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# Monitoring of Pesticides Residues in Italian Mineral Waters by Solid Phase Extraction and Gas Chromatography Mass Spectrometry

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## ABSTRACT

Twenty-two pesticides and metabolites, selected on the basis of regional priority lists, were surveyed in thirty Italian mineral waters springs for three years by a procedure based on solid phase extraction in combination with gas chromatography coupled with mass spectrometry detection. The procedure proved to be simple, sensitive and reliable, the limits of detection and relative standard deviations were respectively in the range of 0.002 - 0.04 μg/L and 3% - 7%, recoveries ranged from 86% to 105% at the European Union Maximum Acceptable Concentration (MAC). Pesticide residues were detected in just one of the ninety water samples analyzed but no one exceeding the MAC. These results demonstrate the good quality of Italian mineral waters, not forgetting the need of constant revision and update of the priority list of pollutants.

**Keywords:** Mineral Water, Pesticides, SPE, GC-MS

## 1. Introduction

The packaged waters sector is growing steadily over the last few years. The worldwide consumption of packaged waters can be estimated to be around 200 billion L in 2008, which means that the rate was 25 - 26 L/per capita/year. Data in **Table 1** show the world market of bottled water in 2008 compared to 2003, with Italy being the highest consumption (each citizen consumes 200 L/year). Italian production of bottled water has increased by of 30% over the last 5 years. In Italy there are more than three hundred brands of Italian bottled waters recognized by the European Community, with 46% of bottled waters being in Northern Italy while only 15% in the South [1].

In Italy pesticides consumption for agricultural use for the 2008 was about 150 thousand tons, being the fungicide class the most used (63.4%) followed by insecticide and acaricide (10.5%). Almost half of the pesticides are used in the Northern regions, the 12 percent in the central the remaining in the Southern [2]. Several studies have provided evidence that pesticides can be transferred rapidly at high concentrations beyond the root zone, therefore leaching of pesticides from agricultural soils may threaten the quality of drinking water resources [3,4].

Generally, pesticide residue analysis is carried out following several steps, e.g. extraction from sample matrix, clean up and final chromatographic separation and determination. Thus, environmental water samples cannot be analysed without some preliminary sample preparation.

In this sense, liquid-liquid extraction (LLE) has been employed for many years as the routine technique for the extraction of pesticides from environmental water samples. However, LLE presents some disadvantages such as being time-consuming and requiring consumption of large amounts of organic solvents, so this technique has been replaced by other methodologies such as SPE, solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) or liquid phase microextraction (LPME). Despite the advantages of these microextraction techniques, SPE is still widely accepted as the best technique for isolating pesticide residues in water samples, because it is fast, accurate, precise, consumes small volume of organic solvent, does not involve costly material and a wide range of selective sorbent materials are available. The most widely used sorbents are C8 and C18 chemically bonded to silica, carbon black and polymeric resins. The sensitivity of this technique can be increased in micropollutants from water and has now become the method of choice in order to carry out simultaneously the extraction and concentration of many pesticides and metabolites in aqueous samples [5-7].

The most widely used methods for the analysis of pesticides in water are based on GC and LC. Although conventional detectors such as electron capture detection and UV absorbance detection can be used, identification based

 

