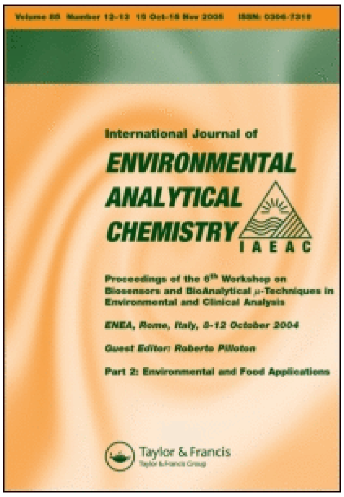

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EVALUATION OF PESTICIDE CONTAMINATION OF GROUND WATER IN TWO AGRICULTURAL AREAS OF PORTUGAL

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In two Portuguese agricultural areas, "Beira Litoral" and "Ribatejo e Oeste", several pesticides regularly applied in vineyards, maize, potato, tomato for industry, apple, pear and rice were detected in ground water.

Atrazine was the most frequently detected, being found in 70% of the total of 79 sites selected in the year 2000, followed by its metabolites desethylatrazine and desisopropylatrazine with frequencies of detection, respectively, of 56% and 48% and by simazine (37%), alachlor (25%), metolachlor (24%) and metribuzin (15%). Other pesticides and metabolites i.e. 3,4-dichloroaniline, dimethoate, α and β-endosulfan, lindane, molinate and prometryn were also detected but at lower occurrences. Pesticides were detected mainly in ground water wells used for irrigation purposes, although in some locations they were also found in water wells used for human consumption. In this study, it was also observed a seasonal variation of pesticide residues in ground water of shallow and deep wells.

Keywords: Pesticides; contamination; Ground water; Portugal

INTRODUCTION

The preservation of water quality, particularly of ground water, has been considered a priority, being pesticides contamination looked with great concern, due to the persistence that these compounds usually have in ground water and to the use of this resource in human consumption. Pesticide treatments in agricultural areas have been responsible for the contamination of water resources worldwide. In Portugal, several pesticides, particularly herbicides, have also been detected in ground water.

The evaluation of exposure of Portuguese ground water to pesticides started in the beginning of the 1990s. Initially the studies were focused on atrazine in maize areas [1,2] and then were enlarged to other pesticides and agricultural ecosystems [3–5].

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In these studies, which evaluated only exposure to herbicides, atrazine, simazine and alachlor were the most frequently found [5,6].

In order to determine ground water contamination to a larger number of pesticides a study was performed during the year 2000, in two important agricultural regions of Portugal, where these products are regularly used. In this paper, the results of their occurrence and dynamic in ground water are presented.

EXPERIMENTAL

Study Area

The studies were developed in "Beira Litoral" and "Ribatejo e Oeste" Agricultural Regions, due to the hydrogeological vulnerability of some of their areas [7], evaluated by DRASTIC index and to the relevance of ground water resources in Centre and Tagus–Sado hydrographic Regions [8] where these agricultural areas are located (Table I). In fact, in "Beira Litoral" a large area has DRASTIC indices between 160 and 226 and in "Ribatejo e Oeste" several locations, namely along river Tagus, also show similar indices [7].

"Beira Litoral" is situated in the Western Middle Cenozoic fringe, ranging from the Triassic to Recent and which are almost sedimentary. The formations are basically carbonates (limestone, marl and dolomite), clay and sand. "Ribatejo e Oeste" is located in the sedimentary basins of the Tagus and Sado, made up of formations which range in age from the Palaeogene to Recent. They occur in the terminal part of the hydrographic basins of these two rivers. The Cenozoic formations consist mainly of limestone, sandstone, siltite, argillite and marl, whereas the Recent formations consist of sandy and sandy-argillaceous material of alluvial origin. The detrital levels are of great hydrogeologic significance. They contain the most important water reservoirs in Portugal with depths attaining 500 m.

