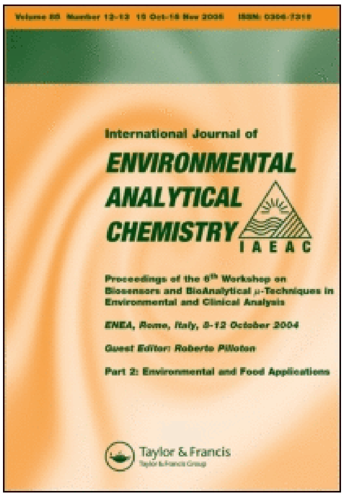

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SURVEY OF GROUND WATER PESTICIDE POLLUTION IN RURAL AREAS OF CATALONIA (SPAIN)

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A systematic survey of the quality status of the main aquifers in rural areas of Catalonia (Spain) regarding pesticide pollution has been carried out. A total number of 139 wells, distributed among 13 different hydrogeological units have been sampled and analyzed by GC-MS and GC-ECD, during the period 1997–98. Pesticides monitored were selected among triazine herbicides, organochlorine and organophosphorus insecticides. A positive presence of pesticides has been detected in 84.2% of the samples analyzed, 23.7% of them exceeding the requirements of the EU drinking water Directive (98/83/CE). Organochlorine insecticides were present in 62.6% of the samples, triazines in 49% and organophosphorus insecticides in 28.8%. The results obtained have been interpreted by Principal Component Analysis.

Keywords: Groundwater quality; Pesticides; Principal Component Analysis

INTRODUCTION

The common and extensive use of pesticides in agriculture, usually involving a wide broadcast application and spread out in large crop field areas, is recognized to be a major source of diffuse contamination, typically by runoff to surface waters or by leaching to the underlying aquifers[1–3]. Of particular concern are the later ones, since they are oftenly used as supply resource for human drinking purposes.

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For that reason, and because there is no EU Directive specifically addressed to establish quantitative limits of pesticides in ground waters, their quality is oftenly referred to drinking water standards.

European legislation, through the recently issued Directive 98/83/EEC[4], has fixed the maximum acceptable level of total pesticides in drinking water at 0.5 μg/l, and for individual compounds at 0.1 μg/l. Being these values quite strict, it was considered of interest to carry out an extensive pesticide monitorization program of the ground waters (hydrogeological units) of Catalonia (Spain), in order to ascertain the degree of accomplishement of the aforementioned Directive.

Under this scope, the areas to be prospected, should combine a significative agricultural activity (thus involving a definite potential risk of pesticide pollution) with an use of the aquifers for human consumption.

Therefore, in the present study we are extensively reporting data regarding pesticide contamination of ground waters in the area under consideration (Catalonia, see Figure 1), gathered during 1997 and 1998. It is worth mentioning that, whereas a substantial amount of information about pesticides on surface waters was already available for Catalonia[5–8], to the best of our knowledge, the corresponding data on ground waters were lacking.

