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Screening and determination of pesticides in soil using continuous subcritical water extraction and gas chromatography–mass spectrometry

Pablo Richter^{a,b,*}, Betsabet Sepúlveda^a, Rodrigo Oliva^a, Katia Calderón^a, Rodrigo Seguel^a

^aFundación Centro Nacional del Medio Ambiente, Universidad de Chile, Av. Larraín 9975, La Reina, Santiago, Chile

^bDepartamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile

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Abstract

In the present work the efficiency of water under subcritical conditions for the extraction of pesticides having a broad spectrum of polarities from soils was evaluated. The pesticides under study were carbofuran, hexachlorobenzene, dimethoate, simazine, atrazine, lindane, diazinon, methylparathion, alachlor, aldrin-R, metholachlor, chlorpyrifos, heptachlor epoxide, dieldrin, endrin, 4,4-DDT and metoxichlor. Optimization studies were carried out using a blank soil (Non-Polluted Soil 1, CLN-1, RTC) and a real soil which were previously spiked with the pesticide mixture and aged for 60 days. A laboratory-made aluminum oven with controlled temperature was used to carry out the leaching process with subcritical water, where it is placed a pre-heater and the extraction cell. The following variables were studied, keeping the pressure controlled about 1200 p.s.i.: the extraction temperature, the time of static and dynamic extraction and the flow-rate of water (1 p.s.i.=6894.76 Pa). The extraction efficiency of the pesticides increases with the temperature trending to the quantitative extraction at temperatures near to 300 °C. After the extraction process, the analytes were transferred quantitatively to 5 ml dichloromethane, before the determination by GC–MS. The results indicate that under the optimized conditions mostly of the analytes are extracted quantitatively in 90 min with recoveries quite similar to those obtained by the standard Soxhlet extraction procedure. Alternatively, by using an extraction time of 25 min, the method can be used as screening for all the pesticides, with recoveries depending on their polarity.

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1. Introduction

Usually the concept of quality in analytical

chemistry is mainly associated with the fact of reaching the maximum level of analytical properties for a given method. The quality is defined in terms of the representativity of the sampling, the accuracy of the results, and the precision, selectivity and sensitivity of the analytical process of measurement. In other words, this vision represents the metrological approach of quality.

*Corresponding author. Fundación Centro Nacional del Medio Ambiente, Universidad de Chile, Av. Larraín 9975, La Reina, Santiago, Chile. Fax: +56-2299-4172.

E-mail address: prichter@cenma.cl (P. Richter).

But quality is not only related with the achievement of a high level of analytical features, but also it must to be related to the client's satisfaction, in terms of rapidity and opportunity of the information. This is particularly valid in the environmental field of the analytical chemistry, in which some situation of emergency requires rapid information to make appropriate decisions. In this instance the screening approach is preferred instead an accurate but time consuming method. In this context, the development of more rapid and efficient methodologies for the sample preparation of solid matrices is a significant trend in modern analytical chemistry.

The preservation of the environment and human health from exposure to persistent organic pollutant is nowadays a priority objective in developed countries. In this sense, pesticides constitute a very important group of target compounds owing to their high toxicity and their unavoidable use in agricultural practices. Chile is a country with intensive agricultural production and the use and commercialization of organochlorinated pesticides has been gradually prohibited since 1984, however because they were used extensively they probably still remain in the environment. Therefore, the rapid monitoring of organochlorinated pesticides together with those congeners actually authorized is imperative from an environmental point of view.

Regulatory agencies and private laboratories around the world monitor pesticide residues. Most of the methods developed for this purpose are based on Soxhlet extraction procedures [1–5]. Despite that this kind of technology is old, complicated and time-consuming (between 8 to 36 h), most standard official methods for extraction of organics are still based on it. Sonication or shaking are other faster traditional leaching techniques for organic analytes, but also consume large quantities of solvent, are labor intensive, and require special equipment [6,7]. More recently, modern technologies [8–19] including the use of new sources of energy have been described, such as microwave-assisted extraction (both normal and focused microwaves), supercritical fluid extraction, accelerated solvent extraction and subcritical water extraction.