Main Crops and Pesticides Used in the Study Areas

In Centre Region the main crops are vineyard, maize, potato, rye and bean [9]. In "Ribatejo e Oeste" vineyard, maize and potato are also important crops, as well as sunflower, tomato for industry and orchards [10].

The priority crops considered for this study were those in which pesticides where regularly applied, namely maize, potato, tomato for industry and vegetables, and which are intensively irrigated, and yet vineyard and orchards. Rice was also selected since it is a

TABLE I Ground water resources of Portuguese hydrographic regions [8]

Hydrographic region	*Resources* (km^3)
North	0.04
Centre	19.70
Tagus–Sado	102.12
Alentejo	4.87
Algarve	2.69
Portugal (Continental)	129.42

crop growing in some areas of "Beira Litoral" and "Ribatejo e Oeste", with a large consumption of pesticides.

The compounds introduced in larger quantities in the studies areas are the fungicides copper (both sulfate and oxychloride), fosetyl-aluminium, mancozeb, propineb, sulfur, zineb, the herbicides alachlor, amitrol, atrazine, bentazone, dimepiperate, EPTC, glyphosate, metolachlor, metribuzin, molinate, paraquat, prometryn, propanil, quinclorac, simazine, and the insecticides carbofuran, dimethoate, endosulfan, lambdacyhalothrin and lindane, being some of them the most used pesticides in Portugal [11].

The selection of pesticides to be analysed was based on pesticide use and on their ground water contamination potential, based on calculations using fugacity model (Level 1) [12] and a leaching index [13]. Organic pesticides with high affinity for the water compartment or with high leaching potential were given priority for the field studies. The selection also took in account the availability of multiresidue methods for their identification and quantification.

The herbicides and metabolites alachlor, atrazine, desethylatrazine, desisopropylatrazine, metolachlor, metribuzin, molinate, prometryn, propanil, 3,4-dichloroaniline and simazine, as well as the insecticides dimethoate, lindane and α and β-endosulfan were selected for analysis.

Selected Sites for Ground Water Sampling

Water sampling was carried out in 79 sites, being most of them drilled holes with water pumping system.

In "Beira Litoral" a total of 43 sites were considered (nine drilled holes, three wells and three springs used for human consumption and 8 drilled holes and 20 wells used for irrigation purposes) and in "Ribatejo e Oeste" a total of 36 sites were selected (14 and 22 drilled holes used, respectively, for human consumption and irrigation purposes).

Analytical Methodology

Chemicals

Pesticide grade ethyl acetate and dichloromethane obtained from Riedel-de-Haën (Seelze, Germany) and methanol from Merck (Darmstadt, Germany) were used. Pesticide standards, with certified purities equal or higher than 96.1%, were purchased from Riedel-de-Haën (Seelze, Germany).

Sample Preparation

A six-station manifold extraction disk apparatus from 3 M Empore was used, as well as membrane extraction disks, with 47 mm diameter and 0.5 mm thick, also from 3 M Empore and distributed by Varian (Harbor City, CA, USA).

The protocol was as follows: each disk was placed in the 3 M Empore apparatus and washed with 5 mL of solvent mixture ethyl acetate + dichloromethane (1 : 1, v/v), and then conditioned with 5 mL of methanol and 10 mL of deionised water. The water sample (1 L) was loaded and the SDB-phase was rinsed with deionised water (10 mL). The disk was dried for 20 min in the apparatus with vacuum to remove residual water that could cause degradation of some pesticides. After sample extraction, the pesticides trapped in the disk were collected in elution tubes using 3×5 mL of solvent mixture ethyl acetate + dichloromethane (1 : 1, v/v) for elution. After careful evaporation of the solvent to 1 mL using a gentle stream of nitrogen, extracted residues were carefully transferred to a graduate tube and were evaporated to a final volume of 200 µL for GC–MS detection.

