, an aqueous ultrasound-assisted solid-liquid extraction followed by SPE proved to be a promising 3-PBA extraction technique.

Aqueous solid-liquid extraction followed by SPE

Selection of SPE cartridge and method

Previous assays were performed using aqueous solutions of 3-PBA to optimize the SPE extraction step. A total of four different SPE cartridges were tested for a concentration of 100 μg L^{-1} of 3-PBA prepared in water. For SPE, the protocols were adapted from the Phenomenex^{R}-recommended protocols. The recovery results (%) are shown in Fig. 3 for triplicate replicates.

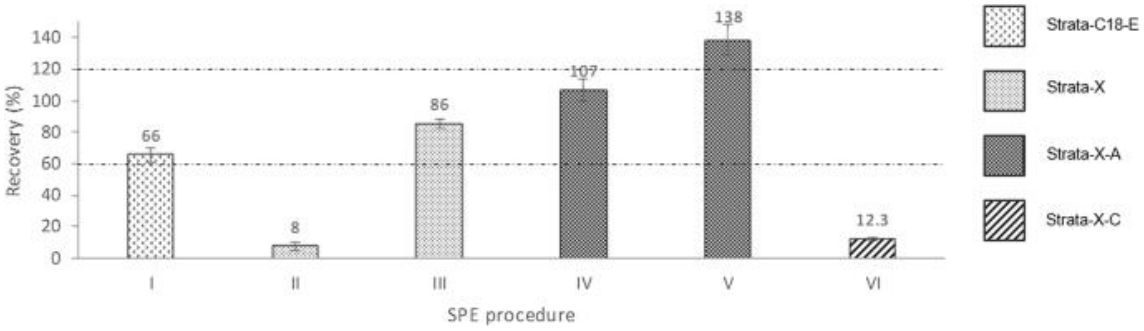


Fig. 3 Recoveries of 3-PBA extraction in water using different SPE cartridge. I to VI are the different solid-phase extraction procedures tested for the different cartridges
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By analyzing the recoveries of the various SPE columns, it is possible to verify that those that are within the limits recommended for pesticide residue analysis in the range of 70 to 120% with RSD ≤ 20 (Albaiges 2016) are the procedure III with Strata X cartridge and the procedure IV with Strata X-A cartridge (see Table 2). These results are in accordance with the properties of 3-PBA (acid compound, pka of 3.92). Thus, these cartridges/procedures were chosen to optimize 3-PBA SPE extraction for the soil samples.

Optimization of soil extraction

Comparing the recoveries of the same amount of 3-PBA adding in soil and adding in water, lower results in soils were obtained. Because, probably, the 3-PBA extraction from soil was not efficient, so, an optimization of the soil extraction procedure was required. The effect of using the buffer, ammonium acetate 100 mM as extraction solvent instead of water was evaluated for both cartridges (Fig. 4a) and the best recovery was found for the cartridge Strata X with ammonium acetate as the soil extraction solvent (49.2 ± 4.3%). The influence of the amount of soil (Fig. 4b) was also tested (5, 10, and 15 g soil).

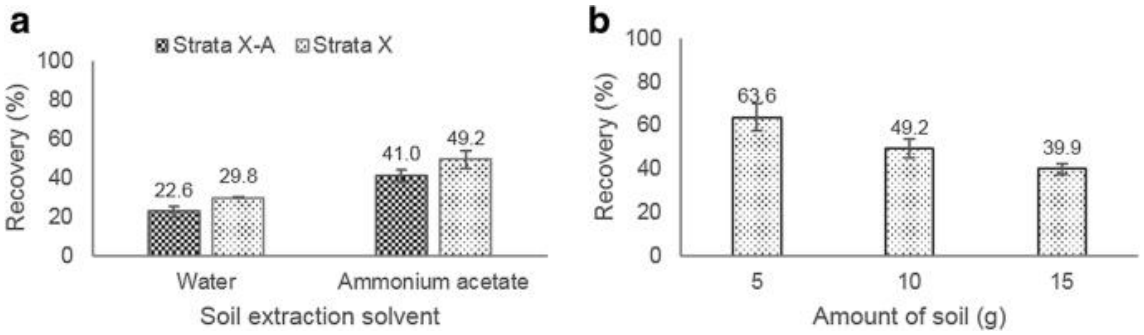

Fig. 4 Optimization of soil extraction by changing **a** extraction solvents and **b** ratio of mass of sample per volume of solvent

