

Evaluation of the Pesticide Contamination of Groundwater Sampled over Two Years from a Vulnerable Zone in Portugal

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A monitoring program of pesticides was implemented in the “ZV1” vulnerable zone (Directive 91/676/EEC) in Portugal, in order to assess the impact of intensive horticulture practices on groundwater contamination. The monitoring network comprised 23 sampling points sampled every 3 months during a 2-year period. Forty-two pesticides belonging to varied chemical families, including current pesticides, persistent organic pollutants (POPs), and degradation products, were analyzed by solid-phase microextraction (SPME) and gas chromatography with electron-capture detection-thermoionic specific detection (GC-ECD-TSD) or mass spectrometry (GC-MS). Statistical treatment was performed by descriptive analysis followed by chemometric multivariate analysis. The latter included cluster analysis, linear discriminant analysis, and factor analysis. Twenty-two pesticides were quantitated, 20 pesticides were not detected, and metalaxyl, benalaxyl, quinalphos, pirimicarb, and prometryn were only qualitatively detected. The most frequently detected pesticides (% of samples analyzed) were lindane (53%), pendimethalin (49%), endosulfan sulfate (44%), and endosulfan (38%) while those that most frequently exceeded the 0.1 $\mu\text{g L}^{-1}$ European Union (EU) limit were pendimethalin (13%), endosulfan (12%), endosulfan sulfate (11%), and atrazine (9%). 45% of the samples exceeded the EU limit for individual pesticides while 27% exceeded the limit set to the sum of pesticides (0.5 $\mu\text{g L}^{-1}$). Principal component analysis revealed five principal components that were attributed to environmental/agrochemical managing factors. The broad range of pesticides investigated combined with the intensive character of the local agriculture contributed to the diversity of pesticides that were detected. However, the frequency of pesticides above the EU regulatory limit is comparable to that found in the literature concerning different Portuguese and European regions.

KEYWORDS: Environmental monitoring; vulnerable; groundwater; pesticides; lindane; endosulfan; pendimethalin; multivariate analysis

1. INTRODUCTION

Pesticide regulation falls within two approaches: exhaustive study of new candidate pesticides regulated under the European Union (EU) Directive 91/414/EEC, which advocates that pesticides shall not be found as water contaminants under normal usage practices, and monitoring studies, as a means to disclose the present contamination status and assess the impact of newly implemented measures. In Europe, monitoring groundwaters has received somewhat less attention compared to surface waters, and comprehensive monitoring surveys are urgently necessary

(1). The quality of groundwater, as far as the pesticides content is concerned, has been traditionally assessed in the European Union in respect to the 98/83/EC Directive, which establishes the quality criteria of water intended for human consumption, since this is one of the most sensitive uses of groundwater (2, 3). Recently, a specific regulation has been introduced addressing the groundwater quality (4). Besides the limit set for individual pesticides at 0.1 $\mu\text{g L}^{-1}$ (0.03 $\mu\text{g L}^{-1}$ for cyclodienes, except endosulfan), we shall call special attention also to the limit set for the sum of pesticides (0.5 $\mu\text{g L}^{-1}$) in intensively cultivated areas, because of the large number of pesticides that may coexist.

Pesticide contamination of groundwater might be anticipated when the mitigation capacity of the soil system is exceeded, especially when enhanced productivity agriculture is carried out on hydrogeologically vulnerable soils. The agriculture developed in the Mediterranean region has a strong reliance on pesticides

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(1, 2, 5). Monitoring studies carried out under realistic agronomic conditions provide a reliable insight on the threat posed to groundwater quality (6). The presence of pesticide residues in groundwater as a result of their agricultural application, with special emphasis on herbicides, is a common finding (7–10). In 1999, the European Environment Agency (EEA) reported on the status of groundwater quality in Europe, and several pesticides were ranked according to their ubiquity (2). As essential to producing monitoring data is the sound interpretation of the main trends inside often massive data sets. Combining advanced statistical exploratory features to resolve chemical issues, chemometrics is a powerful tool to reveal the most meaningful factors (11). Less obvious patterns can be highlighted in an amalgamated data matrix, namely the deduction of correlated variables, sample grouping, and outlier detection as well as definition of the sources of data variation (12, 13).

To elucidate the impact of the intensive horticulture performed in a vulnerable zone (Directive 91/676/EEC) located in Portugal, a monitoring study of pesticides was carried out comprising groundwater and soils, for a 2-year period. Herein, the results of water samples will be dealt with by descriptive and multivariate statistical approaches, whereas the main findings for soil samples have been published before (14). Vulnerability to pesticides in areas already known as vulnerable to nitrates is a highly relevant matter not thoroughly investigated so far, to our knowledge. The data gathered will help clarify this relationship. Geographical and temporal patterns will be investigated on a regional basis.

2. EXPERIMENTAL PROCEDURES

2.1. Characterization of the Samples and the Sampling Area.

To conform to the EU Directive 91/676/EEC, the protection area of the free aquifer between Esposende and Vila do Conde was designed as Vulnerable Zone no. 1 (ZV1). Although this Directive aims at reducing or impeding the contamination of the underlying aquifers by nitrates of agricultural origin, some reports correlate the concentrations of nitrate with those of pesticides (10, 15–17); thus, pesticide contamination is also a relevant topic to be investigated.

The Portuguese seashore has been mapped using the DRASTIC vulnerability index, which ascribes a value above 180 (highly vulnerable) to extensive regions included in the ZV1 (18). Although it gives a first indication of the need for protective measures, Worrall and Kolpin (19) argue that, in certain circumstances, the interdependence of the hydrogeological factors and the pesticide chemical properties may appertain higher significance to the likelihood of groundwater contamination than each factor by its own. The ZV1 is located in the littoral north of Portugal with an enclosed area of 57.3 km². In 1997, when it was established, it was delimited by the Atlantic ocean on the West, the A28 highway on the East, the Cávado river in the North, and the Ave river in the South. This is the present study area, although in the future the ZV1 will be enlarged. A map depicting the ZV1 and the selected sampling sites is shown in **Figure 1**. The local aquifer is unconfined and shallow, with a phreatic depth as low as 2–4 m in certain areas and less than 9.1 m in most areas. The majority of the cultivated area consists of sandy dunes of sedimentary origin, particularly the central region, where the fields are dug in the ground. This creates a unique configuration and climate conditions. Due to the high permeability of the soils, groundwater is easily available.