Gas Chromatography–Mass Spectrometric Analysis

Gas Chromatography–Mass Spectrometric analyses were performed with a Varian ChromPack CP-3800 Gas Chromatograph coupled with a Saturn 200 GC/MS equipped with an Ion Trap detector, from Varian (Walnut Creek, CA, USA). A J&W DB-5MS 30 m × 0.25 mm Low Bleed/MS column was used (Folfom, USA). Helium was employed as carrier gas at 12 psi. The injector, interface and mass spectrometric detector temperatures were, respectively, 270, 260 and 190°C. The column temperature was programmed from 50 to 170°C at 10°C min^{-1}, from 170 to 180°C at 1°C min^{-1}, from 180 to 200°C at 5°C min^{-1}, being 6 min at this temperature and then from 220 to 240°C at 15°C min^{-1}, with final time of 4 min. Ionization mode was by Electronic Impact (EI). Ions used for identification and quantification were the following (in parentheses): alachlor (160 + 188), atrazine (200 + 215), desethylatrazine (172 + 187), desisopropylatrazine (158 + 173), dimethoate (87 + 125), α-endosulfan (195 + 241), β-endosulfan (195 + 241), lindane (181 + 219), metolachlor (162 + 238), metribuzin (144 + 198), molinate (98 + 126), prometryn (184 + 241), propanil (161 + 163 + 217), 3,4-dichloroaniline (161 + 163 + 126) and simazine (186 + 201).

Recoveries and Detection Limits

The recoveries obtained through the methodology used for the pesticides to be studied ranged between 81 and 100%, except for α-endosulfan, with a recovery of 73%. On the other hand the detection limits were lower than 0.023 µg/L for all the studied pesticides.

RESULTS AND DISCUSSION

In 72% of the 79 studied sites pesticide residues were detected in ground water. This high frequency of pesticide detection is probably due to the hydrogeological vulnerability of the selected agricultural areas.

In 40% of the sites the detected levels (one or more pesticides) were lower than 0.1 µg/L, in 32% of them residues were above that value, being in 10% higher than 1 µg/L (Table II).

TABLE II Frequency of pesticide detection by quantified levels (one or more pesticides), in ground water of the two Portuguese agricultural areas

Agricultural area	*Frequency of detection (%)*				
	ND	≤ 0.1 µg/L	0.1–0.3 µg/L	0.3–1.0 µg/L	> 1.0 µg/L
"Beira Litoral"	31	43	12	5	9
"Ribatejo e Oeste"	25	36	14	14	11
Total	28	40	13	9	10

ND – not detected.

TABLE III Pesticide occurrence (one or more pesticides) in ground water sampled in two Portuguese agricultural areas from drilled holes, wells and springs used for irrigation and human consumption

	No. and % of studied sites			
	No. of sites	*Sites with no detection*	*Sites with detection*	*Sites with detection > 0.1 µg/L*
Irrigation water				
Total	50	5 (10%)	45 (90%)	24 (48%)
Drilled holes	30	5 (17%)	25 (83%)	14 (47%)
Wells	20	0 (0%)	20 (100%)	10 (50%)
Drinking water				
Total	29	17 (59%)	12 (41%)	1 (3%)
Drilled holes	23	16 (70%)	7 (30%)	0 (0%)
Wells	3	0 (0%)	3 (100%)	1 (33%)
Springs	3	1 (33%)	2 (67%)	0 (0%)

In the irrigation wells pesticides and/or metabolites (one or more pesticides) were frequently found at levels above 0.1 µg/L (50%), showing that shallow ground water is easily contaminated with pesticides. They were also found in the majority of irrigation drilled holes (83%), with levels above 0.1 µg/L in 47% of the sites (Table III). Pesticides and/or metabolites were also detected in ground water sampled from drilled holes, wells and springs used for human consumption, but in general their occurrence was below 0.1 µg/L (Table III).

The pesticides and/or metabolites most frequently found were the herbicides atrazine (70% of positive frequency), used in maize; its metabolites desethylatrazine (56%) and desisopropylatrazine (48%); simazine (37%), used in vineyards and orchards; alachlor (25%) and metolachlor (24%), used in maize and metribuzin (15%), used in tomato and potato, and which have already been detected in ground water in previous studies [1–6]. The herbicides molinate, prometryn, propanil metabolite 3,4-dichloroaniline and the insecticides dimethoate, α and β-endosulfan and lindane were also detected, but at lower frequency (Table IV).