It has been demonstrated recently [19] that pressurized liquid extraction (PLE) is a good alternative compared with traditional Soxhlet extraction for the

extraction of herbicides. A critical comparison between these techniques indicates that PLE uses much less solvent (40 ml) than Soxhlet extraction which uses at least 200 ml. On the other hand, PLE is much faster because quantitative extraction takes 30 min compared to 8 h required by Soxhlet extraction.

Subcritical water extraction is based on a principle similar to that of PLE, but in this instance the solvent is water, whose high temperature and pressure strongly reduces its dielectric constant, viscosity and surface tension. That makes water an effective solvent for leaching a number of organic compounds that have a broad spectrum of polarity in solid samples.

Further, water does not exhibit toxicity-associated problems like organic solvents and its subcritical capabilities can be easily achieved with low-cost laboratory devices, without require either much laboratory space or glassware.

Besides its use in analytical chemistry as a solvent for extraction, subcritical water has been used also for pilot-scale decomposition of organic pollutants in soil and oils [20–22], and in the extraction of plant essential oils [23,24].

Regarding the subcritical water extraction (SBWE) of pesticides, it has been observed that by increasing the water temperature the solubilities of the triazine pesticides increased approximately threefold in pure water for each 25 °C temperature increment. Much higher solubility was obtained when hot water was modified with a co-solvent such as urea or methanol [25]. The solubility of the pesticide propazine was enhanced 4300-fold as the temperature of water was increased from 25 to 200 °C [26].

The aim of this work was to evaluate the efficiency of water, under subcritical conditions, for the extraction from soils of a group of typical pesticides used in agriculture, in order to develop a screening/quantitative analytical method. The following pesticides were evaluated: carbofuran, hexachlorobenzene, dimethoate, simazine, atrazine, lindane, diazinon, methylparathion, alachlor, aldrin-R, metholachlor, chlorpyrifos, heptachlor epoxide, diel-drin, endrin, 4,4-DDT and metoxichlor.

After optimization of extraction parameters, the method was applied to samples of soils collected in the VI Region of Chile and the results were com-

pared against a conventional Soxhlet extraction method.

2. Experimental

2.1. Reagents

Deionized water (NANOpure ultrapure water system; Barnstead, Dubuque, IA, USA) was used throughout. Pesticides were purchased from Supelco (Bellefonte, PA, USA, 4-8743). A stock standard solution of each compound at 1000 $\mu\text{g/ml}$ was prepared in acetone (Omnisolv, Merck, Darmstadt, Germany). A mixed standard solution was prepared in acetone at a final concentration of 10 $\mu\text{g/ml}$ for each compound, which was used to spike the soils and for calibration purposes. A series of mixed standard was prepared in acetone, containing each standard at a concentration of 0.01–1.0 $\mu\text{g/ml}$. During each sequence of sample analysis, linearity was checked by including the mixed standard solutions in the sequence. Dichloromethane (GC-MS/pesticide-grade analysis, Fisher Scientific, Fair Lawn, NJ, USA) was used as final extractant. A certified reference material Non-Polluted Soil CLN Soil 1 (manufactured by Resource Technology, RTC,

USA) was spiked at the 10 mg/kg level and used to optimize the SBWE proposed method.

2.2. Instruments and apparatus

The schematic build-up of the extraction unit is shown in Fig. 1. All tubes (1/16 in., 1/8 in. O.D.; 1 in.=2.54 cm) were made from SS 306 stainless steel. Connections were made using Swagelok fittings. The following valve type was employed: Swagelok needle valve SS-ORS2 (5000 p.s.i. allowed pressure; 1 p.s.i.=6894.76 Pa).

The extraction chamber consisted of a laboratory-made oven (a 28×12×5 cm aluminum block with controlled temperature). A temperature controller BTC-704-41521000; Spec.: J, 0–400 °C was used to maintain the temperature. Inside the chamber a preheated coil (2 m stainless steel tube SS-316, 1/16 in., 0.1 mm I.D.) was present to keep the programmed temperature and was followed by the extraction cell (a 12 mm I.D. empty HPLC column, Supelco). The deionized water for the extraction was pumped using a HPLC pump (Waters Model 600 pump) operated in the constant pressure mode. For extraction, the working range of pressure inside the system was kept between 1000 and 2000 p.s.i.