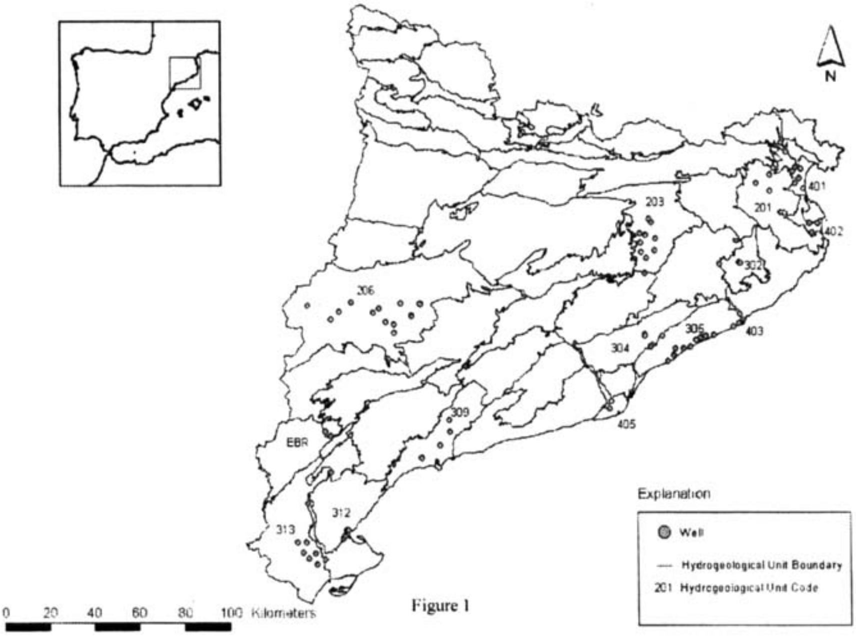


FIGURE 1 Location of survey area, hydrogeological units prospected and sampled wells

The survey network covers 13 different hydrogeological units (see Figure 1 and Table I), fulfilling the above mentioned conditions. Sampled wells (139) were selected to be representative of the corresponding aquifers and were mostly unconfined and located in detritic quaternary materials.

TABLE I Hydrogeological units monitored

Code	*Description*	*Samples Analyzed*
201	Empordà depression	4
203	Paleogene unit of Vic plain	10
206	Detritic Oligocene unit of Lleida plain	20
302	Selva depression	3
304	Vallès depression	8
305	Granitic unit of Maresme	25
309	Camp de Tarragona depression	4
312	Mesozoic unit of Cardó-Vandellós	5
401	Fluvial-deltaic unit of Fluvià-Muga rivers	17
402	Fluvial-deltaic unit of Ter river	6
403	Fluvial-deltaic unit of Tordera river	19
405	Fluvial-deltaic unit of Llobregat river	7
EBR	Ebro alluvial	11

Compounds examined were organochlorine insecticides (18 compounds), organophosphorus insecticides (19 compounds), and triazine herbicides (7 compounds) (see Table II). They were mostly selected in accordance with the extent of their use, like some triazine herbicides (*i.e.*, simazine, atrazine), and/or their environmental harmness. This is particularly the case of some organochlorines, such as DDT and its metabolites DDD and DDE, aldrin-endrin-isodrin, hexachlorobenzene or hexachlorocyclohexane, all of them included in the so called "black list" (list I) of the Directive 76/464/EEC[9] concerning toxic and environmentaly harmful substances. The analysis of pesticides in water samples is fully documented in the literature, either by liquid (LC) or gas chromatography (GC), after a suitable liquid-liquid[8,10,11] or solid-phase extraction (SPE)[7,10,12–14]. In the present study pesticides were determined by GC-MS and, for organochlorines by GC-ECD, followed by identity confirmation by GC-MS. The procedures used were taken from the U.S. Environmental Protection Agency: respectively, method 625 (liquid-liquid extraction)[11], and a slightly modified version of method 525.1 (solid-phase extraction)[12]. To cope with the substantial amount of experimental results obtained, and in order to get a better insight in the eventual relationships between geographic crop distribution and the type of pesticides found (or in other words, to identify the different "sources" of pesticide pollution), it was considered of interest to perform a multivariate analysis using well known techniques, such as Principal Component Analysis (PCA), succesfully applied in similar problems of water contamination by organic micropollutants[15–20].

