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Multiresidue analysis of aromatic organochlorines in soil by gas chromatography-mass spectrometry and QuEChERS extraction based on water/dichloromethane partitioning. Comparison with accelerated solvent extraction

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ABSTRACT

A novel multiresidue method was developed for the simultaneous analysis of 34 organochlorines, including chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins, in soil by GC-MS, using a QuEChERS-based extraction. The conventional QuEChERS method was optimised and, for the first time, the use of a non miscible-water solvent was required. The method was compared to ASE extraction, versatile technique widely used for the soils' extraction and QuEChERS-based method was shown to be the most efficient in terms of recoveries, simplicity and rapidity. For ASE, recoveries between 42% and 85% were obtained for the majority of the compounds. However, due to the high pressure, all volatile compounds were lost. In opposite, QuEChERS extraction allowed detection and quantification of all the compounds with recoveries between 60% and 100%. Moreover, no additional clean up by dispersive SPE on PSA was necessary, which allowed reducing the cost of the analysis.

Performance of the method was assessed. The method was linear over the range of concentration of 10–5000 $\mu g\,kg^{-1}$. Precision, expressed as intra-day precision and inter-day variation was verified at three concentrations. Limits of detection were from 2 to 50 $\mu g\,kg^{-1}$ and limits of quantification from 7 to 170 $\mu g\,kg^{-1}$ for the majority of the compounds (chlorobenzenes and chlorinated hydrocarbons and olefins), except for chlorophenols. The method was further applied to different soils coming from a contaminated industrial site, where a new environmental remediation process, using phytoremediation, was tested. The results showed that the method could be applied to any kind of soils (mineral or organic) and was appropriate to very volatile compounds which were not available with conventional technique.

1. Introduction

Environment pollution, including water and soil pollution, has drawn public and government attention over the last few decades. Indeed, presence and migration of pollutants – mainly persistent, bioaccumulable and toxic contaminants – in the environment may cause human toxicity if they encounter the food chain.

In this context, several decontamination treatments have been developed like adsorption on charcoal for water [1,2] or excavation followed by incineration for soils [3,4]. Nevertheless, these treatments are expensive and difficult to implement.

Thus, alternative methods, based on phytoremediation, have been developed. Phytoremediation is a green technology that uses plants to remediate soils, surface waters or groundwaters from organic or inorganic contaminants [5]. It has been widely applied to remove a wide range of compounds, including petroleum [6], PCB [7], chlorinated solvents [8] or heavy metal [9] from soils. Phytoremediation has also been successfully used for the remediation of phenols [10], pesticide [11] or metals polluted waters [12] but fewer studies are available.

Recently, phytoremediation has been applied to decontaminate groundwater passing under an industrial site polluted by organochlorines, including chlorobenzenes, chlorophenols, chlorinated hydrocarbons and chlorinated olefins. The phytoremediation process was carried out by spreading contaminated groundwater on pilots full of peat and where aquatic plants are growing.

In this context, the aim of this work is to develop a multiresidue method to extract and analyse simultaneously organochlorines belonging to 4 different classes from peat soils. This method should

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enable the quantification of the organochlorines available in pilots' soils and the evaluation of the process efficiency (combination between the amount detected in the soils, the plants, the air and in the groundwater upstream and downstream from the pilot).

Several extraction methods of organochlorines from soils have been reported in the literature since 1990s. However, most of the related work concerns organochlorine pesticides and only few studies deal with chlorobenzenes and multiresidue methods.

The main implemented extraction methods are solvent extraction [13], soxhlet extraction [13,14], ultrasonic solvent extraction [15], microwave-assisted solvent extraction (MASE) [14,16], accelerated solvent extraction (ASE) [14,17–19] and supercritical fluid extraction (SFE) [13,20]. MASE offers higher recoveries than soxhlet extraction and ultrasonic solvent extraction. However, to absorb microwaves, MASE requires polar solvents which tend to co-extract matrix interferences [16]. Also, SFE is more efficient than solvent extraction, particularly for apolar components in soils with high organic carbon contents, like peat. Furthermore, SFE makes clean extracts and, contrary to soxhlet extraction, no additional clean-up is required [13]. ASE offers numerous advantages: it is a quite quick method which uses low amounts of solvents and allows using solvents with a wide range of polarities. Moreover, the high pressure and temperature conditions enable a better penetration of the solvent into the matrix, and therefore the breaking of the intermolecular bonds [17].

In general, all these methods are effective but they are time-consuming, solvent-consuming for some ones, or require expensive apparatus. Recently, a new method known as QuEChERS was developed by Anastassiades et al. [21] for the analysis of pesticides having a wide range of polarities in fruits and vegetables. QuEChERS method – acronym for quick, easy, cheap, effective, rugged and safe – is based on an acetonitrile extraction/partitioning with buffered salts, followed by a dispersive solid phase extraction (dSPE). Normalised in Europe in 2009 [22], this technique has been successfully used for the extraction of pesticides in several matrix (fruits and vegetables [23,24], fruit juice [25], honey [26]. . .) and was also applied to analyse veterinary drugs from milk [27] or drugs in plasma [28]. It has been recently applied to soil matrices, for the extraction of pesticides [29], organochlorine pesticides [30], phenols [31] and some organochlorines (chloroform, 1,2-dichlorobenzene and hexachlorobenzene) [32]. In this matrix, quantification of pesticides in the range of 1–100 $\mu g\,kg^{-1}$, depending on the detection mode (MS or MS–MS) was possible. Limits of quantification between 1 and 10 $\mu g\,kg^{-1}$ were obtained for the phenols and chlorophenols after derivatization [31].

In opposite to other methods, QuEChERS offers good recoveries and good sensibility, even in the cases of multiresidue methods concerning compounds with a wide range of polarities. For example, Romero-Gonzales et al. analysed 90 pesticides belonging to different families at concentration below 5 $\mu g\,kg^{-1}$ with recoveries of 70–100% [25].

In this work, we took advantage of these characteristics and developed a multiresidue QuEChERS-based method for the extraction of chlorobenzenes, chlorophenols, chlorinated hydrocarbons and olefins from soils, using gas chromatography coupled with mass spectrometry. At the same time, we developed an extraction method by ASE (chosen for its rapidity and its versatility), and compared the two methods.