The quantitation was performed using a Hewlett-Packard Model 6890 high-resolution gas chromatograph.

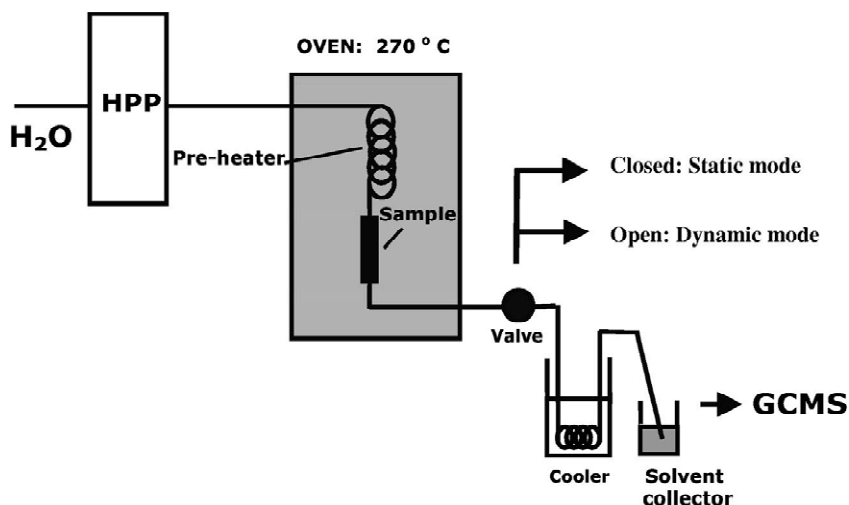


Fig. 1. Subcritical water extraction manifold. HPP, High-pressure pump.

graph coupled to an 5973 mass-selective detector, equipped with a 30 m HP-5MS column (0.25 μ m film thickness, 250 μ m I.D., Hewlett-Packard).

2.3. Spiking procedure

For optimization of variables and recovery studies a blank soil (Non-Polluted Soil 1, CLN-1, RTC) and a real Alfisol soil from the VI Region of Chile were considered. The latter soil contains 8.6% organic matter, 26.6% clay, 14.0% silt, and 59.4% sand. A spiked soil preparation was made by diluting a stock mixture of the pesticide standard in 250 ml of acetone and mixing into amber bottles with 200 g of soil to obtain a final concentration of 10 mg/kg. The bottles were placed in a hood, and the solvent was slowly evaporated under continuous stirring. The spiked soil were aged for 60 days at room temperature and thereafter stored at 4 °C.

2.4. General analytical procedure

The spiked soils and real soil samples were separately extracted according to the following procedures.

2.4.1. Subcritical water extraction

Samples (300 mg) were weighed and loaded into an extraction cell located inside the aluminum chamber–oven extractor. The oven was coupled to a heating device located on the upper part of the chamber and electronically controlled through a thermocouple until reaching a temperature of 270 °C. Then, water was pumped through the system to extract the analytes from the soils at a flow-rate of 2 ml/min for 25 or 90 min, depending if screening or quantitative purposes are required, respectively. After the subcritical water extraction was done, the pesticides already in a water phase were transferred quantitatively by liquid–liquid extraction to 5 ml of dichloromethane prior their characterization by gas chromatography–mass spectrometry (GC–MS). The optimization of the extraction considered the following variables: extraction temperature, static and dynamic extraction time, and flow-rate of water.

2.4.2. Conventional Soxhlet extraction

Spiked soil samples were treated using the con-

ventional Soxhlet extraction procedure. A detailed description of the analytical procedure used for extraction of those samples is described previously [5]. Basically it consists of the extraction by Soxhlet using methylene chloride–acetone (1:1, v/v) as the solvent extraction system (20 h), then the extract after evaporation to 5 ml in a Kuderna-Danish concentrator is characterized by GC–MS.