TABLE II Pesticides analyzed and recoveries

Organochlorine Insecticides	*Method EPA 625[11] (n=9)*		*Method EPA 525.1[12] modified (n=9)*	
	Recovery %	*Std. Dev. %*	*Recovery %*	*Std. Dev. %*
Endrin aldehyde	100	19	90	26
Endrin	120	14	94	23
β-HCH	115	13	88	11
α-HCH	96	7	87	9
δ-HCH	109	11	86	13
Lindane(γ-HCH)	103	6.2	90	12
HCB	81	5	65	15
4,4'-DDT	123	12	93	17
4.4'-DDD	112	13	85	15
4.4'-DDE	116	16	79	11
Heptachlor	109	6	85	24
Heptachlor epoxide	115	12	62	8
Aldrin	99	7	76	16
Isodrin	120	10	84	13
Dieldrin	114	12	92	11
Endosulfan I	119	12	79	18
Endosulfan II	113	13	74	11
Endosulfan sulfate	90	17	71	10
Organophosphorus Insecticides	*Recovery %*	*Std. Dev. %*	*Recovery %*	*Std. Dev. %*
Ethion	100	4	74	6
Fenitrothion	99	8	79	11

Chlorpyrifos	87	9	78	4
Diazinon	79	8	80	4
Parathion	92	5	73	4
Parathion-methyl	92	6	75	13
Chlorfenvinphos	119	6	116•	11
Malathion	105	10	97	7
Azinphos-ethyl	123	15	101	7
Azinphos-methyl	-[a]	–	107	12
Phorate	-[a]	–	65	6
Methidathion	113	2	90	17
Dichlorfenthion	106	2	65	11
Fenchlorphos	102	3	68	13
Bromophos-ethyl	99	2	64	15
Bromophos-methyl	110	2	70	12
Tetrachlorvinphos	117	3	95	15
Phosalone	-[a]	–	102	16
Coumaphos	-[a]	–	93	17
Triazine Herbicides	*Recovery %*	*Std. Dev. %*	*Recovery %*	*Std. Dev. %*
Simazine	103	8	76	11
Atrazine	103	8	92	14
Prometryn	98	9	91	16
Propazine	103	9	95	16
Ametryn	96	9	89	15
Terbutryn	95	13	96	15
Prometon	84	13	89	14

a. Recovery not determined

Summarizing, the aim of the present work is to present, for the first time and on a systematic way, the current status of the ground waters on the most important crop field areas of Catalonia, as regards as pesticide contamination is concerned, together with an interpretation of the results by means of a PCA, thus allowing to characterize the different hydrogeological units studied, and, if possible, to relate them to the agricultural practices supported.

EXPERIMENTAL

Sampling

Water samples were collected from the points indicated in Figure 1, during the period 1997–98. Samples (2 l) were kept on glass bottles fitted with teflon-lined caps, leaving no head-space and preserved in cold (not exceeding 5°C) until analysis (not later than 7 days after collection).

Chemicals and reagents

Pesticide standards were obtained from Cromlab (Barcelona, Spain). Suprasolv-grade dichloromethane, ethyl acetate, n-hexane, isooctane, 2-propanol and acetone were purchased from Merck (Darmstadt, Germany). Anhydrous Na_2SO_4 was purchased from Panreac (Barcelona, Spain) and was heated overnight at 400 °C and kept dry until use. Surrogate standards nitrobenzene-d_5, 2-fluorobiphenyl and 4-terphenyl-d_{14} and internal standards anthracene-d_{10} and decachlorobiphenyl were from Supelco (Bellefonte, PA, U.S.A.). C8 EC (end-capped) solid-phase extraction cartridges of 500 mg were supplied by IST (Mid Glamorgan, U.K.).

Sample solid-phase extraction procedure

Pesticide SPE was carried out according to the modified method 525.1 from the U.S. Environmental Protection Agency[12]. 5 ml of 2-propanol were added to 1 l of sample just before extraction. Cartridges were conditioned with 2-propanol (10 ml) and rinsed with reagent grade water (10 ml). Conditioning of cartridges and loading of samples onto the cartridges was done at less than 30 ml/min flow, using vacuum control in a manual device. Sample bottles were rinsed with reagent water (10 ml), that was subsequently eluted too through the column. The sorbent was dried by centrifugation and the analytes eluted with two portions of 2 ml and one portion of 1 ml of acetone/ethyl acetate (75:25) at free vacuum flow-rate.