2. Experimental

2.1. Reagents and standard solutions

Certified reference standards, all of >97% purity, were purchased from Sigma–Aldrich (St. Quentin Fallavier, France). Hexane and acetone, of pesticide residue grade were obtained from Fisher Scientific (Sigma–Aldrich, St. Quentin Fallavier, France) and dichloromethane, pestanal grade, from Riedel de Haën (Sigma–Aldrich, St. Quentin Fallavier, France).

Diatomaceous earth (hydromatrix) was purchased from Varian (Les Ulis, France) and anhydrous sodium sulphate 99.8% purity from Carlo Erba (Peypin, France).

QuEChERS tubes were obtained from Agilent Technologies (Massy, France).

Individual stock solutions at 5 $g\,L^{-1}$ were prepared in acetone or dichloromethane, depending on the organochlorine solubility. A working standard mixture solution at 100 $mg\,L^{-1}$ in dichloromethane of each compound was prepared for extraction optimisation.

To validate the method, working solutions at concentration of 1, 10 and 100 $mg\,L^{-1}$ of each compound were prepared in dichloromethane. These solutions were used to prepare a five-point matrix-matched calibration in the concentration range of 10–5000 $\mu g\,kg^{-1}$ (10, 100, 500, 1000, 5000 $\mu g\,kg^{-1}$).

The solutions were stored at −18 °C.

2.2. Preparation of spiked soils

Peat samples came from pilots based on an industrial French site and fed by contaminated groundwater. These pilots are carried out to study the phytoremediation process.

Collected soils were frozen at −18 °C at laboratory until analysis.

All the experiments needed to optimise extraction and validate the method were performed using uncontaminated peat (blank peat). In order to imitate the samples coming from pilots which were waterlogged, the blank peat was soaked with 18 mΩ water.

Then it was spiked with the mixture of organochlorines at the defined concentrations and set at room temperature during 24 h to promote interactions.

2.3. GC–MS analysis

GC–MS analysis were carried out using a Hewlett-Packard (HP) 5973 mass spectrometer coupled with a HP 6890 gas chromatograph and an Automatic Liquid Sampler (Agilent Technologies, Massy, France).

Separation was performed on a JW (Agilent Technologies, Massy, France) DB-VRX 60 m × 0.32 mm ID × 1.80 μm column, with helium as carrier gas at a constant flow of 2 mL min^{-1}. Oven temperature was maintained at 37 °C for 1 min, then ramped at 20 °C/min up to 50 °C (held 5 min), 10 °C/min up to 110 °C, 1.5 °C/min up to 150 °C and finally 10 °C/min up to 260 °C (held 20 min). 1 μL of sample was injected in the pulsed splitless mode (pulse pressure: 25 Psi) at 260 °C. Transfer line temperature was set at 260 °C, source at 230 °C, and quadrupole at 150 °C. Ionisation was performed in the electron impact mode at 70 eV and the quadrupole analyser operated in the SIM mode (selected ion monitoring) with 3 or 4 ions, depending on the specificity of the mass spectra of the compound. Target (T) and qualifiers (Q1, Q2, Q3) ions used for identification and quantification are presented in Table 1 according to European guideline SANCO 2007/3131. Quantification was performed on the Target ion T.

Data acquisition and reprocessing were performed using the MSD ChemStation version D.02.00.275

2.4. ASE extraction

ASE extraction was performed on an ASE 200 system (Dionex,Voisins-le-Bretonneux, France).

For extraction optimisation, a 2 g portion of blank soil was mixed with 4 g anhydrous Na_2SO_4, placed in a 34 mL stainless steel

Table 1
Organochlorine retention time and MS acquisition parameters of the GC–MS method.

Name	*RT* (min)	Ion T	Ion Q1	Ion Q2	Ion Q3
1,2-Dichloroethylene cis	8.92	61	96	98	
1,2-Dichloroethane	10.2	62	64	49	98
1,2-Dichloropropane	11.83	63	62	65	76
Trichloroethylene	11.9	130	132	95	134
Tetrachloroethylene	15.7	166	164	168	131
Chorobenzene	17.21	112	114	77	
1,1,2,2-tetrachloroethane	19.35	83	85	95	87
Cumene	20.58	105	120	77	
Phenol	22.21	94	66	39	
2-Chlorophenol	24.18	128	130	64	39
1,3-Dichlorobenzene	25.41	146	148	111	75
1,4-Dichlorobenzene	25.72	146	148	111	75
1,2-Dichlorobenzene	27.28	146	148	111	75
Hexachloroethane	29.84	117	119	201	121
1,3,5-Trichlorobenzene	34.45	180	182	145	74
2,4-Dichlorophenol	36.36	162	164	63	98
4-Chlorophenol	36.58	128	130	65	
1,2,4-Trichlorobenzene	37.71	180	182	145	74
2,6-dichlorophenol	39.16	162	164	63	98
Hexachlorobutadiene	40.13	225	190	260	227
1,2,3-Trichlorobenzene	40.53	180	182	74	145
1,2,3,5-Tetrachlorobenzene	50.31	214	107	179	
1,2,4,5-Tetrachlorobenzene	50.43	214	107	179	
2,4,6-Trichlorophenol	51.49	196	198	97	132
2,4,5-Tricholorophenol	51.82	196	198	97	132
1,2,3,4-Tetrachlorobenzene	54.22	216	214	179	108
Pentachlorobenzene	63.62	250	248	108	215
2,3,4,6-Tetrachlorophenol	64.39	232	230	131	166
Alpha HCH	68.18	183	219	217	
Hexachlorobenzene	69.00	284	286	142	249
Beta HCH	69.3	183	219	217	
Lindane	69.74	183	219	217	
Pentachlorophenol	69.75	266	268	165	95
Delta HCH	70.45	183	219	217	

T: Target ion.
Q1, Q2, Q3: Qualifier ions.

vessel and spiked with the mixture of organochlorines at 1 mg kg^{-1} of each compound. Stagnant volume of each vessel was filled with diatomaceous earth and the cell was set at room temperature during 24 h to promote interactions. Extraction was carried out with dichloromethane at 40 °C and 10 MPa with a pre-heat time of 5 min, followed by a 10 min static extraction and a 100% flush volume.

2.5. Optimisation of QuEChERS extraction

The conventional QuEChERS method using acetonitrile was compared with a modified method using dichloromethane.