The monitoring network used in this study is shared with the national groundwater quality system which was established to support the implementation of the above-mentioned EC Directive. Initially it comprised 25 sampling points that were later reduced to 23, since sites 3, 7, and 23 were withdrawn while site 2A was added. The wells are of 1.2–1.6 m width and vary in depth from 7 to 15 m. The selected wells are used for irrigation purposes and are located in the fringe of the cultivated fields or even inside them. Particularly those lying along the eastern boundary are excavated on consolidated rock of schistic

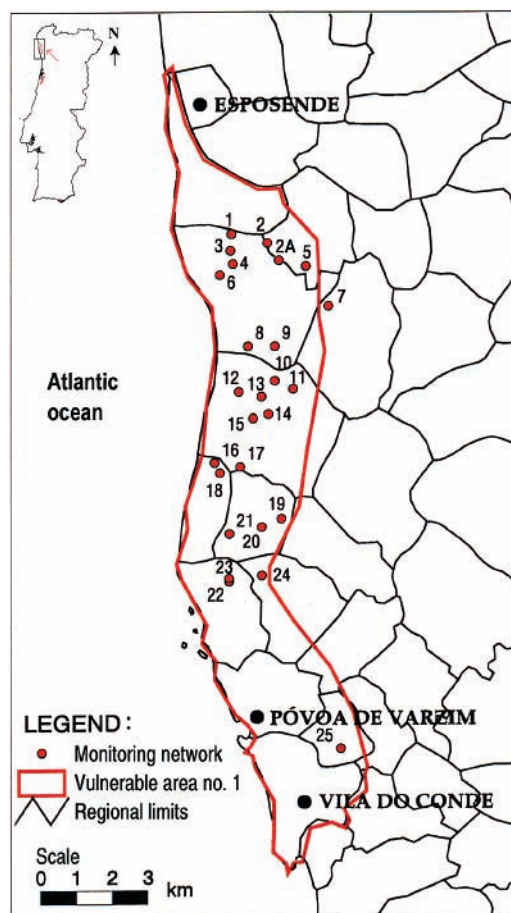


Figure 1. Map of vulnerable zone no. 1 (ZV1) designed in the framework of the 91/676/EEC Directive and showing the distribution of the sampling points considered in the present study.

and granitic type. The most popular vegetables produced in the intensive regime are tomatoes, beans, cucumbers, peppers, varieties of melon, lettuce, onion, carrots, garlic, and different types of cabbage and broccoli, either cultivated in the open air or in greenhouses. Maize, grass, and potatoes are the main crops produced in the humic cambisols of sites 5, 19, 22, and 25.

The groundwater composition is related to the soil nature: in sandy soils (central region, sites 8–18, see map) pH is typically >6.5 and conductivity goes up to 1200 $\mu\text{S cm}^{-1}$ whereas in humic soils pH is <6.5 and conductivity does not exceed 800 $\mu\text{S cm}^{-1}$. Nitrate levels are unrelated with such data, but concentrations >150 or even >300 mg L⁻¹ can be found from sites 12 to 22.

2.2. Sampling Schedule and Analytical Work. The evaluation of pesticide residues in water samples was carried out concurrently to the testing of the soil samples during a 2-year period. Collection of samples was performed in eight sampling events with an approximate schedule every trimester, as follows: September 2001, February, April, July, and November 2002, and March, July, and October 2003. Water samples were collected from the homogenized top meter of each well. An aliquot was transferred to a 40 mL amber glass vial and capped tightly with a screw cap holding a Teflon lined silicone septum. At randomly selected sampling points, duplicates were also collected and field blanks were obtained. All samples were transported to the laboratory in refrigerated containers and kept in a cool environment (4 °C) till their analysis. The analytical methodology was tailored for this monitoring program, and it was adaptable as new pesticides were identified and included in the course of the project. More sophisticated methods were applied as soon as they were developed, taking profit of the knowledge gathered in previous samplings. These multiresidue methods based on solid-phase microextraction (SPME) were conveniently optimized, validated, and calibrated each time a new sample set was to be analyzed. Briefly, the sample preparation included

extraction of a 3-mL sample volume with a PDMS-DVB 60 μm SPME fiber at 60 °C during 60 min. The sample was magnetically stirred, but no correction of the pH or ionic strength was performed (20). The samples collected in September 2001 and February and April 2002 were subjected to quantitative analysis of pesticide residues by gas chromatography and electron-capture detection-thermoionic specific detection (GC-ECD-TSD) while confirmation was carried out by gas chromatography–mass spectrometry (GC-MS), acquiring the full scan mass spectra. In the sampling of April 2002, the analysis was extended to four new pesticides, alachlor, propyzamide, pendimethalin, and procymidone, using GC-MS-MS. Later on, the samples obtained from July 2002 to October 2003 were first analyzed for a group of most frequently detected pesticides by GC-MS-MS (quantitation and confirmation) and, thereafter, for the presence of the remaining pesticides by GC-MS in μSIS mode (quantitation) and scan mode (confirmation). The target list of pesticides comprising organochlorine (OCP), organophosphorus (OPP), triazine, pyrethroid, and miscellaneous pesticides settled in each of the methods, either GC-ECD-TSD, GC-MS, or GC-MS-MS, can be found elsewhere (20, 21). Quality control samples, including blanks, control standards, and replicates, were run as part of each sample set. Shewhart control charts were built with the control standards whereas analysis of sample duplicates generated average values between 86 and 114% with border values of 70 and 133%, except for the case of endosulfan (43%) at a concentration close to the limit of quantitation (LOQ).

2.3. Description of the Data Set and the Initial Pretreatment.

The data array generated in the monitoring program consisted of concentration values for 42 pesticides (the *Z* and *E* isomers of chlorfenvinphos and the $\alpha + \beta$ forms of endosulfan were added) analyzed in 181 water samples (6976 valid observations). Site 13 failed the samplings of February, April, and November 2002 due to our inability to access the well located on a private property. The array contained additional data gaps. Values for propyzamide, alachlor, pendimethalin, and procymidone were initiated only in April 2002. Metribuzin, chlorpyrifos, deltamethrin, tetrachlorvinphos, and chlordane started being monitored only in July 2002, especially the first three pesticides, given the possibility offered by GC-MS. Metolachlor, on the other hand, was shown to be of interest only in November 2002. The threshold limit considered to report pesticide concentration values, expressed in $\mu\text{g L}^{-1}$, was the respective limit of quantitation. The spectral information required to ascertain the identity of the pesticide was obtained by single or tandem mass spectrometry with a spectral fit requisite higher than 700.