The recovery values range between 39.9% for 15 g and 63.6% for 5 g of soil. It is notorious that the last one (5 g) allows better results. To improve the SPE process after the conditioning step with methanol, the cartridge was equilibrated with the same solution used in soil extraction, i.e., ammonium acetate 100 mM. This change in SPE equilibration step allowed an improvement in the recovery from $63.6 \pm 2.6\%$ when using water to a value of $72.2 \pm 1.1\%$ when the ammonium solution was used. As ammonium acetate is used as the extraction solvent, it is also the best solvent to be used to equilibrate the SPE cartridge, as was proved by the enhancement of 3-PBA recoveries. The optimized process is shown in Fig. 5.

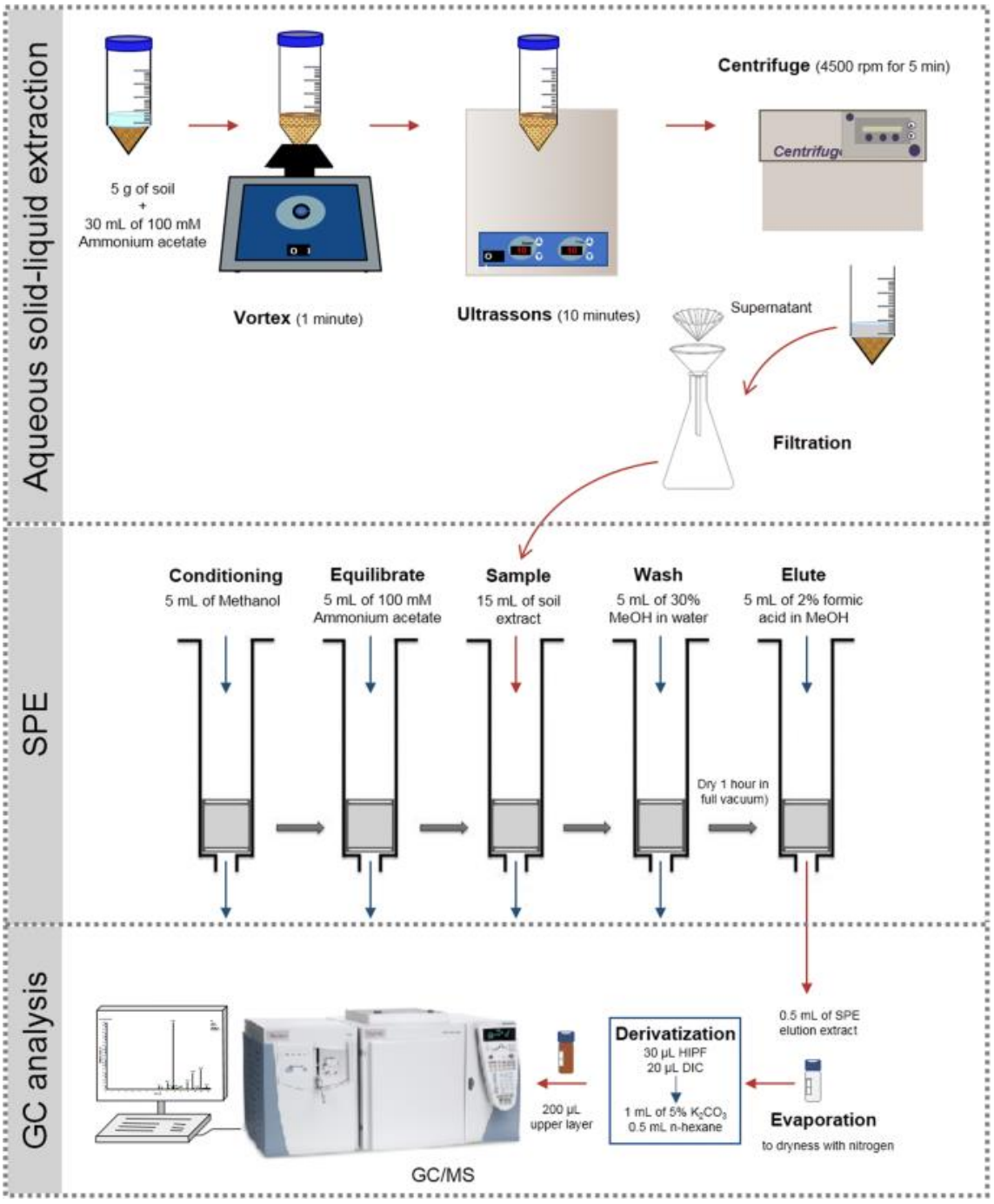