For the extraction based on classic QuEChERS method, 5 g of wet peat spiked at 1 mg kg^{-1} was extracted with 15 mL of acetonitrile in presence of buffered salts (4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate dehydrate and 0.5 g di-sodium hydrogen citrate sesquihydrate). The volume of acetonitrile was adjusted to the sample and water quantities, and set to 15 mL. The extract was vortexed vigorously during 1 min and centrifuged for 2 min at 5000 rpm. Then 5 mL of the upper layer was purified on 150 mg PSA and 950 mg $MgSO_4$, and the purified extract was analysed by GC-MS.

For the extraction with dichloromethane, the same procedure was applied on 5 g of soaked peat spiked at 1 mg kg^{-1}, replacing acetonitrile with 15 mL of dichloromethane.

2.6. Modified QuEChERS extraction

The optimised QuEChERS method was as follow: 2 g of soaked peat spiked at 1 mg kg^{-1} was weighed in a 50 mL polypropylene tube and extracted with 15 mL of dichloromethane. The extract was shaken vigorously. Afterwards, 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate dehydrate and 0.5 g di-sodium hydrogen citrate sesquihydrate were added and the mixture was vortexed vigorously for 1 min. After 2 min centrifugation at 5000 rpm, 1.5 mL of the upper layer was transferred in a GC vial and analysed by GC-MS.

3. Results and discussion

3.1. GC–MS separation

Compounds of interest are mainly a mixture of chlorobenzenes and chlorophenols isomers (see Table 1). For each family, isomers have similar properties, like polarities and volatilities, which make the separation difficult. Furthermore, they have analogous mass spectra (same ions with same ions ratio) and therefore cannot be identified when they are co-eluted. To separate all the compounds, it was necessary to use an apolar column with a 60 m length and different ramps of temperature. Particularly, a 1.5 °C/min ramp from 100 to 150 °C was necessary to separate 1,2,3,5 and 1,2,4,5-tetrachlorobenzene isomers.

The chromatogram was displayed in Fig. 1. The low sensibility of the chlorophenols can be explained by the presence of a hydroxyl group which tends to interact with the stationary phase of the column. It results into a broad peak tailing. To improve resolution and sensitivity, chlorophenols are generally derivatized [31,33]. However, in our study, analysis concerns compounds belonging to 4 different families and derivatization was not appropriate with the multiresidue method.

3.2. Sample preparation

In order to study the performance of the phytoremediation process, pilots containing peat, and aquatic plants in some cases, were

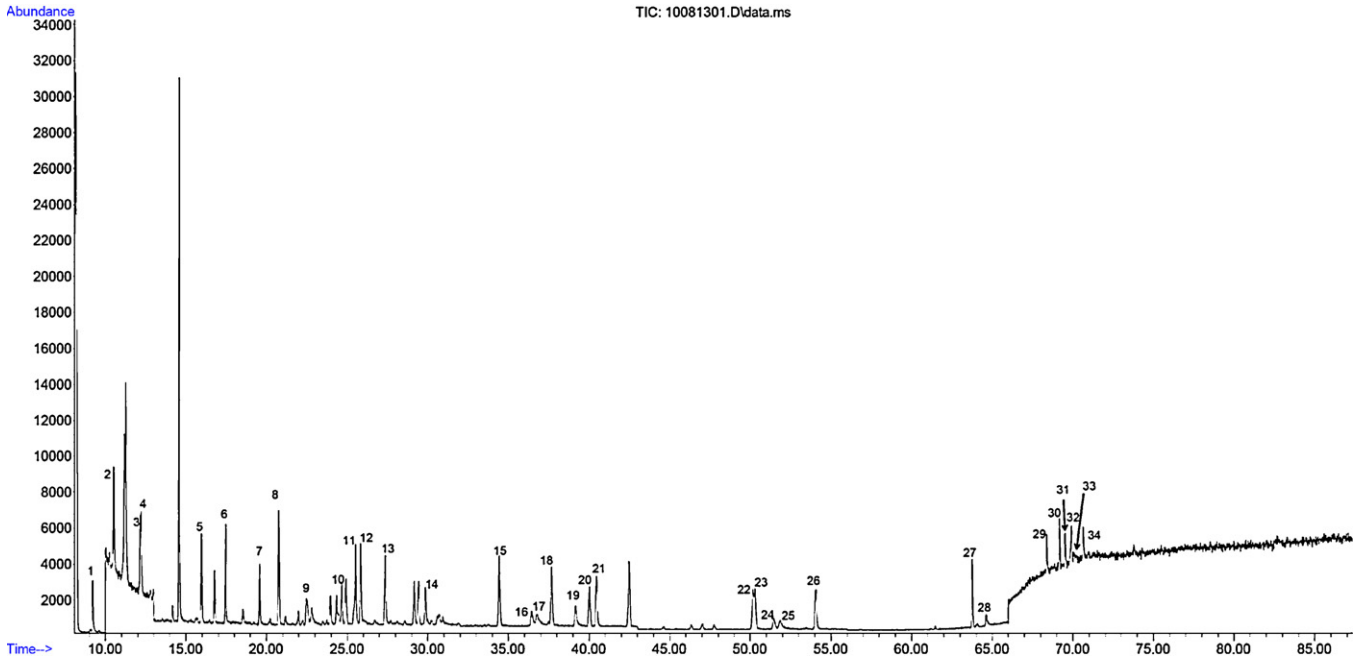

Fig. 1. GC–MS analysis of a spiked peat sample extracted by QuEChERS method. 1: 1,2 dichloroethylene cis; 2: 1.2 dichloroethane; 3: 1.2 dichloropropane; 4: trichloroethylene; 5: tetrachloroethylene; 6: chorobenzene; 7: 1.1.2.2 tetrachloroethane; 8: cumene; 9: phenol; 10: 2-chlorophenol; 11: 1.3-dichlorobenzene; 12: 1.4-dichlorobenzene; 13: 1.2-dichlorobenzene; 14: hexachloroethane; 15: 1.3.5 trichlorobenzene; 16: 2.4 dichlorophenol; 17: 4-chlorophenol; 18: 1.2.4 trichlorobenzene; 19: 2.6 dichlorophenol; 20: hexachlorobutadiene; 21: 1.2.3 trichlorobenzene; 22: 1.2.3.5 tetrachlorobenzene; 23: 1.2.4.5 tetrachlorobenzene; 24: 2.4.6 trichlorophenol; 25: 2.4.5 tricholorophenol; 26: 1.2.3.4-tetrachlorobenzene; 27: pentachlorobenzene; 28: 2.3.4.6 tetrachlorophenol; 29: alpha HCH; 30: hexachlorobenzene; 31: beta HCH; 32: lindane; 33: pentachlorophenol; 34: delta HCH.

used. These pilots were continuously fed with water and consequently, peat was waterlogged.