For statistical evaluation, some conversion was required in order to have quantitative data throughout. Since the attained analytical LOQs were generally far below the 0.1 $\mu\text{g L}^{-1}$ limit, in practice, concentrations below the LOQ can be considered negligible and meaningless. Thus, the following criteria were adopted: nonquantifiable results were considered as zero; quantifiable results for which identity confirmation was not achieved were also assumed as zero. A few pesticides were only qualitatively investigated in the samples, since they were considered at a later stage and had not been subjected to extensive method validation. The occurrence of trifluralin, fenthion, endrin aldehyde, azinphos ethyl, metalaxyl, benalaxyl, quinalphos, pirimicarb, and prometryn will be discussed, briefly.

2.4. Statistical Analysis of the Monitoring Results. The thorough interpretation of monitoring data requires that both univariate and multivariate statistical approaches be employed. While the former gives an uncomplicated summary of original data arguments organized by either pesticide (variable) or sample/site (case), the latter allows the deconvolution of internal relationships that lay latent in an intricate data matrix. The relevant environmental information embedded in the data matrix was first explored by means of descriptive parameters, such as frequencies, minimum and maximum values, mean, median, values above and below a reference limit, etc. Then, a stepwise multivariate analysis followed. Hierarchical cluster analysis was used as an unsupervised exploratory technique to discover unanticipated natural affinities within the data, considering associations of both pesticides and samples. The squared Euclidean distance was used as the interval measure for clustering, preferably using Ward's linkage method. Raw data were computed after standardization based on *Z*-scores by variable.

All variables that assumed a constant value equal to zero all across the samples and dates were eliminated from any multivariate statistical handling. With the purpose to reduce the "noise" present in the data, which was seen in preliminary trials to disturb the resolution of the main trends, a simplification strategy was adopted. It was based on the assumption that variables characterized by a standard error of the mean higher than the mean itself, concomitantly with a few nonzero data values (less than 5/181), should be unsuitable to display a consistent pattern linked to the environmental behavior of the pesticides. This criterion led us to additionally exclude the following pesticides from multivariate analysis: dimethoate, terbuthylazine, diazinon, metribuzin, parathion, fenamiphos, 4,4'-DDE, λ -cyhalothrin, and α -cypermethrin. It should be stressed that the requisite of a completely fulfilled matrix without data gaps to carry these calculations forced the exclusion of the two first samplings from multivariate analysis but not from descriptive analysis. Clusters of samples were further examined with the assistance of linear discriminant analysis (LDA) in order to check the discriminant capacity of the variables. Finally, factor analysis was applied to reveal the main sources of data variance, thus allowing the interpretation of eventual relationships between the pesticide results and the environmental mechanisms or agrochemical procedures that explain them. Computation was based on the correlation matrix. All the statistical multivariate handling was performed using the SPSS 14.0 for Windows software (SPSS Inc., Chicago, IL).

3. RESULTS AND DISCUSSION

3.1. Occurrence of Pesticides in Groundwater Samples.

In this monitoring program we have found pesticides from all activity classes: insecticides, herbicides, and fungicides. The pesticides metalaxyl (3), benalaxyl (11), quinalphos (5), pirimicarb (10), and prometryn (2) were only qualitatively detected, and the number of contaminated samples is quoted in parentheses. These pesticides were recognized by their characteristic mass spectra through meticulous search of the mass spectrometry chromatograms. To the best of our knowledge, a great lack of information exists regarding the presence of some of these pesticides in groundwaters; thus, this prior information vividly recommends their inclusion in future analytical work. Trifluralin, fenthion, endrin aldehyde, and azinphos ethyl were not found as contaminants in the investigated area. Propyzamide, alachlor, pendimethalin, procymidone, and metolachlor were identified by their mass spectra in an early stage of the survey; thus, they were included in the analytical methods for quantitation in the subsequent samples.

The following 20 pesticides are not considered water contaminants since they were always absent from the samples: dichlorvos, hexachlorobenzene, simazine, propazine, fonofos, parathion-methyl, simetryn, heptachlor, heptachlor epoxide, fenitrothion, malathion, aldrin, isodrin, chlordane, tetrachlorvinphos, endrin, 4,4'-DDD, 4,4'-DDT, azinphos-methyl, and deltamethrin. Fifteen of these were probably not used during 2001–2003, but the list includes nine OCPs that ought to be analyzed due to their persistence in the environment and bioaccumulation potential. Fonofos, parathion-methyl, azinphos-methyl, malathion, and deltamethrin were applied during that period, but the first three pesticides entered decline and were soon banned.

The focus of the following statistical description will be reserved to those 22 pesticides effectively quantitated in the samples, as shown in **Table 1**. This table shows the distribution of the pesticide concentrations by a few ranges of interest, namely in respect to the drinking water quality directive. Some pesticides, such as diazinon, parathion, 4,4'-DDE, and cyhalothrin, were detected in a few samples and never exceeded 0.1 $\mu\text{g L}^{-1}$. On the contrary, some pesticides found just as infrequently were quantified in excess of that limit (i.e.,

Table 1. Occurrence^a of Pesticides in Groundwater with Respect to the Regulatory Limit Enforced by the 98/83/EC Directive