The final determination by GC–MS was carried out according to the following parameters: column: HP-5MS (30 m \times 0.25 mm, 0.25 μ m), carrier gas: helium (1.2 ml/min, constant flow), temperature program: 70 °C (hold 2 min) to 150 °C at 25 °C/min, 150 to 200 °C at 3 °C/min, 200 to 280 °C at 8 °C/min, 280 °C (hold 3 min); total 35 min, injection volume: 2 μ l splitless, injector temperature: 250 °C.

The MS transfer line was held at 280 °C and the quantitations were based on calibration with standard pesticides using the mass spectrometric parameters [selected ion monitoring (SIM) mode] shown in Table 1. Peak identification of pesticides was based on the retention times and full scan spectra of the standards and soil samples. Quantitation was based on SIM for the molecular ion of each analyte.

2.5. Samples

Soil samples were collected from agricultural fields in September 2002 from the VI Region (central Chile). The samples were air-dried, sieved to 2 mm, homogenized and placed in glass brown bottles. One non polluted soil sample was spiked with pesticides as described above, to assess the optimization studies. The samples were stored in a refrigerator at 4 °C prior to analysis.

3. Results and discussion

Recently, we applied the subcritical water extraction approach to the determination of low-polarity compounds such as polycyclic aromatic hydrocarbons (PAHs) in airborne particles from the Santiago (Chile) metropolitan area [15]. The proposed approach was useful as a quantitative method to characterize low-molecular-mass PAHs and simultaneously as a screening method for high-molecular-

Table 1
Analytical features of the method

Pesticide	Ion mass*	Retention time (min)	LOD ($\mu\text{g}/\text{kg}$)	Recovery (%)		Repeatability, RSD ($n=6$) (%)
				25 min	90 min	
(1) Carbofuran	164, 149	6.41	30.9	97.3	106.7	2.3
(2) Hexachlorobenzene	284, 286	12.40	9.2	37.6	78.6	9.1
(3) Dimethoate	87, 93	12.72	18.0	43.3	90.2	33.8
(4) Simazine	201, 186	12.93	16.0	95.0	95.0	9.9
(5) Atrazine	200, 215	13.31	14.3	88.0	88.0	6.5
(6) Lindane	183, 219	14.20	36.2	66.0	72.0	11.5
(7) Diazinon	179, 304	14.47	16.4	54.0	107.9	12.5
(8) Methylparathion	263, 109	16.53	3.2	85.3	98.3	18.5
(9) Alachlor	160, 188	16.95	14.5	78.6	91.0	10.7
(10) Aldrin-R	263, 265	18.38	7.4	44.1	78.3	7.1
(11) Metholachlor	162, 238	18.79	5.2	74.8	100.0	11.9
(12) Chlorpyrifos	97, 197	19.12	29.3	14.2	51.7	17.9
(13) Heptachlor epoxide	353, 355	20.51	19.3	75.8	96.7	4.2
(14) Dieldrin	79, 149	23.59	22.0	72.2	103.4	2.33
(15) Endrin	265, 263	24.46	137.1	69.9	96.7	5.9
(16) 4,4-DDT	235, 237	26.63	6.0	17.5	65.8	10.1
(17) Methoxychlor	227, 228	28.43	3.2	22.5	86.7	3.4

* First and second ion mass correspond to target and qualifier ions, respectively.

mass PAHs, because the recoveries are not quantitative for molecular masses over 202.

The situation of pesticides is different than that of PAHs, because in the former compounds it is possible to find a broad spectrum of polarities, consequently variables related to the leaching process would affect the extraction of each compound in a different way.

3.1. Effect and optimization of variables

It is known that the soil composition drives the pesticide mobilization in a soil matrix. Soil is a complex matrix of inorganic and organic constituents. The specific portion of the soil to which a contaminant interacts will depend on both the compound and the matrix, as well as the time of contact between them. The most realistic situation for evaluation of an extraction technique is the use of a native contaminated soil. However, because it is practically impossible to find a natural matrix contaminated with all the analytes under study, the use of a spiked soil that has been allowed to age appears a good model for evaluation of the leaching technique.