In the literature, soils are usually air-dried at room temperature [17,34] or in a heating plate [32]. However, analytes of this study were very volatile (boiling point at 80 °C for the most volatile ones) and any water elimination would have lead to the loss of these compounds. Then, in order to have the same humidity degree for all the samples, blank peat was soaked with water. That way, extraction efficiency was not influenced by the water amount.

3.3. ASE extraction

3.3.1. Optimisation of ASE extraction

Temperature and solvent of ASE extraction were optimised in order to improve the extraction and to limit the loss of volatile compounds. Three temperatures were tested (40 °C, 60 °C and 100 °C) and the best efficiency was shown to be at 40 °C. Also, dichloromethane was proven to be a better extraction solvent than more polar solvents as acetone, or more apolar solvents as dichloromethane/hexane (50/50) (data not shown). Recoveries obtained with the extraction at 40 °C with dichloromethane are reported in Table 2. We obtained recoveries between 42% and 85% for the majority of the compounds except for the more volatile ones where recoveries were less than 35%. Indeed, for these compounds which have a boiling point inferior to 200 °C, we observe their loss by evaporation, due to the high pressure during extraction. In a general way, HCH were more efficiently extracted than chlorophenols, followed by chlorobenzenes and chlorinated hydrocarbons and olefins. This can be explained by their volatility which increases proportionally.

3.3.2. Performance of ASE extraction

Repeatability of the extraction was evaluated by extracting 3 peat samples spiked at 1 mg kg^{-1} (see Table 2). Extraction was repeatable for the less volatile compounds with RSD < 25%; for the most volatile analytes, we obtained RSD between 13% and 46% showing that the method was not repeatable for these analytes. These results can be explained by the low recoveries.

Linearity was verified using matrix-matched calibration solutions over the range of 100–5000 μg kg^{-1} (see Table 2).

Limits of detection and quantification were estimated from the matrix-matched calibration and were defined as the analyte concentrations giving a signal-to-noise of 3 and 10 respectively (see Table 2). LOD ranged from 58 to 540 μg kg^{-1} and LOQ from 194 to 1800 μg kg^{-1} for the less volatile compounds. For pentachlorophenol, higher values were obtained (LOD: 2700 μg kg^{-1} and LOQ: 9000 μg kg^{-1}) due to its low sensitivity in GC (see Section 3.1).

For the 5 most volatile compounds, no signal was detected at 5000 μg kg^{-1} due to their loss by evaporation. Thus, performance parameters, i.e., correlation coefficient, LOD and LOQ could not be calculated.

3.4. QuEChERS extraction

3.4.1. Optimisation of QuEChERS extraction

Ethyl acetate and acetonitrile are the two solvents generally used for QuEChERS extraction [21] as they give high extraction recoveries of pesticides in fruits and vegetables. Acetonitrile is the most used for its ability to separate easily from water with the addition of an appropriate mixture of salts (anhydrous magnesium sulphate and sodium chloride). However, according to ASE extraction, dichloromethane was the most suitable solvent for the extraction of organochlorines compared with more polar solvents (see Section 3.3).

Considering this, we compared conventional QuEChERS method using acetonitrile with extraction using dichloromethane (see protocol of extraction in Section 2.5). After extraction with acetonitrile or dichloromethane, the extract was purified by dispersive SPE on PSA in order to remove organic acids contained in peat. The results are displayed in Fig. 2.

Table 2
Performance of ASE extraction: recovery (R) with RSD (%) at 1 mg kg^{-1}, linearity range, correlation coefficient (R^2), LOD and LOQ.

Name	Recovery R (%)	RSD (%)	R^2 100–5000 μg kg^{-1}	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
1,2-dichloroethylene cis	0%	N.A[b]	N.A[b]	N.A[b]	N.A[b]
1,2-Dichloroethane	0%	N.A[b]	N.A[b]	N.A[b]	N.A[b]
1,2-Dichloropropane	0%	N.A[b]	N.A[b]	N.A[b]	N.A[b]
Trichloroethylene	0%	N.A[b]	N.A[b]	N.A[b]	N.A[b]
Tetrachloroethylene	0%	N.A[b]	N.A[b]	N.A[b]	N.A[b]
Chorobenzene	4%	42%	0.975[a]	340	1135
1,1,2,2-Tetrachloroethane	29%	18%	0.992	58	194
cumene	4%	46%	0.953[a]	183	610
phenol	61%	16%	0.999	80	268
2-Chlorophenol	70%	13%	0.999[a]	188	625
1,3-Dichlorobenzene	27%	29%	0.999	100	333
1,4-Dichlorobenzene	31%	29%	0.999	89	298
1,2-Dichlorobenzene	35%	26%	1.000	107	355
Hexachloroethane	21%	33%	0.998[a]	354	1178
1,3,5-Trichlorobenzene	42%	23%	1.000	85	282
2,4-Dichlorophenol	68%	19%	0.999	339	1130
4-Chlorophenol	68%	25%	0.999	285	949
1,2,4-Trichlorobenzene	56%	15%	0.999	65	218
2,6-Dichlorophenol	62%	17%	1.000	238	794
Hexachlorobutadiene	34%	20%	0.999	100	333
1,2,3-Trichlorobenzene	57%	13%	1.000	117	390
1,2,3,5-Tetrachlorobenzene	61%	17%	0.999	173	577
1,2,4,5-Tetrachlorobenzene	67%	12%	0.998	129	429
2,4,6-Trichlorophenol	71%	14%	1.000[a]	431	1438
2,4,5-Tricholorophenol	75%	17%	0.999[a]	453	1512
1,2,3,4-Tetrachlorobenzene	67%	13%	1.000	143	475
Pentachlorobenzene	72%	9%	1.000	129	430
2,3,4,6-Tetrachlorophenol	70%	8%	0.999	221	735
Alpha HCH	74%	8%	1.000[a]	345	1151
Hexachlorobenzene	67%	9%	0.999[a]	472	1574
Beta HCH	81%	12%	0.999[a]	492	1639
Lindane	85%	13%	1.000[a]	542	1808
Pentachlorophenol	N.A[c]	N.A[c]	N.A[c]	2708	9028
Delta HCH	64%	10%	0.999[a]	493	1644

N.A.: non available.
[a] Correlation coefficient calculated on the range 500–5000 μg kg^{-1}.
[b] Parameters non available as the compounds were non detected (recovery 0%).
[c] These parameters can not be evaluated as LOD was superior to 2700 μg kg^{-1}.