	N ^b	<LOQ	LOQ < N ≤ 0.1 (%)	0.1 < N ≤ 1.0 (%)	N > 1.0 (%)	N > 0.1 (%)	mean	median	range
desethylatrazine (DEA)	181	169	0	8 (4.4)	4 (2.2)	12 (6.6)	3.4	0.58	0.14–34
dimethoate (DIM)	181	179	0	0	2 (1.1)	2 (1.1)	81	81	48 to 1.1 × 10 ²
atrazine (ATR)	181	145	19 (10.5)	14 (7.7)	3 (1.7)	17 (9.4)	2.4	0.096	0.015–42
terbutylazine (TER)	181	180	0	1 (0.6)	0	1 (0.6)	0.16	0.16	0.16
lindane (LIN)	181	85	88 (48.6)	8 (4.4)	0	8 (4.4)	0.034	0.007	0.001–0.58
diazinon (DIA)	181	178	3 (1.7)	0	0	0	0.040	0.016	0.013–0.092
propyzamide (PPY)	136	119	12 (8.8)	4 (2.9)	1 (0.7)	5 (3.7)	0.26	0.027	0.003–2.9
metribuzin (MTB)	115	114	0	0	1 (0.9)	1 (0.9)	2.8 × 10 ²	2.8 × 10 ²	2.8 × 10 ²
alachlor (ALA)	136	104	25 (18.4)	4 (2.9)	3 (2.2)	7 (5.1)	0.97	0.015	0.002–18
chlorpyrifos (CLP)	114	93	16 (14.0)	5 (4.4)	0	5 (4.4)	0.096	0.021	0.003–0.58
parathion-ethyl (PAR)	181	177	4 (2.2)	0	0	0	0.035	0.026	0.010–0.078
pendimethalin (PEN)	136	69	49 (36.0)	12 (8.8)	6 (4.4)	18 (13.2)	0.71	0.030	0.008–18
chlorfenvinphos (CLF)	181	152	15 (8.3)	13 (7.2)	1 (0.6)	14 (7.7)	0.20	0.049	0.008–1.0
procymidone (PCY)	136	104	24 (17.6)	7 (5.1)	1 (0.7)	8 (5.9)	0.42	0.040	0.015–11
endosulfan (ENS)	181	113	47 (26.0)	18 (9.9)	3 (1.7)	21 (11.6)	0.24	0.043	0.003–4.2
fenamiphos (FEM)	181	180	0	1 (0.6)	0	1 (0.6)	0.25	0.25	0.25
4,4'-DDE	181	179	2 (1.1)	0	0	0	0.005	0.005	0.003–0.006
dieldrin (DIE)	181	137	43 (23.8)	1 (0.6)	0	1 (0.6)	0.021	0.014	0.002–0.10
endosulfan sulfate (ENSS)	181	102	59 (32.6)	20 (11.0)	0	20 (11.0)	0.095	0.034	0.002–0.92
λ-cyhalothrin (CYH)	181	180	1 (0.6)	0	0	0	0.059	0.059	0.059
α-cypermethrin (CYP)	181	177	1 (0.6)	2 (1.1)	1 (0.6)	3 (1.7)	0.46	0.21	0.052–1.4
metolachlor (MET)	69	58	7 (10.1)	3 (4.3)	1 (1.4)	4 (5.8)	0.24	0.041	0.007–1.6

^a An estimation of the mean and median concentrations in the data set, as well as the maximum and minimum measured concentrations. All the values are given in $\mu\text{g L}^{-1}$. ^b N = number of samples having each pesticide in the given interval.

terbutylazine and fenamiphos) or in high excess (i.e., dimethoate and metribuzin). One of the most frequently used indicators to assess the severity of groundwater contamination is given by the percentage of detections above the $0.1 \mu\text{g L}^{-1}$ limit. From this standpoint, it must be emphasized that pendimethalin, endosulfan, and endosulfan sulfate are detected in more than 10% of the samples, followed by atrazine, chlorfenvinphos, and desethylatrazine. Whether their occurrence is due to their high intensity of use or the favorable leaching properties, endosulfan and endosulfan sulfate never reached concentrations as high as the rest, probably due to their adsorption to soil (22). In this group of compounds, we readily identify two pesticide degradation products, endosulfan sulfate and desethylatrazine. Although desethylatrazine appeared in fewer samples than atrazine, the concentrations were high to extremely high. It is noteworthy that desethylatrazine was detected in the absence of the parent compound, particularly in sites 12, 16, and 17 (see **Table 2**). A similar finding occurs with endosulfan sulfate, illustrated in site 22.

Atrazine was detected above $0.1 \mu\text{g L}^{-1}$ up to twice as frequently as alachlor, despite some commercial formulations containing both compounds. Indeed, atrazine is classified according to the GUS index as a potential leacher, while alachlor is a transient leacher and less persistent (7, 22). **Table 1** also indicates that four pesticides out of the six measured above $10 \mu\text{g L}^{-1}$ are herbicides. **Figure 2** displays the total frequency of pesticide detection, regardless of the concentration and above $0.1 \mu\text{g L}^{-1}$. From the 27 pesticides present in water samples, 8 are herbicides, 12 are insecticides, 3 are fungicides, 1 is a nematicide, and 3 are degradation products. Obviously, the list depends on the total list of species tested for. Although lindane was the pesticide mostly detected (53%) and ubiquitous (present in all but one sampling site), it should be noted that a few samples exceeded the EU limit (4%), which contrasts with pendimethalin (13%), endosulfan (12%), and endosulfan sulfate (11%), that reached also much higher maximum concentrations. Since lindane is a medium/high persistence pesticide ($t_{1/2} = 191$ days) and has sufficient water solubility (7.3 mg L^{-1}) to reach groundwater, besides its toxicity as an endocrine disruptor (23, 24), it was not included in the positive list of pesticides of the

EU (Annex I, Directive 91/414/EC). Lindane has been banned in Portugal since 2002. Nevertheless, an increase in residue levels was noticed in three sites in the sampling of October 2003. Its high detection frequency might be explained by physicochemical, analytical (low LODs), geomorphologic (vulnerability), and agricultural (soil insecticide) considerations, but the concentrations are rather low. Lindane has also been detected with a similar pattern in the U.S.A. (New Jersey, California, Mississippi, and South Carolina) and Europe (Italy) (24, 25). Also persistent, dieldrin was still detected after 2 decades of banning with a noteworthy frequency (24%), but the levels were markedly low, while 4,4'-DDE appeared sporadically at trace levels. In a ranking order, then follow the herbicides and OPP insecticides, that range in **Figure 2** from atrazine (20%) to desethylatrazine (7%) and metolachlor (16% of 69 samples).

Cerejeira et al. (8) found triazine and chloroacetanilide herbicides (the only classes that were surveyed from 1991 to 1998) in Portuguese groundwaters. In the "Ribatejo and Oeste" region, central Portugal, atrazine (64%), simazine (45%), and alachlor (25%) were the pesticides detected most often. The maximum residue levels of atrazine and alachlor were slightly lower than our results, but in a similar proportion. Subsequently to this study, Batista et al. (26) extended the program to the vulnerable area of "Beira Litoral" and widened the range of pesticides to include some other herbicides, degradation products, and insecticides. The detection frequency was in the following sequence: atrazine (70% of the samples), desethylatrazine (56%), desisopropylatrazine (48%), simazine (37%), alachlor (25%), metolachlor (24%), metribuzin (15%), endosulfan (6%), lindane (6%), and dimethoate, prometryn, molinate, and 3,4-dichloroaniline (5% each). However, their occurrence at levels above $0.1 \mu\text{g L}^{-1}$ was less than 10%, except for the case of atrazine (19%). Compared to these studies, the range of pesticides investigated in our work is much wider, which was reflected in the diversity of pesticides that were detected. Additionally, the crops produced in both regions also differ: here the green vegetables dominate the cultivations in intense rotation and no fruit trees or vineyards are grown, although both regions have maize crops.