The reason for using a certified non-polluted soil for optimization studies was the certified absence of

organic pollutant on it. However the contents of organic matter and clay in this soil are low (0.5 and 3.3%, respectively). In order to determine if the immobilization of pesticides in this blank soil agree with a representative condition, we compare the response by using a real Chilean soil from an agricultural region, which was spiked under the same conditions. In this soil the contents of organic matter and clay were 8.6 and 26.6%, respectively.

3.2. Effect of temperature on pesticide extraction

The effect of the temperature on pesticide extraction was checked using different temperatures in the range of 50–300 °C. As shown in Fig. 2, for some representative compounds, the best efficiency was found at 300 °C. The behavior observed for each pesticide depends on its polarity. The highly polar carbofuran presents a high solubility even at 50 °C. At 100 °C this compound is quantitatively extracted. The less polar pesticides show a consequently lower solubility to 50 °C, higher temperatures being required for their extraction. As can be seen in Fig. 2, the solubility of the pesticides increases with the temperature trending to the quantitative extraction at temperatures near to 300 °C. In order to study the possible thermolability of some analytes at high

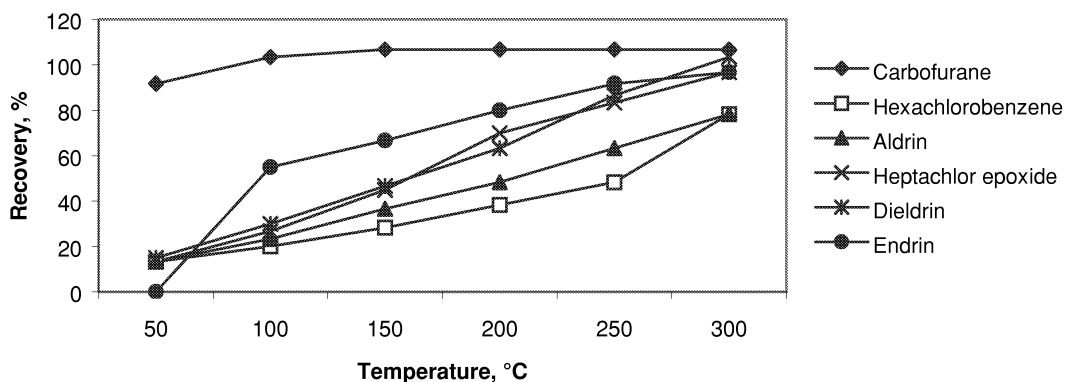


Fig. 2. Effect of the temperature on the subcritical water extraction of pesticides from soil. Dynamic extraction time, 90 min; static extraction time, 0 min; flow-rate of water, 2 ml/min.

temperature, the same study was carried out for all pesticides in the interval 250–300 °C, determining the recovery in 10°C increments in this interval. It was observed that for all pesticides the maximum recoveries were obtained between 260 and 280 °C, falling significantly for some compounds beyond this range, probably due to water under this condition decomposing those compounds that are thermolabile or prone to hydrolytic attack. Taking this effect into consideration a temperature of 270 °C was selected as optimum.

According to Crescenzi et al. [9] when the extraction temperature increased from 90 to 130 °C, the extraction of terbutylazine, alachlor and metholachlor increased by approximately 20%. The extractions did not further increase either by setting the extraction cell temperature at temperatures above 130 °C or by increasing the extractant volume. In the present study we found a different effect for alachlor and metholachlor, the extraction increased until 260 °C reaching a recovery between 90 to 100%, and then the recovery started to decrease until it reached 55% at 300 °C.

On the other hand, thermostability is an important issue in pesticide determination, because it has been established that high temperature shows some evidence of decomposition for some pesticides. For example, extraction performed at 130 °C dramatically decomposed phenylurea pesticides such as monolinuron and linuron [9]. Further, it has been observed that 99% of dehalogenation of lindane occurred

when a water solution is exposed to static subcritical conditions at 200 °C for 60 min [27].