Dichloromethane was the best solvent extraction for chlorinated hydrocarbons and olefins, and for chlorobenzenes. HCH are most efficiently extracted with acetonitrile. For chlorophenols, we obtained higher recoveries with acetonitrile; however, their extraction with acetonitrile is less repeatable and RSD ranged up to 53%. Furthermore, they were retained on PSA phase. In order to improve their recovery, an extraction with a mixture of acetonitrile/dichloromethane 50/50 was also performed (data not shown). The recovery of the tri- and tetrachlorophenols slightly increase but we observe a simultaneous increase of RSD. Thus, as we can see in the Fig. 2, extraction with dichloromethane without purification by dispersive SPE on PSA was a good compromise.

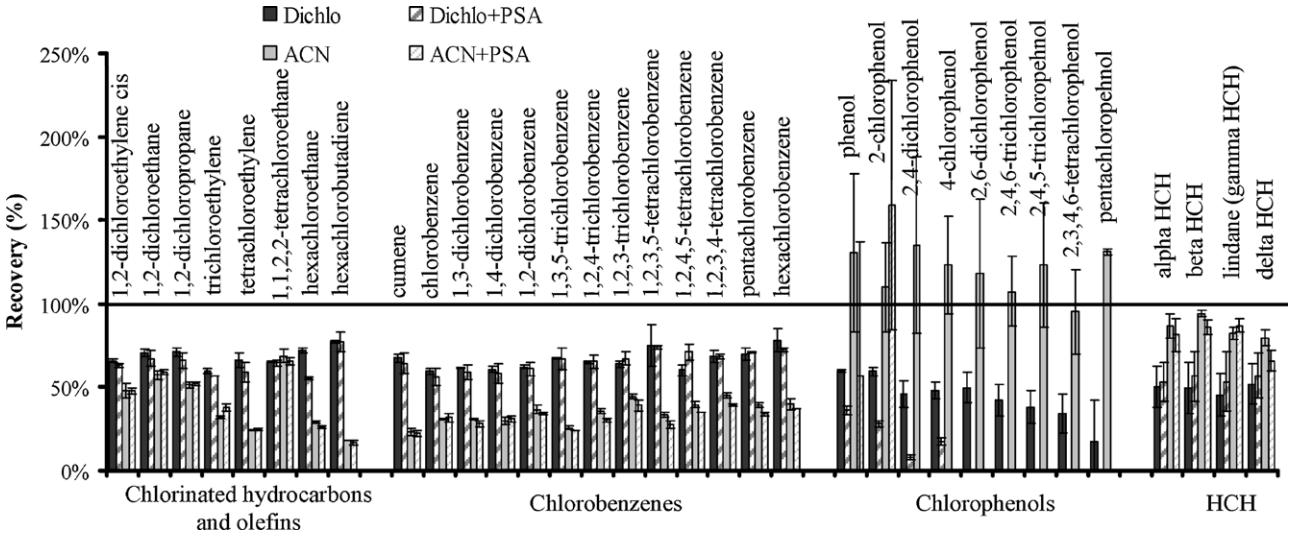

Fig. 2. Optimisation of QuEChERS extraction. Comparison between conventional QuEChERS procedure (acetonitrile with and without PSA), and dichloromethane extraction with and without PSA.