1 g of anhydrous Na_2SO_4 was added to the extract to remove any water present. The vial was placed on a vortex mixer for few seconds, then allowed to settle and evaporated under a gentle stream of nitrogen. Further, the Na_2SO_4 was rinsed several times with isooctane and the resulting extract concentrated to 100 µl for HRGC/MS and/or HRGC/ECD analysis. Grab samples were spiked with nitrobenzene-d_5, 2-fluorobiphenyl and 4-terphenyl-d_{14} (surrogate standard mix-

ture). Anthracene-d_{10} and decachlorobiphenyl (internal standards) were added to the extracts.

Sample liquid-liquid extraction procedure

Pesticide liquid-liquid extraction was carried out according to the method 625, from the U.S. Environmental Protection Agency[11]. 1 l of sample was added with surrogate standard mixture (nitrobenzene-d_5, 2-fluorobiphenyl and 4-terphenyl-d_1) and extracted twice with dichloromethane (150 ml and 100 ml) by stirring for 10 min. The organic extracts were combined and dried with anhydrous Na_2SO_4. Dichloromethane was removed under reduced pressure, first in a round bottom flask and further in a conic flask, until a volume of 0.5 ml. The concentrate was transferred to a 1 ml conic vial, washing the flask with isooctane, and dried under N_2 stream until a final volume of 100 μl for HRGC/MS and/or HRGC/ECD analysis. Internal standards (anthracene-d_{10} and decachlorobiphenyl) were added to the extract.

HRGC Analysis

The HRGC/MS analysis were performed on an integrated quadrupol GC/MS MD-800 from Fisons (Manchester, U.K.). Helium was used as carrier gas (at a constant flow of 1.2 ml/min) in a DB-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The program was from 90°C (held 5 min) to 240 °C at 6°C/min and to 310 °C (maintained for 10 min) at 10°C/min. Injector temperature was 280°C, and the injection mode was splitless for 90 s. The scanning was 40–500 m/z at 1 scan/s. The data were processed with the Masslab software that include the spectra libraries NIST (62,235 spectra) and Wiley 5th ed. (138,111 spectra).

The HRGC/ECD analysis were performed on a Shimadzu GC-9A model gas-chromatograph equipped with an ECD-9 model detector of the same firm. Helium was used as carrier gas at a flow of 2.6 ml/min in a DB-5 column (30 m × 0.2 mm i.d., 0.25 μm film thickness). The program was from 130 °C (held 1 min) to 140 °C (mainained for 1 min) at 12°C/min, and from 140°C to 310°C at 4°C/min; the final temperature was further held for 10 min. Injector and detector temperature were 290°C and the injection mode was splitless for 1 min.

Multivariate Statistics: Principal Component Analysis

Multivariate data structure was examined by Principal Component Analysis. The three groups of pesticides, triazine herbicides, organophosphorus and organochlorines were processed separately. The starting data matrices were composed by the whole set of sampling points (n = 139), and the pesticides analyzed in each group. To avoid the presence of "zeros" (i.e., concentration values below the limit of detection), those were replaced by a fictitious value equal to half of the limit of detection. Data were not scaled, but they were converted to logarithmic units and the covariance matrices used. PCA calculations were performed with the S-Plus 4.5 software package (Mathsoft, Inc., Cambridge, MA).

RESULTS AND DISCUSSION

Analysis

As mentioned above, pesticides analyzed were extracted from the samples by either SPE (modified U.S. EPA method 525.1[12]) or liquid-liquid (U.S. EPA method 625[11]), being the former the choice of preference, because its greater operation simplicity. In fact, the SPE method was actually applied in the majority of the samples anlayzed, being the alternative liquid-liquid method only used in those few cases in which the presence of particulate suspended material was causing difficulties in the SPE operation procedure.