Fig. 5 Scheme of the optimized procedure for 3-PBA determination in soil

Method performance

A complete method validation comprising linearity, selectivity, sensitivity, accuracy, precision, and ruggedness was performed. In addition, matrix effect was studied. An organic agricultural soil with 3.70% of TOC content and a pH of 6.91 was used for method validation. At 3-PBA retention time (11.9 min), no interferences from endogenous substances were detected. Consequently, a good separation was obtained

under the described GC/MS conditions. A chromatogram of a soil sample spiked with 600 ng g^{-1} of 3-PBA is depicted in Fig. 6.

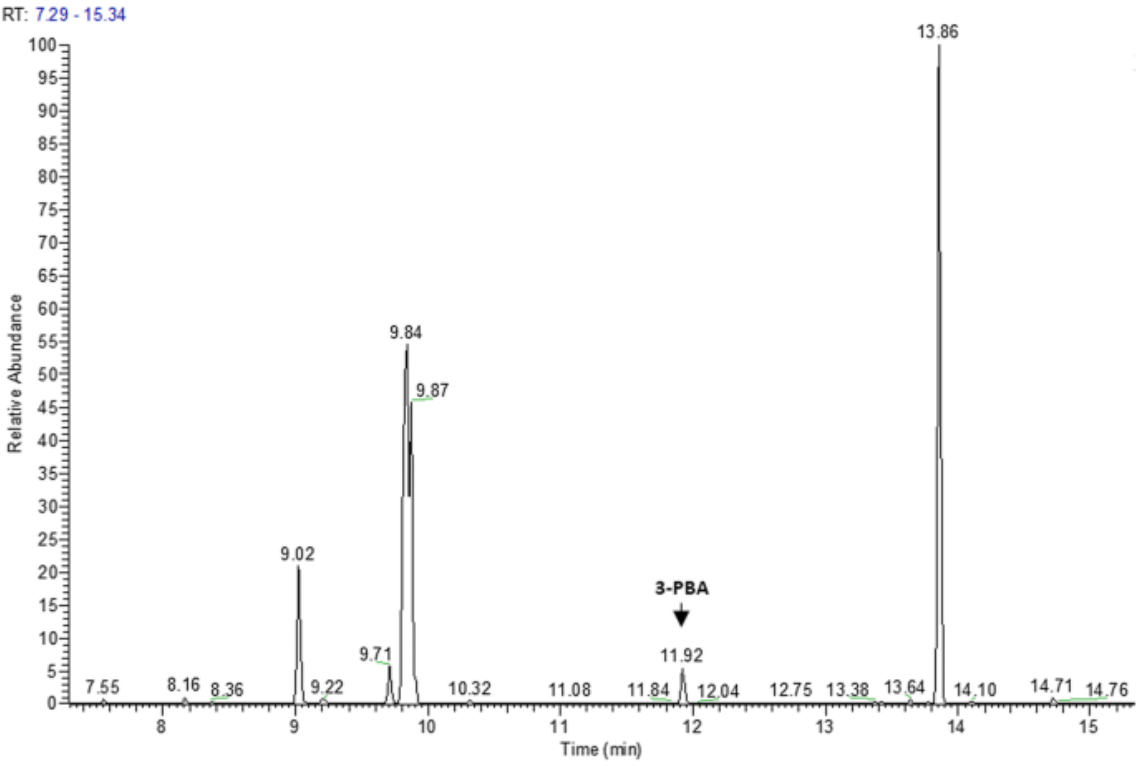

Fig. 6 Gas chromatography/mass spectrometry under selected ion mode chromatogram of 3-PBA at a spiking level of 600 ng g^{-1} in the soil sample