Although the detection of some of the pesticides was relatively frequent, their occurrence at levels above 0.1 µg/L was much lower (Table IV), showing that pesticides are commonly present in ground water, in the studied areas, but in most cases at low levels. However, in some cases, high levels, of pesticide residues were detected (Table IV). The pesticides most frequently detected at levels above 0.1 µg/L were atrazine (19%), metolachlor (10%), the metabolite desethylatrazine (6%) and alachlor (6%), all of them used in maize, an important irrigation crop in the two Agricultural Regions under study.

The highest detected levels were for metolachlor (17.0 µg/L), molinate (16.3 µg/L), atrazine (11.2 µg/L), alachlor (8.0 µg/L), 3,4-dichloroaniline (3.8 µg/L), α-endosulfan (1.4 µg/L), dimethoate (1.2 µg/L) and lindane (1.1 µg/L) (Table IV). These high values found in some of the sites are most probably due to point contamination, occurring during spray tank preparation and chemigation by back siphoning and by direct transport of residues through the drilled hole or well. In studies of other authors [14–16] high levels of several pesticides have also been detected in ground water, both in Europe and North America.

Some of the pesticides most frequently found in this study were also frequently detected in ground water worldwide. In a review presented by Funari and collaborators [14], from studies carried out in Europe and North America, atrazine showed the highest degree of frequency in ground water (38% of positive frequency), followed by alachlor (10% of positive frequency). In a U.S. National study, carried out during 1993–1995 [16], the compounds most frequently detected were atrazine (38%), desethylatrazine (34%), simazine (18%), metolachlor (15%) and prometon (14%).

During the year 2000, the seasonal variation of residues in ground water was followed, showing a dynamic of the residue levels through the sampling period, which is thought to be dependent of several factors, namely hydrogeological properties of the area and cultural practices, particularly spray treatment period and irrigation. Some examples are presented in Figs. 1–4. It can be observed that, in general, there

TABLE IV Occurrence of pesticides and metabolites, in ground water, from two Portuguese agricultural areas

Pesticide or metabolite	*Occurrence (%)*	*Occurrence (%) > 0.1 μg/L*	*Maximum detected level (μg/L)*
alachlor	25	6	8.0
atrazine	70	19	11.2
desethylatrazine	56	6	0.31
desisopropilatrazine	48	0	0.09
3,4-dichloroaniline	5	2	3.8
dimethoate	5	5	1.2
α-endosulfan	6	5	1.4
β-endosulfan	6	1	0.69
lindane	6	5	1.1
metolachlor	24	10	17.0
metribuzin	15	4	0.65
molinate	5	4	16.3
prometryn	5	0	0.07
simazine	37	4	0.22

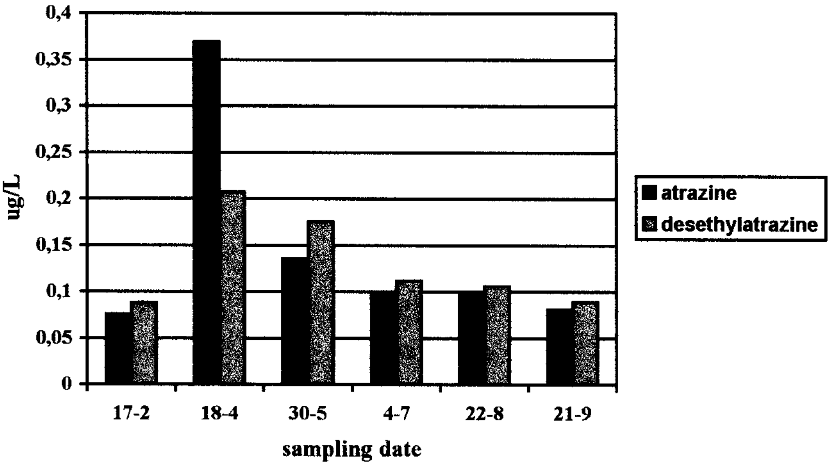

FIGURE 1 Seasonal variation of atrazine and its metabolite desethylatrazine, in a drilled hole with 15 m depth, from "Ribatejo e Oeste" (Portugal), during 2000.