3.3. Effect of time and flow-rate on extraction

The effect of static time in the extraction efficiency appears to be negligible. Some tests were done to check this effect, however there was no clear evidence showing the importance of this variable. This result is consistent with the studies made by Hawthorne et al. [28] with soils contaminated with PAHs, metolachlor and pendimethalin. They observed that the extraction of these pesticides and PAHs from the soils with subcritical water did not depend on kinetics, and only appeared to depend on the soil/water distribution equilibrium during the extraction.

On the other hand, the dynamic time on the extraction efficiency was found quite important. As can be seen in Fig. 3, for some representative compounds, in the interval 5–25 min of dynamic extraction all pesticides are extracted to a good extent, which indicates that with a 25-min extraction we can use the method for screening purposes (Table 1). The precision obtained at 25 min of extraction, expressed as relative standard deviation (RSD), was between 3.0 and 25%. By increasing the dynamic extraction time, additional amounts of pesticides continues to be recovered little by little. The quantitative extractions for all analytes are almost achieved at 90 min (Table 1). This time would

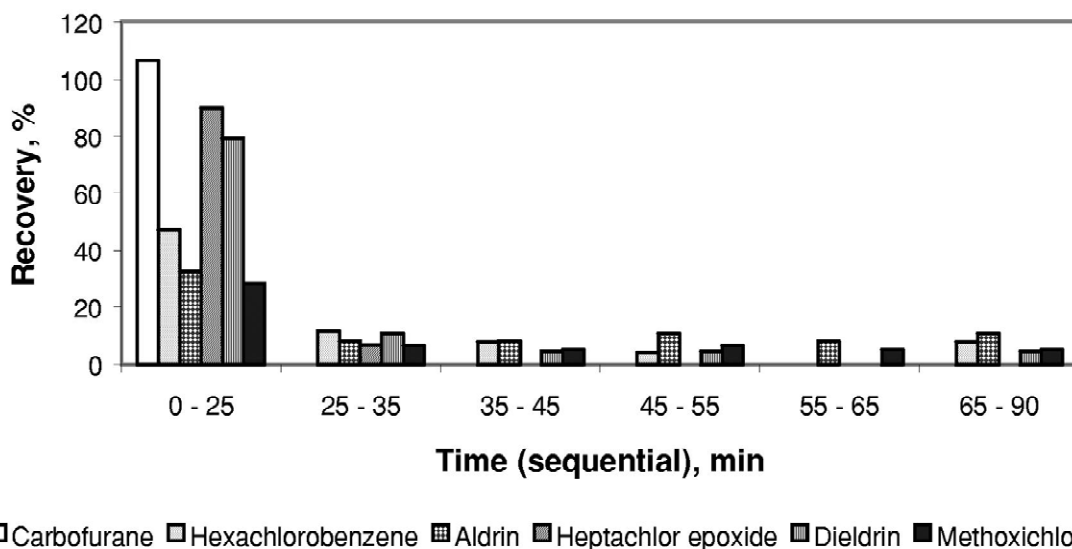


Fig. 3. Effect of dynamic extraction time on the subcritical water extraction of pesticides from soil. Temperature 270 °C, static extraction time, 0 min; flow-rate of water, 2 ml/min. Different temperature extractions were performed sequentially using the same soil sample.

correspond to the quantitative method. This effect was studied at an extraction temperature of 270 °C.

Kamer et al. [29] reported a comparison of the recoveries of pesticides such as: diazinon, malathion, chlorpyrifos, chlordane and DDT, from a spiked sand using different extraction techniques, including static batch subcritical water extraction. Conventional Soxhlet had a much higher average recovery (74%) compared with static batch SBWE (9%). In this instance, it is possible to associate the low recovery obtained by batch SBWE with the eventual re-adsorption of the analytes when water is cooled in contact with the sample after the leaching period.