Table II shows the percent recovery values and percent relative standard deviations (RSD) obtained on spiked samples (ca. 50 ng/l) for both methods. In general terms, values are similar to the reference EPA methods[11,12], and can be considered acceptable according to them for the majority of compounds analyzed (recoveries of 70 to 130% and RSD below 30%). Only few compounds, namely, hexachlorobenzene, heptachlor epoxide, phorate, dichlorfenthion, fenchlorphos and bromophos-ethyl, had recoveries sligthly below 70% (62 to 68%) in the SPE method.

Data description

In Figure 2, we are reporting the frequencies found for the presence of the diverse pesticide compounds in the set of samples analyzed. A positive presence of pesticides has been detected in most of the samples (84.2%). Organochlorine insecticides were present in 62.6% of the samples, triazines in 49% and organophosphorus insecticides in 28.8%. These results can be explained, in general trends, taking into account their physico-chemical properties, such as persistence (half life) and mobility (solubility and adsorption), that govern their environmental behaviour, together with the extent of their use. Thus, for instance, the pres-

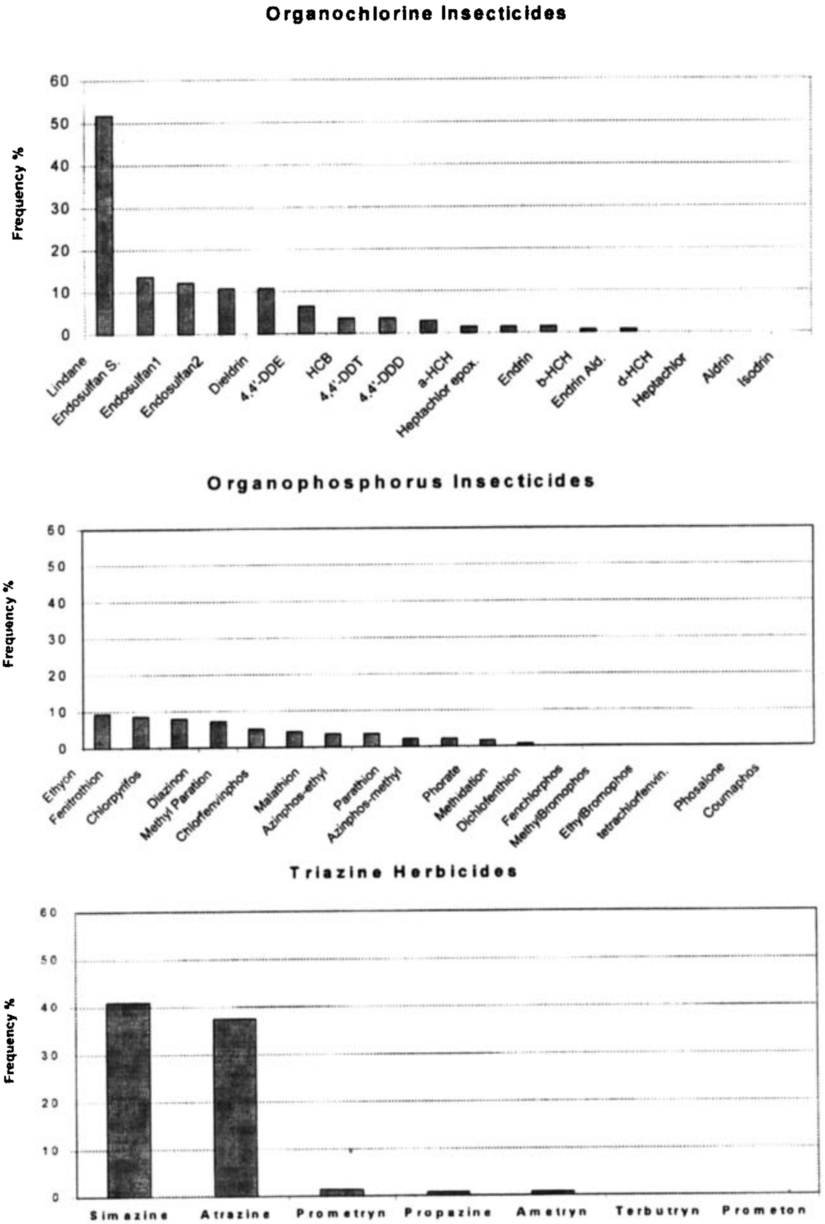


FIGURE 2 Detection frequencies (%) of pesticides analyzed