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The ME (%) was obtained from the ratio of linear relationships from the slopes in reagent-only and in match-matrix calibrations and is equal to 91.0% (< 100% ionization suppression) which represents a low ionization suppression (less than 10%). Therefore, for soil samples, match matrix calibration curve was necessary for this method to improve its accuracy. A good linear relationship was obtained between the response and their corresponding concentrations (90–1080 ng g^{-1}) with an $R^2 = 0.9989$. The obtained LOD and LOQ were of 4.0 and 13.3 ng g^{-1}, respectively.

Validation of both accuracy and precision of the optimized method were obtained for three spiking levels (90, 600, and 1080 ng g^{-1}, $n = 3$ for each spiking level) and the results are shown in Fig. 7. Overall, the recoveries ranged from 70.3 to 93.5% and RSDs ranged from 1.1 to 3.4%. The precision of the method was assessed in terms of repeatability

(intraday) and reproducibility (inter-day) for 3-PBA at the medium spiking level concentration (600 ng g^{-1}) and the results were equal to 5.0% and 4.8%, respectively.

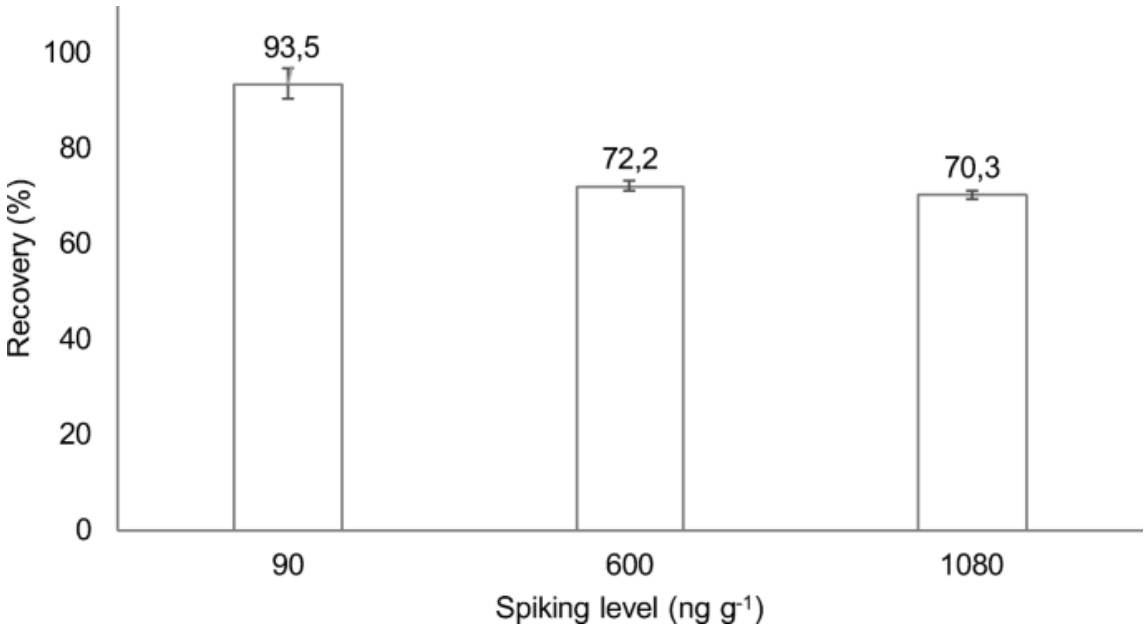

Fig 7 -Recoveries obtained with extraction at three spiking level concentrations (90, 600, and 1080 ng g^{-1}) ($n = 3$)

The results showed that the proposed method could be used for effective monitoring of 3-PBA in soil samples.