Table 2. Contamination of Water Samples above the Limits Set by EU Directive 98/83/EC and Detected Pesticides, Arranged by Sampling Site

site no.	no. of quantitated pesticides above 0.1 $\mu\text{g L}^{-1}$								no. of samples		detected pesticides (and frequency)
	Sept 2002	Feb 2002	April 2002	July 2002	Nov 2002	March 2003	July 2003	Oct 2003	sum above 0.5 $\mu\text{g L}^{-1}$	no. of pesticides quantitated	
1			1							5	LIN (3), CLP (1), PEN (2), CLF (2), DIE (1), ENSS (1)
2			1	1		1	3		4	2	ATR (2), LIN (3), ALA (5), CLP (2), PEN (6), CLF (2), DIE (4)
2A		1	1	1	1	2	1	1	4	1	ATR (1), LIN (2), CLP (2), PEN (5), PCY (1), ENS (7), DIE (2), ENSS (7)
4			2			1	4	1	2	1	ATR (5), LIN (3), ALA (2), CLP (1), PAR (1), PEN (5), ENS (6), DIE (1), ENSS (6), MET (3)
5						1				3	ATR (2), LIN (1), PEN (3), ENS (3), ENSS (2)
6		2	2	5	1	3	2	2	7		DEA (1), DIM (2), ATR (6), LIN (8), DIA (1), PPY (4), ALA (2), CLP (4), PEN (6), CLF (3), PCY (5), ENS (2), 4,4'-DDE (1), ENSS (4), CYP (3)
8	1	3	1	2	3	3		2	5		LIN (7), CLP (1), PEN (4), CLF (7), PCY (2), ENS (7), DIE (5), ENSS (7)
9							1		1	3	ATR (2), LIN (3), MET (3)
10			1					1		1	ATR (2), LIN (5), ALA (2), PEN (2), ENS (3), DIE (1), ENSS (4), MET (2)
11	1	3				1		2	2		LIN (7), ALA (1), CLP (1), PEN (3), CLF (3), ENS (7), ENSS (7)
12				1	1	1	1	3	4	1	DEA (3), LIN (6), PPY (4), ALA (3), CLP (2), PEN (5), ENS (1), DIE (3), MET (1)
13		NA ^a	NA		NA	1		1			ATR (1), LIN (2), CLF (2), PCY (3), DIE (3)
14										5	LIN (1), PEN (2), ENS (1), DIE (1), ENSS (1)
15				1		2		2		1	LIN (7), PPY (1), CLP (1), PEN (6), CLF (2), PCY (1), ENS (2), ENSS (1)
16			1		2			2	2	2	DEA (2), LIN (4), PPY (1), CLP (1), PEN (2), ENS (2), FEM (1), DIE (1), ENSS (3)
17	2	2		2	4	4	2	2	3		DEA (5), LIN (5), PPY (4), ALA (1), PAR (1), PEN (4), PCY (2), ENS (8), ENSS (7)
18	1					2			2		LIN (7), CLP (1), PEN (6), PCY (4)
19										5	LIN (1), ALA (1), PAR (1), PEN (1), CLF (1), ENS (1), DIE (1), ENSS (1)
20			3	3	1		2	6	4		DEA (1), ATR (4), LIN (8), PPY (2), MTB (1), ALA (4), CLP (2), PAR (1), PEN (5), CLF (1), PCY (6), ENS (6), DIE (4), ENSS (7), CYH (1), MET (2)
21			1	1				1	3	1	LIN (2), CLP (1), PCY (4), ENS (4), DIE (1), ENSS (7)
22	1							1	1		ATR (3), LIN (5), ALA (3), 4,4'-DDE (1), DIE (8), ENSS (5)
24	1	1	1	2	1	1	4		2		ATR (1), LIN (4), ALA (2), CLP (1), CLF (1), PCY (4), ENS (8), DIE (8), ENSS (8)
25			3	3	2	2	1		3	1	ATR (7), TER (1), LIN (2), DIA (1), PPY (1), ALA (6), ENS (1), ENSS (1), CYP (1)
no. of samples	6	6	12	11	9	14	12	12			
no. of pesticides	7	12	18	22	16	25	23	25			

^a NA indicates that the sample was not available.

Most such studies in Europe have been focused on herbicides. According to Scheidleder et al., the pesticides that raise higher concerns in the EU are atrazine, simazine, lindane, desethylatrazine, heptachlor, metolachlor, bentazone, DDT, diclorprope, MCPA, and metoxychlor (2). Papadopoulou-Mourkidou et al. (6) have investigated the impact of intense agriculture (predominantly maize, wheat, and cotton crops) in the subsoil water in northern Greece. Atrazine and prometryn were the most frequently found pesticides (>30% of samples). Atrazine was found above 0.1 $\mu\text{g L}^{-1}$ in 73% of the positive samples, whereas prometryn was found in around 20% of them. Alachlor and propanil were other herbicides detected in phreatic water while

carbofuran and paraoxon-methyl were not very frequent, although their levels were relatively high. Papastergiou and Papadopoulou-Mourkidou (9) detected with a descending frequency the following pesticides, atrazine > desethylatrazine > alachlor = metolachlor, in groundwater collected from drinking and irrigation water wells of five maize producing areas. On the other hand, the decreasing order of concentrations was the following: metamitron (single case) > atrazine > metolachlor > desethylatrazine > alachlor. Similarly to the case of our study, atrazine was quantitated with higher frequency than desethylatrazine. Conversely to this study, our results point to a significant degradation of atrazine before reaching groundwater,