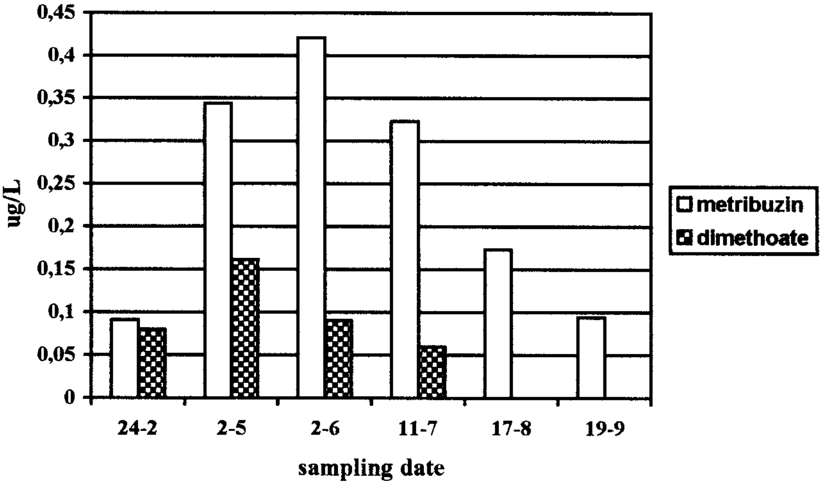

FIGURE 2 Seasonal variation of metribuzin and dimethoate, in a drilled hole with 18 m depth, from "Ribatejo e Oeste" (Portugal), during 2000.

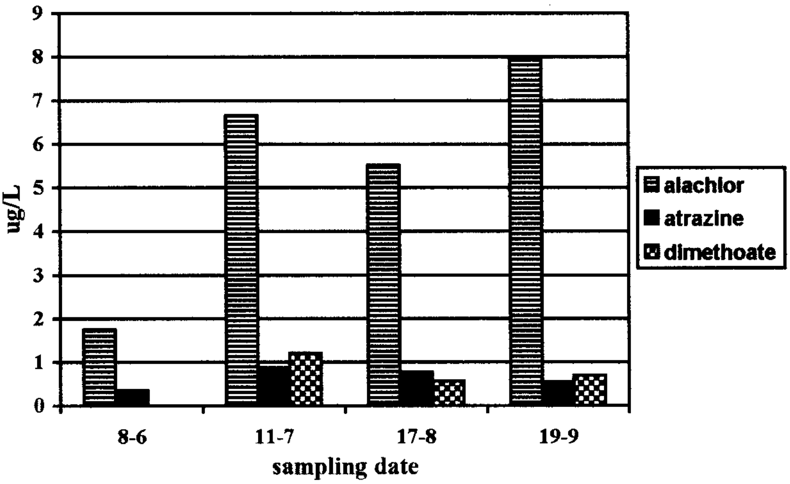

FIGURE 3 Seasonal variation of alachlor, atrazine and dimethoate, in a drilled hole with 235 m depth, from "Ribatejo e Oeste" (Portugal), during 2000.

is an increase of residue levels after the period of pesticide application, especially in the case of herbicides, which are used generally in Spring, from March to May. The highest residue levels were observed after pesticide treatment and during the irrigation period. The pronounced dynamic observed in shallow ground water, from drilled holes (illustrated in Figs. 1 and 2, respectively with 15 and 18 m depth) located in areas with a water table at ca. 5 m, could result from residues transport through the soil by preferential flow. Some authors have also pointed out seasonal variation of pesticide residues [17–20]. As in the present study, the lower levels are usually observed before Spring treatments and higher values occurring after that period, namely during irrigation period.