**Table 1. List of the pesticides studied.**

| Pesticide | Type | logKow* | Chemical class | Rt min | MS ion | LOD** µg/L | Max. Limit*** µg/L |
|---|---|---|---|---|---|---|---|
| 1-Molinate | H | 2.88 | Thiocarbamate | 11.14 | 1,265,583 | 0.005 | 0.05 |
| 2-Desethylatrazine | H | 1.49 | Triazine | 13.86 | 172,174,187 | 0.005 | 0.05 |
| 3-Trifluralin | H | 5.27 | Dinitroaniline | 14.19 | 306,264,307 | 0.002 | 0.05 |
| 4-Benfluralin | H | 5.29 | Dinitroaniline | 14.29 | 29,226,445 | 0.002 | 0.05 |
| 5-Desethyl-terbutilazine | H | 2.3 | Triazine | 14.3 | 186,188,201 | 0.002 | 0.05 |
| 6-Atrazine | H | 2.50 | Triazine | 16.06 | 200,202,215 | 0.003 | 0.05 |
| 7-Propazine | H | 2.94 | Triazine | 16.27 | 214,216,229 | 0.005 | 0.05 |
| 8-Lindane | I-R | 3.69 | Organochlorine | 16.47 | 181,183,217 | 0.01 | 0.05 |
| 9-Terbuthylazine | A-H-M | 3.04 | Triazine | 16.78 | 214,216,173 | 0.005 | 0.05 |
| 10-Diazinone | I-A | 3.30 | Organophosphorus | 17.42 | 179,137,152 | 0.02 | 0.05 |
| 11-Chlorthalonil | F | 3.05 | Substitued benzene | 17.99 | 264,266,268 | 0.003 | 0.05 |
| 12-Metil parathion | I | 2.86 | Organophosphorus | 19.88 | 109,125,263 | 0.005 | 0.05 |
| 13-Alaclor | H | 2.63 | Chloroacetoanilide | 20.29 | 160,188,146 | 0.002 | 0.05 |
| 14-Linuron | H | 3.00 | Urea | 21.56 | 61,248,250 | 0.005 | 0.05 |
| 15-Malathion | I-A | 2.75 | Organophosphorus | 22.10 | 127,125,173 | 0.03 | 0.05 |
| 16-Pendimetalin | H | 5.18 | Dinitroaniline | 24.44 | 252,162,192 | 0.002 | 0.05 |
| 17-Meditathion | I-A | 2.20 | Organophosphorus | 25.91 | 145,85,93 | 0.005 | 0.05 |
| 18-Oxadiazon | H | 4.80 | Unclassified | 27.90 | 175,177,258 | 0.002 | 0.05 |
| 19-Oxadixyl | F | 1.40 | Aniline | 29.50 | 163,132,233 | 0.002 | 0.05 |
| 20-Phosalone | I-A | 4.30 | Organophosphorus | 33.15 | 182,184,121 | 0.005 | 0.05 |
| 21-Azinphos methyl | I-A | 2.96 | Organophosphorus | 33.18 | 77,160,132 | 0.04 | 0.05 |
| 22-Azinphos ethyl | I-A | 3.18 | Organophosphorus | 34.11 | 132,160,77 | 0.02 | 0.05 |

H = herbicide, I = insecticide, A = acaricide, M = microbiocide, R = rodenticide; *Values from Royal Society of Chemistry 1994; **LOD: limit of detection for a signal-to-noise ratio S/N = 3; ***Maximum Acceptable Concentration (Dir. 2003/40/EC).

only on chromatographic analysis (retention time) without the use of spectrometric detection is not suitable as confirmatory method so MS detection has found to be indispensable for high sensitivity and unambiguous detection, confirmation and determination of such residues in different matrices.

The main objective of this study is to determine the occurrence of 22 selected pesticides in 90 mineral water samples coming from three Italian regions, during a three year period (2006-2008) in order to assess the actual impact of the applied practices on the groundwater quality.

## 2. Materials and Methods

### 2.1. Sampling

Mineral water samples were collected in a three year period from 2006 to 2008 in Pyrex borosilicate amber glass (1L) capped with Teflon lined screw caps and stored at 4˚C. The three sampling sites were in the following Italian regions: Emilia (North Italy) the first region for pesticides use in the country, with about 22 thousands tons and 40 springs of bottled mineral waters; Toscana (Centre Italy) with more than 6.6 thousands tons of pesticides used and 37 springs and Campania (South Italy) where in 2008 were used nearly 10 thousands tons of pesticides and has in its territory 18 springs.

Each year, during the summer season, in each region ten wells were sampled, for a total of 90 samples collected. Mineral water samples from Emilia and Toscana had a TDS concentration < 500 mg/l, while those from Campania had a TDS concentration > 500 mg/l and two of them were naturally carbonated with an average $CO_2$ content of 1900 mg/l.

### 2.2. Chemicals and Materials

Pesticide standards of analytical grade were purchased from Riedel de Haen (Seelze, Germany), with a purity >99%. Individual stock standard solution, containing 0.1 µg/ml of each pesticide were prepared in acetone and stored at –20˚C. Working standard mixture solutions were prepared by appropriate dilution with n-hexane and stored under refrigeration (4˚C).