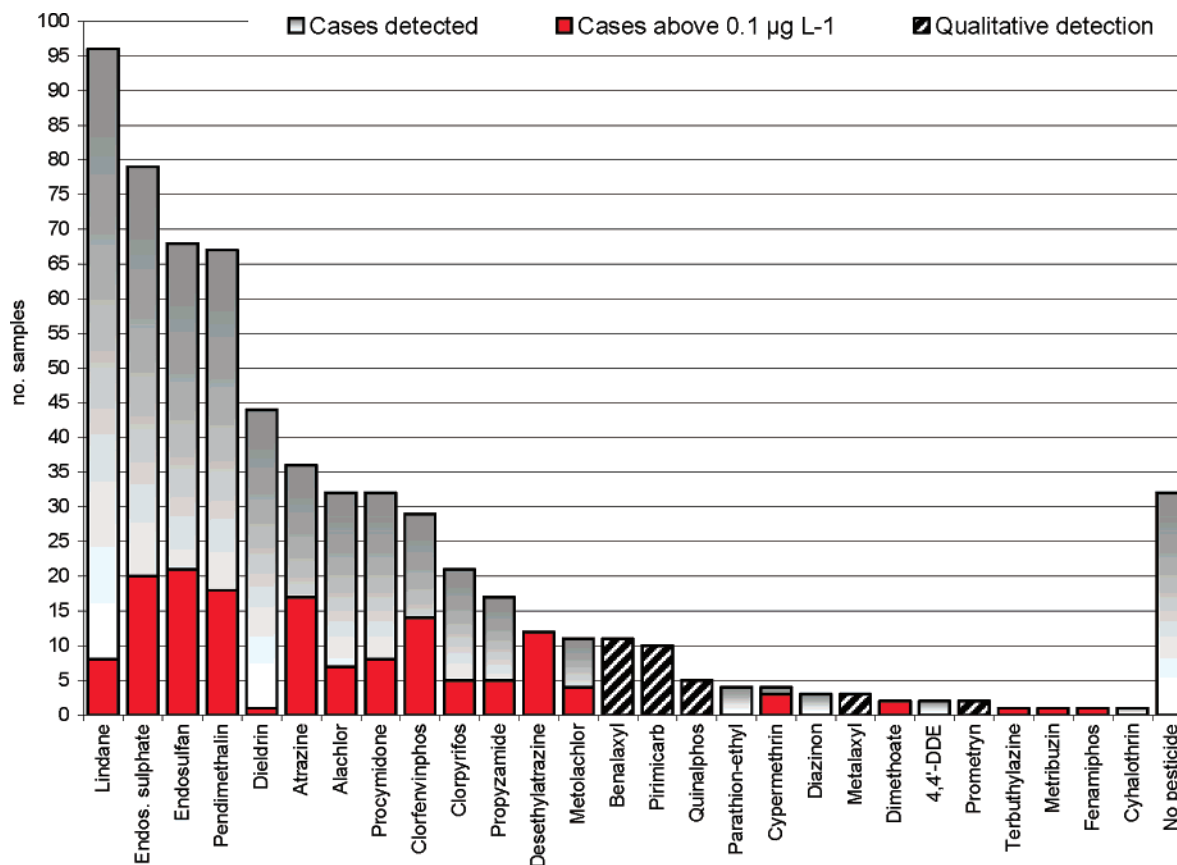


Figure 2. Graphical representation of the absolute occurrence of each pesticide in groundwater and the frequency above the regulatory limit of $0.1 \mu\text{g L}^{-1}$.

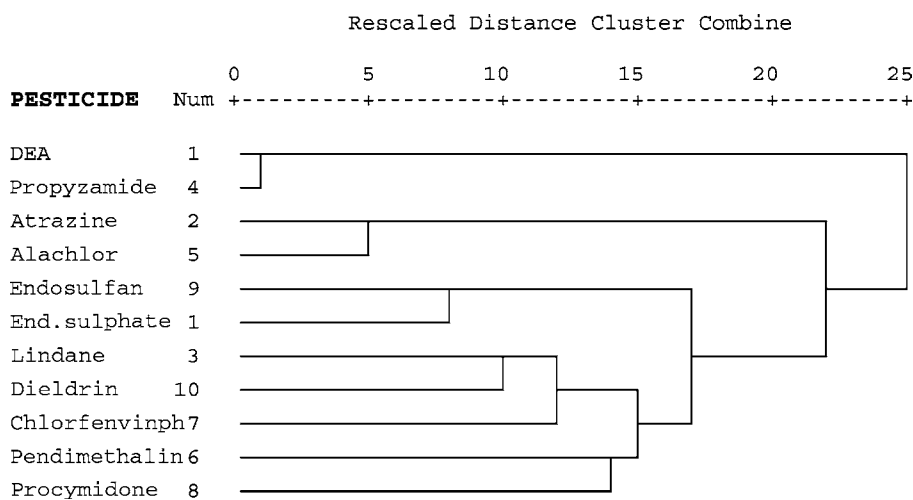
since desethylatrazine levels are usually higher and sometimes occur in the total absence of the parent herbicide. Actually, our findings are not completely exceptional, since Guzzella et al. (1) also detected degradation products of triazines (desethylatrazine and desethylterbutylazine) in greater concentrations than their relative active ingredients, atrazine and terbutylazine. These authors conducted a survey of 5 herbicides and 17 degradation products in intensively cultivated areas of maize and cereals. They concluded that, although atrazine was banned in Italy in 1986, it was still the main groundwater contaminant, present in 100% of the selected samples, and in 30% of them it even exceeded the $0.1 \mu\text{g L}^{-1}$ limit. These results indicate a low degradation rate of pesticides in groundwater. Terbutylazine, used in replacement of atrazine, was detected in 85% of the samples. Alachlor and metolachlor pollution was limited, despite their high usage on maize crops. Due to their quantities and frequency in groundwater, the ubiquity of triazine degradation products in this compartment of the environment is confirmed. Sánchez-Camazano et al. (7) evaluated specifically the inputs of atrazine and alachlor to surface and groundwater from irrigated areas devoted to maize cultivation in central Spain. A notable contamination of groundwater has been reported: atrazine was detected in 87% of the samples (70% $>0.1 \mu\text{g L}^{-1}$) and alachlor in 81%. van Maanen et al. (10) examined the occurrence of pesticides, mainly triazines and organochlorines, in groundwater (well and spring water) in relation with nitrate, in cultivated areas with winter wheat, sugar beet, maize, vegetables, and fruit trees. Higher levels, sometimes exceeding the EU limit, were found in natural springs rather than well water. Again, atrazine was the most ubiquitous pesticide showing a correlation between high concentrations and elevated nitrate levels. Simazine, propazine, and dieldrin were

found in a few samples. The European association of water suppliers and wastewater operators (EUREAU) reported that, in the most affected countries of central and northern Europe, 5–10% of water resources contained pesticides above $0.1 \mu\text{g L}^{-1}$. The pesticides identified to pose a greater threat to groundwater quality were atrazine and metabolites, simazine, mecoprop, and bentazone (27). From the studies above, the type of pesticides that pollute groundwater and their abundance did not change much, at the European level, in relation to the scenario described by the EAA, in 1999 (2).