Application to real samples

The developed and optimized method was applied for the determination of 3-PBA in 11 different agricultural soils. The samples were collected in July 2016. The pH values were similar for all soils and are registered on the Table 3. The determination of TOC was an important part of soil characterization since its presence or absence could influence how chemicals would react in the soil (Correia-Sa et al. 2012). The contents of TOC in agricultural soils range between 1.24 and 5.91%. Only one soil was found to be positive for 3-PBA contamination in real samples, corresponding to soil IV with 23.2 ± 1.7 ng g^{-1}. To confirm this result, more extractions of this soil were done and concentrated 5 times; the final extract was quantified in the linear range of the matrix calibration curve obtaining the same results. As far as the authors know, no references were found reporting the presence of 3-PBA in soil samples.

Table 3 Soil sample characterization mean values with standard deviation (SD)

Soil	pH	Water content (%)	Total organic carbon (%)
I	5.65 (0.09)	14.93 (0.21)	2.79 (0.05)
II	5.51 (0.02)	16.78 (0.09)	2.30 (0.26)
III	5.39 (0.07)	19.33 (0.16)	3.80 (0.08)
IV	7.03 (0.11)	9.46 (0.37)	1.24 (0.06)
V	5.42 (0.07)	17.76 (0.60)	2.36 (0.04)
VI	6.97 (0.05)	21.96 (2.28)	5.70 (0.08)
VII	6.91 (0.00)	9.04 (0.01)	3.45 (0.51)
VIII	6.64 (0.14)	19.00 (0.65)	5.91 (0.55)
IX	4.52 (0.05)	17.22 (0.20)	1.82 (0.13)
X	6.96 (0.04)	2.77 (0.08)	3.20 (0.11)
XI	6.59 (0.03)	17.73 (0.03)	2.25 (0.27)

This metabolite is most frequently detected pyrethroid biomarker (> 67%) as it can enter the human body in various ways (food, the residential environment, soil, and various environmental media containing pyrethroids (Tang et al. 2018). Few reports were found worldwide regarding the presence of the parent compounds (pyrethroid pesticides) in soils due to affinity to organic carbon (Domingues et al. 2007). Most reports were found on the Asian continent, mostly from China followed closely by India. These results could be explained by the high usage pattern of insecticides in China, which has resulted in serious pesticide pollution. The highest concentration found was in Chongqing cropland (906.05 ng g^{-1}) (Tang et al. 2018). In Europe, a study in Spain using a developed headspace solid-phase microextraction detected several pyrethroid pesticides, at concentrations below the generic reference levels established by Spanish legislation in soils (Fernandez-Alvarez et al. 2008). 3-PBA, the pyrethroid metabolite, was previously only detected in human body residues worldwide (Tang et al. 2018). Nothing was found regarding its presence in soil environmental samples nor even methods to determine the metabolites of pyrethroid pesticides in soils.

Conclusions

A new, simple, rapid, and robust analytical method for the determination of pyrethroid metabolite, 3-PBA, in soils was developed based on aqueous solid-liquid extraction with the buffer, ammonium acetate followed by SPE procedure and GC/MS detection. The detection and quantification limits in the low ng g^{-1} range (4.0 and 13.3 ng g^{-1}, respectively) were achieved. The method average recovery levels ranged from 70.3 to

93.5% with a relative standard deviation below 3.4%. Intra- and inter-day precision was under 5.0 and 4.8%, respectively. Good validation parameters such as accuracy, precision, and linearity proved suitability for purpose of the developed method.

The developed method was successfully applied to the analysis of 11 agricultural soils, showing the occurrence of 3-PBA, at levels up to few ng g^{-1} of soil (~ 23 ng g^{-1}). The presence of pyrethroid major metabolite in agricultural soils points out the relevance of extending monitoring programs to the analysis of these compound as well as the parent compounds.

References

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Additional information

Highlights

• An analytical method that combines an aqueous solid-liquid extraction, the SPE procedure, and GC/MS detection has been introduced for determination of 3-PBA in soil samples for the first time

• An SPE method at ng g^{-1} level has been validated for the detection of 3-PBA in soil

• Recoveries at the three fortification levels ranged from 70.3 to 93.5%

• The pyrethroid metabolite, 3-PBA, was detected in agricultural soil sample at levels of few nanograms per gram.

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