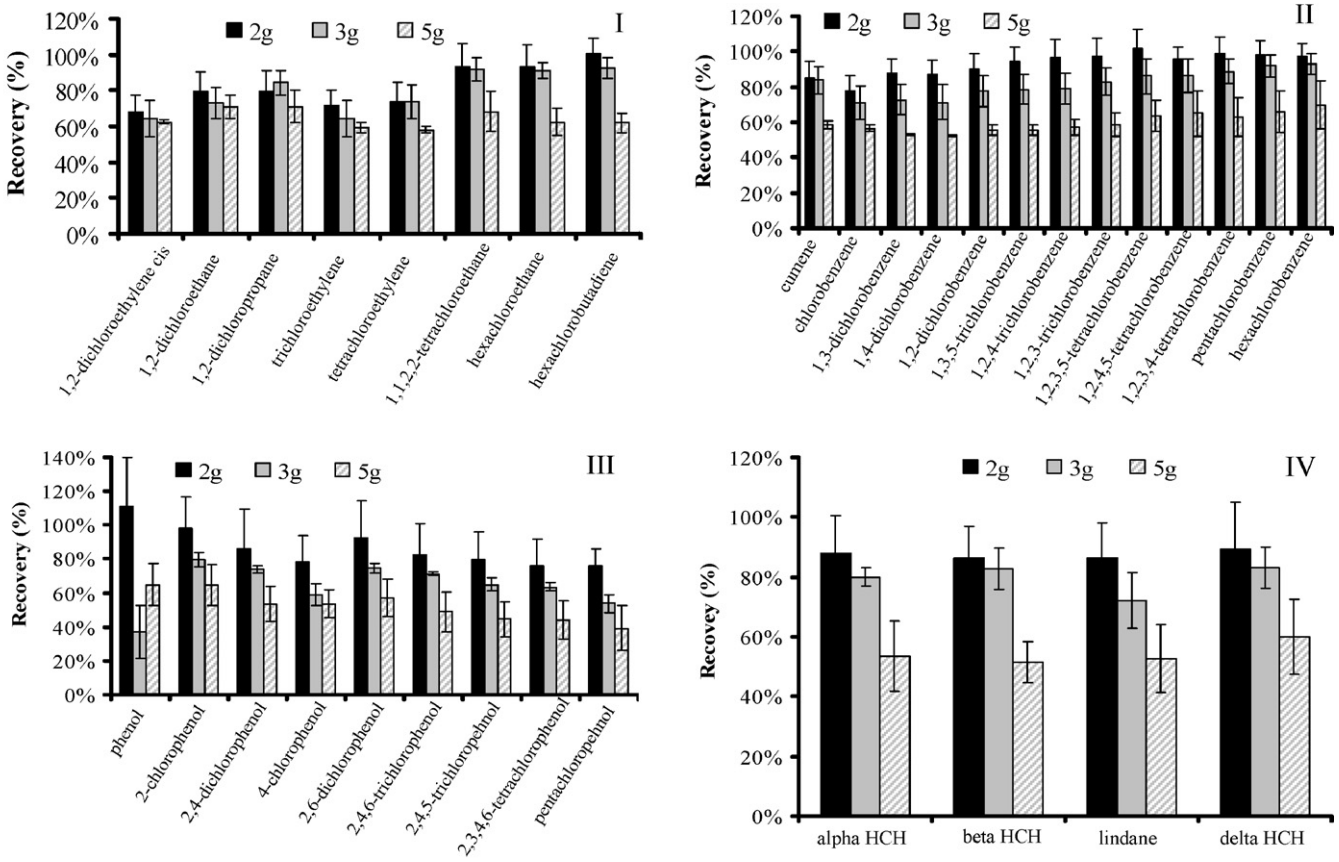

Fig. 3. Influence of the sample amount on the extraction recovery. I) chlorinated hydrocarbons and olefins; II) chlorobenzenes; III) chlorophenols; IV) HCH.

We obtained recoveries between 50% and 78% for 80% of the compounds.

In order to improve the recoveries, we optimized the ratio sample/solvent reducing the sample to 3 and 2 g. Indeed, the ratio water/solvent/salt is a critical parameter in the extraction efficiency as the water amount is higher when the sample amount is larger.

The results are displayed in Fig. 3. For all the compounds, highest recoveries were obtained with small amounts of peat (2 or 3 g). This can be explained by the amount of water which is too important and the amount of anhydrous magnesium is not enough to absorb the water. Thus, 2 g of peat was the most efficient. A representative chromatogram of a peat sample spiked with 1000 $\mu g\,kg^{-1}$ of organochlorines and extracted with this method was displayed in Fig. 1.

However, reducing the sample amount also involves a decrease of the amount of analytes injected in GC. To improve sensibility, we tried to concentrate under nitrogen the extract after QuEChERS extraction. Nevertheless, due to the high volatility of the compounds, we observed an important loss of analytes reaching 85% for the most volatile (1,2-cis-dichloroethylene) (results not shown). In conclusion, concentration was not appropriate for these compounds and the extract was injected directly after extraction.

3.5. Matrix effect

To study matrix effect, a blank peat extracted in the aforementioned conditions and spiked with 20 μL of the solution at 100 $mg\,kg^{-1}$ after extraction (corresponding to a concentration of 1 $mg\,kg^{-1}$ of peat and to a final concentration of 0.133 $mg\,kg^{-1}$ in the GC vial) was compared to a solution at 0.133 $mg\,kg^{-1}$ in dichloromethane.

To display the results, the peak areas of the standard solution in dichloromethane were normalized to 100% (Fig. 4). We observed a positive matrix effect for tetra-, penta- and hexa-chlorobenzenes and for tri-, and tetra-chlorophenols, from 120% to 180%. No matrix effect was observed for the other compounds.

This phenomenon was firstly observed by Erney et al. [35] and can be explained by the presence of active sites in the chromatographic system (in the liner and all along the column) where analytes are adsorbed when they are dissolved in a matrix-free solvent. In the presence of the matrix, the matrix components tend to lock these sites and protect the analytes from adsorption and/or decomposition, ensuring a more complete transfer from injector to column and from column to detector. This phenomenon can explain the higher matrix effect of the organophenols which have a hydroxyl group that can interact with the active sites of the GC.

A way to compensate matrix effect is the use of analyte protectants (AP). This approach was firstly developed by Erney and Poole [36] and was reintroduced by Anastassiades et al. in 2003 [37] and Maštovská et al. in 2005 [38] for the analysis of pesticides in food matrices. It consists of injecting volatile and hydrogen-bonding compounds simultaneously with the pesticides to minimise their interaction with the active sites. However, the most efficient analyte protectants are polar compounds which are soluble in polar solvent like acetonitrile or water, and few soluble in dichloromethane. This reduces significantly the choice of molecules and we focused only on 4 (3-ethoxy-1-2-propanediol, squalene, isopropanol and PEG) at concentrations between 0.5 and 10 $g\,L^{-1}$. Diol is known to protect volatile compounds which elute in the beginning of the chromatogram and squalene for the late-eluting analytes [37]. Isopropanol has been demonstrated to be a good analyte protectant to pesticides and some organochlorines by Barrek et al. [39]. PEG protects intermediate and late-eluting analytes but