Table 2 summarizes the data on individual pesticide detections above $0.1 \mu\text{g L}^{-1}$ and above $0.5 \mu\text{g L}^{-1}$ for the sum of pesticides, arranged by sampling site and date. Pesticide levels above the EU limit appear distributed all across the sampling periods. Only a slight temporal pattern is noticeable considering the sum of pesticide detections by sampling date. In the beginning of the monitoring program, fewer pesticides were detected, probably due to fewer searched analytes. In November 2002, there was a drop in pesticide concentrations, following heavy rain periods in October and mid-November. Water samples collected from sites 14 and 19 never exceeded the individual and total pesticide limits; thus, these groundwaters present a good quality status. Another indicator of the absence of relevant pollution is the total number of samples, by site, where no pesticides were measured. Sites 1, 14, and 19 scored five unpolluted samples out of eight analyzed. In a more critical situation are sites 6 and 8, which combine abundant violations to both the individual and total pesticide limits all across the monitoring scheme. In any of the periods, samples from these sites were free of pesticides, but the same happened in sites 11, 13, 17, 18, 20, and 22, although the results show that, in the latter, an acceptable water quality ($<0.1 \mu\text{g L}^{-1}$) was restored

Table 3. Ten Most Contaminated Samples Found in the ZV1 Area from September 2002 to October 2003

site no.	sampling date	total conc ($\mu\text{g L}^{-1}$)	conc of pesticides $> 0.1 \mu\text{g L}^{-1}$ and (no. of pesticides present)
20	April 2002	2.9×10^2	MTB: 2.8×10^2 /PCY: 11/ENS: 0.21 (9 pesticides)
6	February 2002	1.1×10^2	DIM: 1.1×10^2 /CYP: 0.11 (3 pesticides)
25	July 2002	61	ATR: 42/ALA: 18/TER: 0.16 (8 pesticides)
6	April 2002	49	DIM: 48/PCY: 0.46 (7 pesticides)
6	July 2002	41	ATR: 38/PEN: 1.7/CYP: 1.4/PCY: 0.20/DEA: 0.14 (11 pesticides)
17	October 2003	36	DEA: 34/PPY: 2.9 (4 pesticides)
12	March 2003	18	PEN: 18 (5 pesticides)
12	October 2003	10	ALA: 9.3/DEA: 0.70/PPY: 0.31 (6 pesticides)
6	March 2003	7.9	PEN: 7.5/ATR: 0.15/CLP: 0.12 (8 pesticides)
6	July 2003	6.4	PEN: 6.0/ATR: 0.13 (9 pesticides)

**Figure 3.** Dendrogram obtained by cluster analysis of variables (11 most significant pesticides) based on the squared Euclidean distance measure and Ward's method of linkage.

at some point during the survey. From the 49 (out of 181) samples where the cumulative limit for pesticides was exceeded, we detach the 10 most heavily contaminated samples, as presented in **Table 3**. On the other hand, 32 samples were consistently free of pesticides. Considering that our monitoring studies took place in an intensive horticulture area, another important aspect to address is the diversity of pesticide substances detected in any one sampling site along the 2-year monitoring. From the data presented in **Table 2** it is clear that sites $9 < 18 < 5 = 13 = 14$ were those with less variety of pesticides. On the contrary, the most polluted sites were $20 > 6$, where about 15 different pesticides were found at least once, while the average varied from 6 to 10 individual substances. Most likely, the explanation for this diversity goes beyond the agricultural practices undertaken in the narrow proximity of the wells. As an example, site 6 probably reflects the practices in a larger common area where it is included. In site 19, the number of pesticides contrasts with its low contamination level. It probably reflects a residual residence of pesticides in the aquifer close to the method's LOQs. As a whole, 45% of the samples exceeded the $0.1 \mu\text{g L}^{-1}$ limit and 27% exceeded the $0.5 \mu\text{g L}^{-1}$ limit. No single pesticide violated these limits, *per se*, in more than 13.2% of the samples, but the complex mixture of pesticides and degradation products that have built up in groundwater appears as one of the main factors of concern. Our results improve the knowledge already existing in the literature, since they clearly show that, besides triazines and chloroacetanilides, a wide range of pesticides (> 20) are used in intensive horticulture and reach groundwater, particularly in vulnerable zones. The high pesticide frequency/amount is a

result of local susceptibility in terms of agricultural practices, hydrogeology, and climate conditions that predispose to contamination.

3.2. Cluster Analysis. Hierarchical cluster analysis is an unsupervised multivariate agglomerative technique that seeks for pattern recognition, such as groups of samples or variables (28). Conversely to the descriptive statistics, multivariate data analysis provides a dynamic view of the variables' behavior in multidimensional systems, such as the natural environment. As mentioned in section 2.4, multivariate analysis was applied selectively to a subset of data that could contribute with consistent organic relationships. The pesticides included in the multivariate resolution were those in the left-hand side of the graph in **Figure 2**, till desethylatrazine, except chlorpyrifos. The 11 most significant pesticides and degradation products were clustered, as shown in **Figure 3**. It gives a first overview of the associations between pesticides found in water. Two of them can be immediately highlighted, and not unexpectedly: atrazine/alachlor and endosulfan/endosulfan sulfate. The first consists of a mixture of widely used herbicides, and the second consists of the combination of parent pesticide/degradation product. The former association is a common finding in groundwaters (7, 26). Cluster analysis was also applied to produce a grouping of samples according to their pollution pattern, as far as the above-referred 11 pesticides are concerned (data not presented). The spatial representation of the classes did not allow identifying a clear geographical pattern in pesticide pollution—classes are disperse. The ZV1 area is characterized by intensive horticulture carried out on predominantly sandy soils overlying a shallow aquifer. Additionally, the core of the cultivated area relies on

Table 4. Rotated Canonical Function and Main Loadings (Bold Type) of Principal Factors in Principal Component Analysis^a

	principal components				
	PC1	PC2	PC3	PC4	PC5
sums of squared loadings	1.985	1.674	1.454	1.372	1.024
% of variance	18.045	15.216	13.218	12.472	9.312
	component loadings				
desethylatrazine	0.994	-0.012	0.002	-0.030	0.004
atrazine	-0.018	0.906	-0.014	0.000	-0.007
lindane	0.029	0.143	0.059	0.743	0.173
propyzamide	0.996	0.011	0.012	0.004	0.011
alachlor	0.017	0.907	-0.020	-0.005	-0.011
pendimethalin	-0.033	0.010	-0.131	-0.126	-0.161
chlorfenvinphos	-0.029	-0.060	-0.151	0.586	0.090
procymidone	-0.026	-0.012	0.006	0.010	0.943
endosulfan	0.002	-0.010	0.821	-0.164	0.106
dieldrin	-0.039	-0.079	0.230	0.629	-0.241
endosulfan sulfate	-0.003	-0.018	0.826	0.193	-0.032

^a Rotation method: Varimax with Kaiser normalization.

essentially similar pest protection practices, which reinforces the absence of a clear geographical pattern in pesticide distribution.