A clear advantage of the dynamic extraction process over the batch static alternative is that in the former, the water is cooled outside of the extraction cell, avoiding the possibility of re-adsorption of the analytes on the solid matrix. This is a quite important issue to be considered, since it has been observed in the case of higher-molecular-mass PAHs, that some partitioning back to the solid occurs [10].

It was observed that the flow-rate of subcritical water does not affect the dynamic extraction process between the studied range (1–3 ml/min). A flow-rate of 2 ml/min was selected for further studies.

Finally, the optimal conditions for the subcritical

water extraction method were found in the following set up: aluminum chamber temperature: 270 °C; dynamic time under extraction: 25/90 min (screening/quantitative purposes); water flow-rate through the extraction unit: 2 ml/min.

The solvent extracts were finally characterized by GC–MS. The same GC–MS method and chromatographic conditions were applied to the extracts obtained using both methods (Soxhlet and subcritical water extraction).

Once the variables with the spiked certified non-polluted soil were optimized, the extraction of the spiked pesticides on the real spiked soil was carried out, with the obtained recoveries being statistically equivalent to the recoveries listed in Table 1.

Processing six samples of the spiked real soil under the selected conditions assessed the repeatability of the method (Table 1). The RSDs of the determinations were in the range 2–34%. The detection limits of the combined extraction method and GC–MS technique were determined by spiked soil samples extracted under the optimal conditions. The detection limits of the method for the pesticides were between 3.2 and 137.1 µg/kg, defined at a signal-to-noise ratio of 3 (Table 1).

A critical comparison between the results obtained

using the present method and those obtained by Soxhlet extraction was done. Data for subcritical water conditions (270 °C and 90 min dynamic extraction) are quite comparable to the values obtained for the Soxhlet extractions (recoveries between 72.2 and 121.7%, with RSDs between 0.7 and 1.5%). As can be seen, the precision is better for Soxhlet which shows RSDs always less than 1.5%, compared with the SBWE method which varies between 2.33 and 34%. The main advantages of SBWE over the Soxhlet method is the time involved in the extraction process; SBWE is 10 times faster than Soxhlet extraction. Further, the use of organic solvent in SBWE is less than 10 ml compared with 300 ml for Soxhlet. On the other hand, the SBWE method can be easily automated.

3.4. Analysis of real soil samples

In order to demonstrate the utility of the method, six soil samples collected in agricultural fields from the VI Region (Chimbarongo) of Chile were analyzed for pesticides following the optimized conditions. Taking into account that spiked target compounds are typically extracted from soil more efficiently than native contaminants, after 90 min of dynamic extraction, an additional extraction of 30 min was performed to each sample in order to check if additional amounts of analytes are extracted.

In two samples the only analyte present was hexachlorobenzene at concentrations of 0.25 ± 0.05 and 0.50 ± 0.03 mg/kg. In all samples the concentrations of all other pesticides under study were found below the detection limit (Table 1) of the method. The extraction using 90 min was quantitative for the hexachlorobenzene, since the presence of this pesticide was not observed in the additional extract of 30 min.

The presence of hexachlorobenzene in the analyzed soils is probably associated with the recent prohibition of this pesticide in Chile in January 2002.

4. Conclusions

The current methods of pesticide analysis are typically solvent and labor intensive with the most time and effort spent on sample pretreatment.

In the present work the optimization of variables associated with the extraction of pesticides in soil has been carried out by using the subcritical water extraction system. One important aspect is that quantitation becomes easier and more reliable because the amount of coextracted material is minimized thus eliminating/minimizing background and interfering compounds.

When the extraction is carried out under the optimal conditions the analytes are extracted quantitatively in 90 min as shown by recovery studies by using reference materials. An extraction time of 25 min is sufficient for screening purposes. The method was applied to spiked and real samples of soils. The results provided by the proposed method agree well with those obtained by the conventional Soxhlet method. When a critical comparison is established between the proposed subcritical water extraction and the conventional Soxhlet extraction method, it can be concluded that: (a) the time of analysis is decreased from 20 h to less than 2 h. (b) The organic solvent used in the extraction procedure can be decreased to less than 2%. (c) The precision of the SBWE method is lower than that of the Soxhlet method.

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