Pesticide-quality solvents (n-hexane, acetone, methanol, ethyl acetate) were supplied from J.T. Baker (Deventer, The Netherlands). SPE extraction columns LC18

 

(500 mg, 6 ml) were purchased from Sigma Aldrich. Ultrapure water was obtained from a Milli-Q water system (Millipore, Bedford, MA, USA). An extraction manifold from Alltech (Alltech Associates, Deerfield, USA) was used for the SPE analysis.

## 2.3. Instrumentation

**GC-MS Separation and Determination**

All analysis were performed with Finnigan Trace GC ultra gas chromatograph coupled to a Finnigan Polaris Q mass spectrometer (Thermo Electron Co., Austin, Texas). Separations were conducted on a DB-5 ms fused-silica column, 30 m × 0.25 mm × 0.25 μm film thickness (J&W Scientific, Folsom, CA), with helium as carrier gas, at a flow of 1.0 ml/min.

The column was held at 70˚C ramped 15˚C/min to 150˚C, then up to 200˚C at 3˚C/min and finally ramped at 8˚C/min to 300˚C and held for 5 minutes. A volume of 2 μl of sample extract was injected manually on a PTV injector operating in splitless mode. The injector temperature was set at 60˚C. The mass spectrometer operated in the EI mode. The parameters were set at the following values: an electron energy of 70 eV and a filament emission current of 200 μA. The interface and ion source temperatures were maintained at 250˚C and 200˚C, respectively. The scan mode was used between m/z 40 and 350.

## 2.4. Procedure

Samples of mineral water naturally carbonated were degassed in an ultrasonic bath for 5 min.

**Spe Procedure**

The procedure followed the guidelines EPA Method n 525 [8]. SPE C18 cartridges were conditioned with 5 ml of ethyl acetate, followed by 5 ml of methanol and 10 ml of bidistillated water, without allowing the cartridge to dry out. Then, 2.5 ml of methanol were added to 500 ml of water sample that was passed through the conditioned cartridges at a flow rate of approximately 8 ml/min under vacuum. The cartridges were dried for 10 min under vacuum and afterwards the analytes were eluted from the solid phase with 5 ml of ethyl acetate, traces of water were removed with anhydrous sodium sulphate. The eluate was evaporated to dryness under a stream of nitrogen and the residue was dissolved in 0.5 ml of n-hexane.

# 3. Results

The quality of water for human consumption has always been and still is one of the most serious challenges. Since the late decades, concern about the contamination of water sources has risen due to the increasing number of pesticides detected. Regulations for drinking water are required in order to limit human risks and environmental pollution. These regulations are well defined in Europe, setting at 0.05 μg/l of each pesticide concentration limit in mineral water samples. Consequently, it becomes necessary to provide control laboratories with analytical methods allowing the monitoring of pesticide residues at this trace level, with basic performance data in agreement with the drinking water EC Directives 98/83 and 2003/40 requirements [9,10].

Pesticides used in agricultural practices are several, therefore to ensure an effective quality control it is necessary to develop a list of priority substances to be monitored by the producers themselves who are obliged to carry out annual controls by Italian law. The methodology developed to generate the list of priority substances is based on relevant factors, including for example sale data, the target, their degradation, the environmental distribution, which results from many chemical characteristics such as molecular weight, vapour pressure, solubility in water and octanol/water partition coefficient (Kow). The priority list, that includes the pesticides considered in this study, is developed by the Italian Environmental Protection Agency.

In this study a multiresidue method based on SPE and GC separation with MS detection were utilised to assess the presence of 22 selected pesticides residues in 30 Italian mineral water wells for three years. The method showed to be suitable to the analysis of these compounds since they were detected at low concentrations, according to European Union maximum admissible concentration (**Table 2**). The LODs were calculated multiplying by three the average value of the noise sampled at the retention time of each analyte. Repeatability and reproducibility studies yielded Relative Standard Deviations (RSDs) lower than 7% in all the cases, with recoveries ranging from 86% to 105% evaluated at 0.05 μg/l spiked level. All measurements were performed in triplicate. The typical chromatogram is showed in **Figure 1**. During the screening only in 2007 one sample belonging to an Emilia well had a level of meditathion of 0.01 mg/l which is over our detection limit but under the European Union Maximum Acceptable Concentration (MAC) (**Table 2**).