3.3. Linear Discriminant Analysis. LDA can be used to resolve numerous environmental issues, namely those that deal with the distinction of samples arranged in groups based on a complex set of attributes (12). Here, our purpose was to use LDA as a means to make clear which variables have driven the segregation of groups of samples based on their pesticide content, as seen in cluster analysis. First, we assessed the discriminant capacity that the pesticides input to the discriminant function associated with each class analyzing the Wilks' λ and F values in the test of equality of group means. The F value was always below 75.5, which is a rather low value, indicating that none of the pesticides retain an extremely distinctive feature among the samples. A complex mixture of pesticides is always present in every class.

3.4. Pollution Source Identification by Principal Component Analysis. Principal component analysis (PCA) is one of the most widely used chemometric techniques to seek relevant information in excessively obscured data structures. One of the applications where it proved very useful is the interpretation of water quality data (28–31). The intrinsic dimensionality of environmental data often can be represented by a reduced number of factors that capture most of the inherent variance.

In this study, principal components (PCs) were extracted as a contribution of the 11 pesticides we have been considering. Only factors exhibiting an eigenvalue above 1 were retained. Also, a Varimax rotation was performed to overcome the problem of variables loading on more than one of the PCs. The result is an increased chemical/environmental significance of the PCs. Five PCs were extracted which account for a total variance of 68%. The corresponding loadings matrix is given in Table 4. The PC1 (18% variance) receives a predominant loading from desethylatrazine and propyzamide. To understand the factor behind it, we can search for the samples that contained simultaneously desethylatrazine and propyzamide. These were samples pertaining mainly to sites 12 and 17, which were dedicated to grow lettuce, brassicas, and other vegetables where propyzamide finds great preference as an herbicide. The coexistence of desethylatrazine residues indicates that atrazine has been previously used and underwent degradation. However, atrazine is not an herbicide of choice in those cultures and, indeed, it was never detected. In view of the above, the source

might have been neighboring cultivation fields that contributed desethylatrazine to the groundwater fluxes. Some degree of uncertainty remains, since the homogenization of underground waters hampers a clearer explanation of this factor. PC2 (15% variance) receives a prominent simultaneous loading from the herbicides atrazine and alachlor. This is not particularly surprising, since the active ingredients are found together in herbicidal formulations that are sold in massive quantities mainly for the control of weeds in maize cultivation, reaching groundwater, as discussed in section 3.1. The third PC (PC3, 13%) can be unequivocally explained by the occurrence of the metabolite endosulfan sulfate in places that received insecticide treatments with endosulfan. The fourth PC (PC4, 12%) receives loadings mainly from lindane, chlorfenvinphos, and dieldrin. Although chlorfenvinphos has been losing importance as an insecticide in the national sales rank, in the ZV1 horticulture area, chlorfenvinphos is a fairly selected insecticide, as is lindane. The former is sprayed on the plants while the latter is used as a soil insecticide; thus, they can be used complementarily, which might explain their joint detection. Dieldrin was widely detected in trace levels, which allowed its association in PC4. PC5 (9%) was discerned mainly due to the behavior of procymidone. This fungicide is used in selected goods (mainly strawberries and tomatoes) to prevent the growth of mould (*Botrytis* spp.) that can cause them to rot. Hence, it has a distinct behavior from those of pesticides applied to green vegetables. The remaining 32% of the data variance could not be clearly interpreted. Several procedures in intensive horticulture can be responsible for a deviation from rigid patterns, as detailed elsewhere (14). These are linked mainly to the great variability in horticultural practices and crops in a densely cultivated region. Particularly if carried out on vulnerable areas, these conditions are favorable to the accumulation of a complex mixture of pesticides and degradation products in groundwater. Additionally, the mobility of pesticides in water media hampers the establishment of direct relations to the activities carried out at the surface, at a farm level. Regardless, only pendimethalin was not implicated in any distinctive data pattern identifiable by PCA.

In summary, 22 of the 42 sought pesticides were detected in groundwater. These pesticides spanned a range of chemical classes and comprised 8 herbicides, 12 insecticides, 3 fungicides, and 1 nematicide, together with three degradation products. These include metalaxyl, benalaxyl, quinalphos, pirimicarb, and prometryn, which were only qualitatively detected and should be considered in future analytical work. Other pesticides might have been present but would not have been detected by the analytical methods. The most frequently detected compounds (in descending order) were lindane, endosulfan sulfate, endosulfan, and pendimethalin. Overall, 45% of the samples exceeded the EU limit of $0.1 \mu\text{g L}^{-1}$ for a single pesticide and 27% exceed the $0.5 \mu\text{g L}^{-1}$ limit for combined pesticides. A slight temporal trend in this contamination was discernible, but no systematic geographical pattern was shown by the multivariate data analysis. Five environmental and agrochemical management factors explained 68% of the variability in pesticide distribution, with the most important being the herbicide formulation used on maize, the metabolism of endosulfan, and insecticide combinations applied in horticulture.

ACKNOWLEDGMENT

The authors thank the IAREN for technical support. Acknowledgements are due to DRAEDM and to A. Matos, Região Agrária da Póvoa de Varzim, for his involvement in the

collection of samples and insightful discussions regarding the interpretation of statistical results in light of the field use of pesticides.

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Received for review December 18, 2006. Revised manuscript received May 3, 2007. Accepted May 4, 2007. FCT—Fundação para Ciência e Tecnologia is greatly acknowledged for the Ph.D. Grant PRAXIS XXI/BD/21823/99. The authors thank the IAREN for financial support.