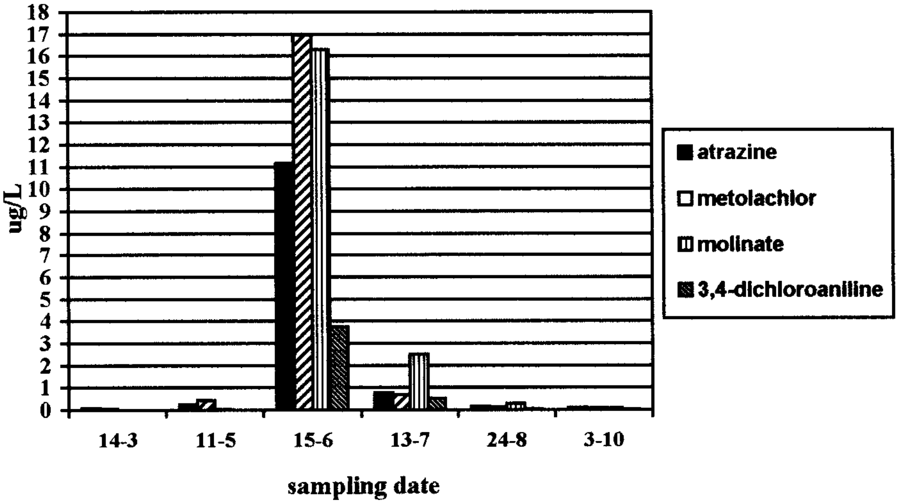

FIGURE 4 Seasonal variation of atrazine, metolachlor, molinate and 3,4-dichloroaniline, in a well with 7 m depth, from "Beira Litoral" (Portugal), during 2000.

The high levels of residues observed in cases of deep drilled holes (Fig. 3) and in shallow wells (Fig. 4), were probably due to point contaminations, as previously referred.

CONCLUSIONS

Residues of the herbicides and metabolites alachlor, atrazine, desethylatrazine, desisopropylatrazine, 3,4-dichloroaniline, metolachlor, metribuzin, prometryn, molinate and simazine, as well as residues of the insecticides dimethoate, lindane and α and β-endosulfan were detected in ground water collected in two important Portuguese agricultural areas. Some herbicides and metabolites were frequently detected in the 79 sampled sites, namely atrazine (70%), desethylatrazine (56%), desisopropylatrazine (48%), simazine (37%), alachlor (25%), metolachlor (24%) and metribuzin (15%). However, their occurrence at levels above 0.1 µg/L was much lower: 19% for atrazine, 10% for metolachlor, 6% for alachlor, 6% for desethylatrazine, 4% for metribuzin and 4% for simazine.

The highest detected levels observed in this study were 17.0 µg/L for metolachlor, 16.3 µg/L for molinate, 11.2 µg/L for atrazine, 8.0 µg/L for alachlor, 3.8 µg/L for 3,4-dichloroaniline, 1.4 µg/L for α-endosulfan, 1.2 µg/L for dimethoate, 1.1 µg/L for lindane, 0.69 µg/L for β-endosulfan, 0.65 µg/L for metribuzin, 0.31 µg/L for desethylatrazine, 0.22 µg/L for simazine, 0.09 µg/L for desisopropylatrazine and 0.07 µg/L for prometryn.

A seasonal variation of residues in ground water related namely with time of pesticide treatment and irrigation was observed. In most cases, there is an increase of residue levels after the period of pesticide treatment and during irrigation period, especially in the case of herbicides, which occurs from March to May. A pronounced variation was observed in shallow ground water, probably as a result of residue transport through the soil by preferential flow, and, in a few cases, both in shallow and deep ground water, due to point contamination of wells and drilled holes.

Pesticide residues found in ground water show that improvement of plant protection and irrigation practices are required. It is necessary to select carefully the pesticides to be used, in each agricultural area, according to its hydrogeological vulnerability applying them as recommended in the labels; providing adequate elimination of pesticides packages and wastes and avoiding direct contamination of the drilled holes and wells.

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