# 4. Discussion

Italy is the nation with highest production and consumption of mineral waters in the world. The results of this three-year study on pesticide residues in 90 mineral water samples coming from three regions with intensive use of pesticides, are reassuring for the quality of Italian mineral waters, being residues detected in just one sample and at a concentration lower than the European Union Maximum Acceptable Concentration (MAC).

The multiresidue analytical method used has proved to be sensitive and reliable. The method does fulfill the detection limits required by the EC Directive, with LOD

 

**Table 2. Results of the pesticides determination in mineral waters (µg/l).**

| Pesticides | Emilia | | | Toscana | | | Campania | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2006 | 2007 | 2008 | 2006 | 2007 | 2008 | 2006 | 2007 | 2008 |
| 1-Molinate | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 2-Desethylatrazine | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 3-Trifluralin | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 4-Benfluralin | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 5-Desethyl-terbutilazine | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 6-Atrazine | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 |
| 7-Propazine | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 8-Lindane | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 9-Terbutilazine | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 10-Diazinone | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| 11-Chlorthalonil | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 | <0.003 |
| 12-Metil parathion | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 13-Alaclor | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 14-Linuron | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 15-Malathion | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| 16-Pendimetalin | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 17-Meditathion | <0.005 | <0.005 | <0.005 | <0.005 | 0.01 | <0.005 | <0.005 | <0.005 | <0.005 |
| 18-Oxadiazon | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 19-Oxadixyl | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 |
| 20-Phosalone | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 | <0.005 |
| 21-Azinphos methyl | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| 22-Azinphos ethyl | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |

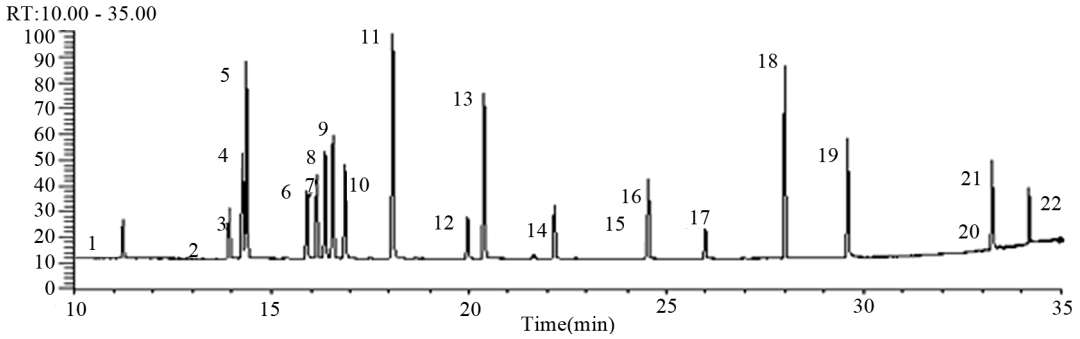


**Figure 1. Total ion GC/MS chromatogram of a 22 pesticides standard mixture. Peaks are listed in Table 1.**

ranging from 0.002 to 0.04 µg/L, and therefore is useful to verify occurrence and frequency of pesticides belonging to a priority list in mineral waters.

Considering the costs and the social relevance that are related to such monitoring activities, appears to be essential that the priority list of pesticides is regularly reviewed and developed on a regional basis.

## 5. Conclusion

The aim of this study was to evaluate the risk to water resources of 22 priority pesticides. It is a significant example of a three year monitoring of a sector with great relevance for economy and public health, involving 90 samples from three sampling sites at high risk of water resources contamination for massive use of pesticides. To our knowledge, this the first example in literature of a such long screening of pesticides in mineral waters coming from areas with intensive agricultural practices. The simple, reliable and sensitive multiresidue analytical method, optimized to assess the presence of these contaminants, has proved to be suitable for routine analysis of pesticides residues in both environmental and drinking waters monitoring.

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