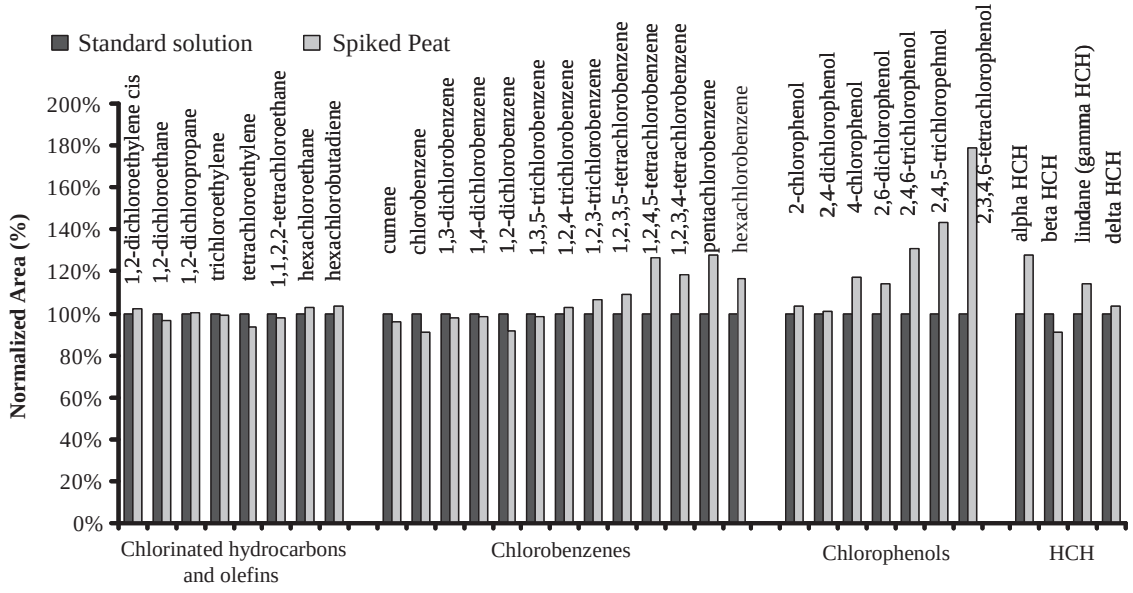

Fig. 4. Influence of the matrix on the organochlorine response.

it deteriorates column performances quite quickly [38]. Nevertheless, among these 4 molecules tested, none of them had an effect on the organochlorines and no protection effect is observed. Indeed, we do not observe any improvement of the peak tailing and any area gain (data not shown). This can be explained by the analyte protectant volatility which is different from that of the analytes. The use of sugars like sorbitol, D-mannitol or D-galacticol would have been more suitable as they protect late-eluting compounds, but they are insoluble in dichloromethane [37].

Thus, to compensate this matrix effect and avoid any over estimation of organochlorines, a matrix-matched calibration was used.

3.5.1. Validation of QuEChERS extraction

The performance of the method, in terms of specificity, recovery, precision (intra-day precision and inter-day precision), limits of detection and quantification, and accuracy was evaluated on three days. Validation was based on reference systems (INTERNATIONAL CONFERENCE ON HARMONISATION Q2(R1), SANCO 2007/3131 and AFNOR NF V 03-110).

Specificity was assessed by the analysis of 3 blank peat samples extracted by the optimised QuEChERS method. No interference was detected at the analytes retention times.

Recoveries were determined by analysing 3 blank peat samples spiked at three concentrations (100, 500 and 1000 $\mu g\,kg^{-1}$ corresponding respectively to the low, medium and high levels of the calibration curve), and compared to three blank peat samples spiked at the same concentration after the QuEChERS extraction. The results for the low concentration are reported in Table 3 (complete data reported in TableS1). We obtained recoveries between 70% and 100% for 85% of the compounds. For 1,2-dichloroethylene cis, recovery was under 60% at 500 $\mu g\,kg^{-1}$, and for tetrachloroethylene and chlorobenzene, at 67%. These recoveries were low but consistent and allowed quantification. For chlorobenzenes, it was shown that the higher the number of chlorines, the higher the recoveries were. It can be explained by their solubility in dichloromethane which would be chlorine-number dependant (data not available). Moreover, RSD were inferior to 25% at the three concentration levels.

Precision, expressed as intra-day precision and inter-day precision, was also verified at the three concentrations, in triplicate. The results for the low concentration are reported in Table 4 and the complete data are reported in TableS2. Extraction was repeatable at each concentration with RSD <9% and reproductible with RSD < 25% for 90% of the compounds. The high value can be explained by the low sensitivity of the compounds.

Linearity was verified using matrix matched calibration in the range of 10–5000 $\mu g\,kg^{-1}$ of peat corresponding to a concentration range of 1.3–667 $\mu g\,kg^{-1}$ in the GC vial. For all the

Table 3
Recoveries and variations ($n=3$) obtained for the QuEChERS extraction of 100 $\mu g\,kg^{-1}$ of organochlorines from peat.

	R (%)	RSD (%)
1,2-Dichloroethylene-cis	71.7%	10.0%
1,2-Dichloroethane	78.8%	12.5%
1,2-Dichloropropane	77.5%	19.0%
Trichloroethylene	72.3%	13.0%
Tetrachloroethylene	74.8%	7.8%
Chorobenzene	72.3%	10.8%
1,1,2,2-Tetrachloroethane	90.2%	8.5%
Cumene	84.3%	7.6%
Phenol	99.2%	9.0%
2-Chlorophenol	95.9%	9.5%
1,3-Dichlorobenzene	84.6%	8.0%
1,4-Dichlorobenzene	84.5%	6.6%
1,2-Dichlorobenzene	88.5%	7.9%
Hexachloroethane	94.8%	10.5%
1,3,5-Trichlorobenzene	92.2%	8.1%
2,4-Dichlorophenol	92.6%	5.2%
4-Chlorophenol	N.A	N.A
1,2,4-trichlorobenzene	94.1%	10.9%
2,6-Dichlorophenol	92.2%	7.3%
Hexachlorobutadiene	99.5%	5.4%
1,2,3-Trichlorobenzene	94.6%	9.8%
1,2,3,5-Tetrachlorobenzene	92.3%	10.0%
1,2,4,5-Tetrachlorobenzene	95.4%	10.7%
2,4,6-Trichlorophenol	87.8%	3.4%
2,4,5-Tricholorophenol	N.A	N.A
1,2,3,4-Tetrachlorobenzene	93.1%	9.3%
Pentachlorobenzene	93.0%	11.7%
2,3,4,6-Tetrachlorophenol	84.1%	6.3%
Alpha HCH	85.7%	9.2%
Hexachlorobenzene	93.9%	8.5%
Beta HCH	92.0%	12.5%
Lindane	82.3%	4.0%
Pentachlorophenol	N.A	N.A
Delta HCH	87.2%	19.4%

N.A: non available (concentration < LOD).

Table 4
Validation parameters of QuEChERS extraction: linearity (range 10–5000 μg kg^{-1}), LOD, LOQ, intra-day precision (n = 3), inter-day precision (n = 3) at 100 μg kg^{-1} and bias at 500 μg kg^{-1} (n = 3).