ence of atrazine and simazine in ca. 40% of the samples analyzed can be related to relatively high water solubilities (respectively, 33000 and 6700 μg/l)[21] or GUS index (Groundwater Ubiquity Score)[22] of 3.68 and 3.34, combined with a widespread application. In the case of lindane, a half life of 400 days[21], a solubility of 6107 μg/l[21], a GUS index of 2.47 and a broad spectrum of use, are in good agreement with its environmental ubiquity (it is present in more than 50% of the samples analyzed).

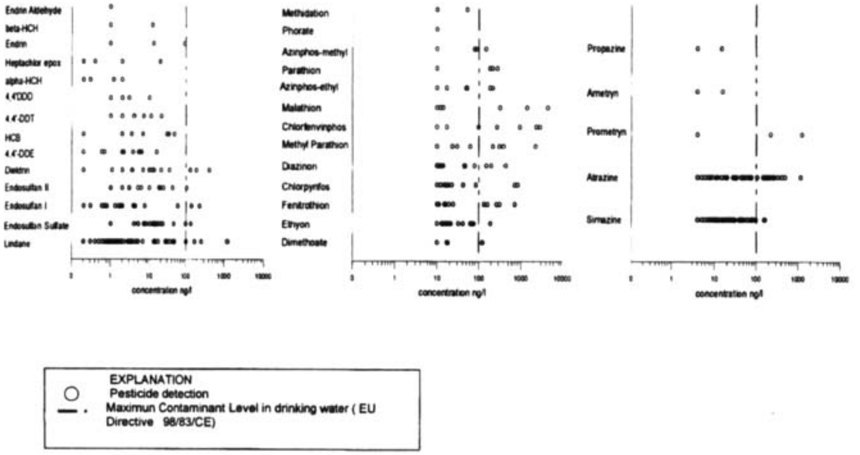


FIGURE 3 Concentration of detected pesticides

A substantial percentage of the samples (23.7%) exceeded the EC Directive (98/83/CE)[4] fulfillment (see Figure 3). Highest concentrations found (exceeding 1000 ng/l) appeared only for lindane (1 sample), malathion (2 samples), chlorfenvinphos (2 samples), methyl parathion (1 sample), prometryn (1 sample) and atrazine (1 sample). Such peak values can be likely interpreted as resulting from a recent product application, particularly for those compounds having relatively short half-lives, like malathion (1 day), methyl-parathion (18.5 days), prometryn (41 days) or atrazine (50 days)[1].

The areas showing the most significative pesticide pollution were the oligocene detritic of the Lleida plain (#206), the Maresme littoral plain (#305), the Empordà depression (#201) and the fluvial-deltaic units corresponding respectively to the rivers Fluvià-Muga (#401), Tordera (#403) and Llobregat (#405)(see Table I and Figure 1). All of them have an intensive agricultural activity based on fruit trees, horticulture, corn and ornamental cultures. Samples with highest pesticide levels corresponded to those soils formed by detritic quaternary materials.

TRIAZINE HERBICIDES

Covariance Matrix					
Variables	simazine, atrazine, prometryn, propazine Ametryn terbutryn, prometon.				
Observations	139				
Importance of Components					
	COMP 1	COMP 2	COMP 3	COMP 4	COMP 5
Standard deviation	0.695	0.295	0.256	0.05	0.046
Proportion of Variance	0.754	0.135	0.103	0.004	0.003
Cumulative Proportion	0.754	0.890	0.993	0.997	1.000

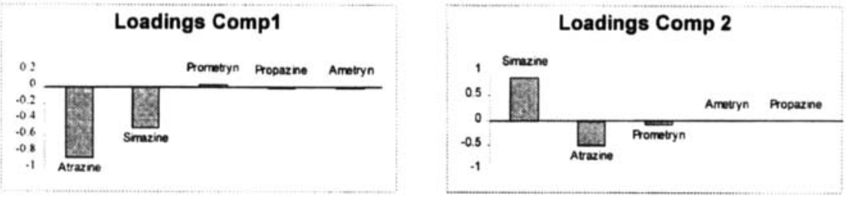


FIGURE 4 Principal Component Analysis for triazine herbicides

In the case of the Lleida plain (#206), it is an aquifer constituted by coarse gravels, in which the water remaining from irrigation plays an important role in the recharge. The aquifers in the Maresme littoral plain (#305) and the fluvial-deltaic units (#401, #403 and #405) are formed by sands of medium to coarse granulometry. In the Empordà depression (#201), the samples analyzed were taken on alluvial sediments. In all cases, they are superficial aquifers, with the freatic level placed at low depth (*i.e*, not more than 10 m).

Principal Component Analysis

Principal Component Analysis (PCA) was performed separately on each pesticide group, but it has been only interpreted for two of them, namely, triazine herbicides and organophosphorus insecticides. The occurrence of points with rather high values and limited data variability in the organochlorine group, made difficult its PCA interpretation.

Application of PCA for triazines results in a quite good model in which the first three components account for more than 99% of variance, respectively 75.4%, 13.5 % and 10.3% (Figure 4). The loadings plot for the first two principal components PC1 and PC2 is also given in the same Figure 4. Both components appear highly loaded by atrazine and simazine, differing in the sign of their respective contributions. Thus, in PC1 both compounds have the same (negative) sign, *i.e.*, they are positively correlated, increasing or decreasing simultaneously, while in PC2 the opposite situation occurs, with simazine and atrazine having positive and negative values respectively (they are inversely or negatively correlated). The third PC is dominated by prometryn. The scores plot of PC1 and PC2 (Figure 5) shows a fairly good grouping among samples belonging to the same hydrogeological unit. Thus, for instance, clusters corresponding to hydrogeological units of Lleida plains (#206), Ebro alluvial (#EBR), and in less extent, Camp de Tarragona depression (#309) or the Vic plain (#203), can be identified.

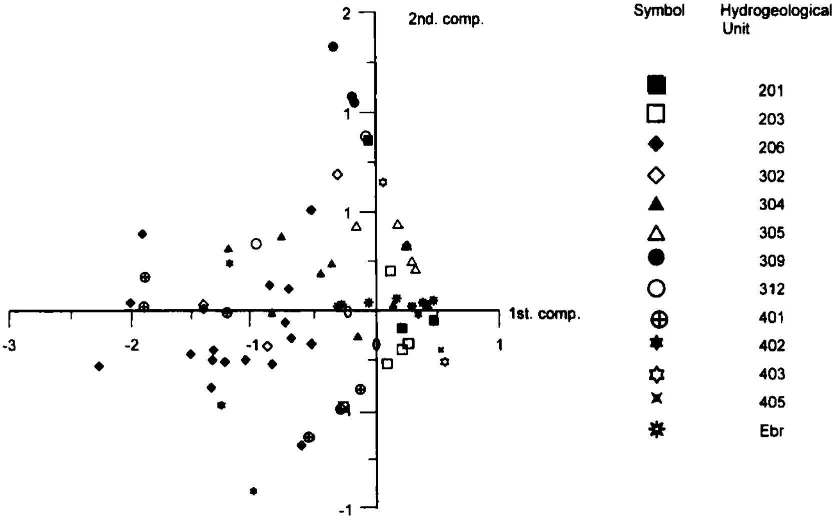
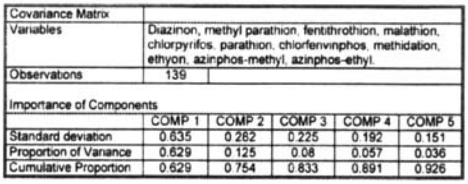