	R^2	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	Intra-day precision (n = 3)	Inter-day precision (n = 3)	Bias
1,2-Dichloroethylene-cis	0.9973	22.7	75.5	3.5%	6.8%	10.1%
1,2-Dichloroethane	0.9984	8.1	27.0	6.5%	12.3%	4.8%
1,2-Dichloropropane	0.9984	36.8	122.7	8.0%	11.6%	2.3%
Trichloroethylene	0.9975	10.7	35.7	6.2%	7.2%	1.3%
Tetrachloroethylene	0.9967	15.0	50.0	5.9%	37.2%	5.5%
Chorobenzene	0.9995	3.1	10.3	8.1%	5.9%	−14.9%
1,1,2,2-Tetrachloroethane	0.9991	5.5	18.2	1.5%	9.2%	−5.0%
Cumene	0.9987	2.1	6.9	6.7%	2.6%	−2.3%
Phenol	0.9952	63.7	212.4	4.3%	20.9%	−15.4%
2-Chlorophenol	0.9965	43.8	145.8	4.3%	3.3%	−5.9%
1,3-Dichlorobenzene	0.9989	4.8	16.0	6.9%	13.5%	−10.1%
1,4-Dichlorobenzene	0.9988	8.1	26.9	6.7%	15.1%	−10.5%
1,2-Dichlorobenzene	0.9989	8.8	29.2	7.4%	12.2%	−11.1%
Hexachloroethane	0.9984	48.6	162.2	6.5%	6.7%	−3.5%
1,3,5-Trichlorobenzene	0.9986	4.8	16.0	6.9%	15.8%	−14.1%
2,4-Dichlorophenol	0.9935	69.2	230.8	2.7%	5.4%	−14.4%
4-Chlorophenol	0.9939[a]	147.5	491.8	N.A	N.A	0.4%
1,2,4-Trichlorobenzene	0.9985	4.1	13.8	8.4%	16.0%	−14.5%
2,6-Dichlorophenol	0.9957	40.0	133.3	4.6%	5.7%	−10.4%
Hexachlorobutadiene	0.9987	14.6	48.8	5.5%	15.3%	−11.8%
1,2,3-Trichlorobenzene	0.9986	4.6	15.4	8.0%	14.6%	−13.5%
1,2,3,5-Tetrachlorobenzene	0.9977	6.0	20.0	5.6%	13.6%	−17.5%
1,2,4,5-Tetrachlorobenzene	0.9976	8.6	28.6	6.0%	15.1%	−19.7%
2,4,6-Trichlorophenol	0.9936	88.2	294.1	2.6%	5.1%	−15.2%
2,4,5-tricholorophenol	0.9938[a]	281.3	937.5	N.A	N.A	−3.7%
1,2,3,4-Tetrachlorobenzene	0.9984	4.7	15.8	6.4%	16.4%	−15.2%
Pentachlorobenzene	0.9984	9.3	31.1	7.4%	15.2%	−15.8%
2,3,4,6-Tetrachlorophenol	0.9954	73.3	244.4	5.6%	8.1%	−14.2%
Alpha HCH	0.9990	61.8	205.9	3.9%	12.8%	−1.4%
Hexachlorobenzene	0.9988	51.2	170.6	4.6%	22.6%	−7.7%
Beta HCH	0.9990[a]	109.1	363.6	3.5%	13.2%	11.2%
Lindane	0.9988	80.4	267.9	4.4%	17.3%	0.7%
Pentachlorophenol	0.9992[b]	635.3	2117.6	N.A	N.A	N.A
Delta HCH	0.9990[a]	115.4	384.6	5.6%	17.1%	8.9%

N.A: non available.
[a] Linearity range: 100–5000 μg kg^{-1}.
[b] Linearity range: 500–5000 μg kg^{-1}

compounds, correlation coefficients (R^2) were superior to 0.99. For the compounds with LOD superior to 100 μg kg^{-1}, correlation coefficients were calculated from 100 to 5000 μg kg^{-1} and from 500 to 5000 μg kg^{-1} for pentachlorophenol.

Limits of detection and quantification were estimated from the matrix matched calibration as the analyte concentration giving a signal-to-noise of 3 and 10 respectively. LOD were inferior to 30 μg kg^{-1} for 50% of the compounds and <100 μg kg^{-1} for 80% of them. The highest LOD were obtained for organophenols which tailed in the chromatographic column. For half of the organochlorines, we obtained LOQ <50 μg kg^{-1} and LOQ <500 μg kg^{-1} for 90% of the compounds. LOQ values reached to 2100 μg kg^{-1} for pentachlorophenol due to its low volatility and chromatographic profile (peak tailing; see Section 3.1).

Accuracy of the method was assessed by determining the concentration of 3 blank peat sample spiked at 500 μg kg^{-1} using matrix-matched calibration, and comparing the calculated concentration with the theoretical concentration (500 μg kg^{-1}). The concentration was set to 500 μg kg^{-1} in order to be over the LOQ of the analytes. Accuracy was expressed as bias between the average calculated concentration and the theoretical concentration (see Table 4). Bias value ranged between −20% and +11% which is within the acceptance criteria (<20%).

Furthermore, the method was applied to 15 peat soil samples coming from pilots. It allowed the quantification of all the compounds in the soils (data not shown). So, in correlation with the amount of organochlorines in the air, the plants and the groundwater, these results may conclude on the phytoremediation process efficiency.

This method was further applied to 2 other soils with different polarities and properties (organics and mineral soils) and the compounds were successfully quantified in the same range (data not shown).

4. Conclusion

Conventional QuEChERS method was applied and optimised for the extraction of 34 organochlorines from soils. The different parameters that affect the extraction, such as solvent selection and ratio sample/solvent were studied. Dichloromethane, a non miscible-water solvent was proven to be a better solvent extraction than usual acetonitrile for QuEChERS extraction, especially for chlorinated hydrocarbons and olefins, and for chlorobenzenes. Moreover, it provides clean extracts without any purification by dispersive SPE and does not require the use of PSA which is an expensive phase. Compared to ASE extraction, QuEChERS-based method is rapid, easy to use, and provides good recoveries, even for volatile compounds.

The method was tested on pilots used in the phytoremediation study. It allows quantification of organochlorines at concentration in accordance with the contents found in phytoremediation soils and then, can be used for the monitoring of phytoremediation or for any analysis of chlorinated contaminants in industrial soils of different nature. Furthermore, this method can be applied for the analysis of very volatile compounds in soils which is not possible with conventional methods which generally require water elimination.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2012.02.048.

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