FIGURE 5 Scores plot of the first two principal components for triazine herbicides

From a joint examination of the loadings plot (Figure 4) and the scores plot (Figure 5), together with the use indications of the herbicides considered[23], the PCA results can be tentatively interpreted as representing each PC a typology of agriculture. From those, negative values of the first PC (high atrazine and simazine contribution) seem to gather in sampled wells placed in areas where extensive irrigation cultures are present, such as corn and fruit trees, as in the Lleida plain (#206) (Figure 5). On the other hand, positive values of the second PC (high contribution of simazine) would reflect an increasing presence of dry cultures (vineyard, olive trees, hazelnut trees etc.), as it is the case of the Camp de Tarragona (#309), Cardó-Vandellós (#312) or Empordà (#201) in Figure 5. The third PC (not represented) characterizes some points corresponding to fluvial-deltaic hydrogeological units, like the Llobregat (#405) and the Tordera

(#403) rivers, and can be typically associated with lowland cultures, such as vegetables, horticulture, potatoes etc.

ORGANOPHOSPHORUS INSECTICIDES



Covariance Matrix					
Variables	Diazinon, methyl parathion, fentithrothion, malathion, chlorpyrifos, parathion, chlorfenvinphos, methidation, ethyon, azinphos-methyl, azinphos-ethyl.				
Observations	139				
Importance of Components					
	COMP 1	COMP 2	COMP 3	COMP 4	COMP 5
Standard deviation	0.635	0.282	0.225	0.192	0.151
Proportion of Variance	0.629	0.125	0.08	0.057	0.036
Cumulative Proportion	0.629	0.754	0.833	0.891	0.926

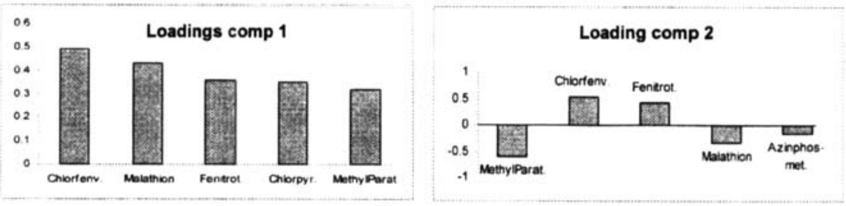


FIGURE 6 Principal Component Analysis for organophosphorus insecticides

Data analysis using PCA for organophosphorus insecticides provides also a reasonably acceptable model, where the first three components explain 83% of the variance, respectively 62.9%, 12.5% and 8% (Figure 6). The first and second PCs are loaded by chlorfenvinfos, malathion, fenitrothion and methylparathion (plus chlorpyriphos and azinphos-methyl in PC1 and PC2 respectively) (Figure 6), differing in the sign of their loading contribution. Whereas in PC1 all the compounds correlate positively, in PC2 they are splitted in two groups inversely correlated: chlorfenvinfos and fenitrotion having a positive loading value, and malathion, methylparathion and azinphos-methyl a negative one. The scores plot of PC1 and PC2 (Figure 7) allows to identify three separate clusters from the whole cloud of points. The first one, corresponding to three points of the Llobregat river delta (#405), is characterized by a positive value of PC1, and is consistent with an horticulture practice. The other two clusters, with similar values of the first PC, are differentiated by the sign of second PC: negative values tend to separate some points belonging to the Lleida plain (#206) hydrogeological unit, and positive values do the same with two points of the Empordà unit (# 201). However, any further interpretation of the results based on the agricultural use of the organophosphorus compounds considered is not straigthforward, mainly because the broad spectrum of application (*i.e.* the lack of specificity) of these insectides, being utilized in a great variety of crop cultures.

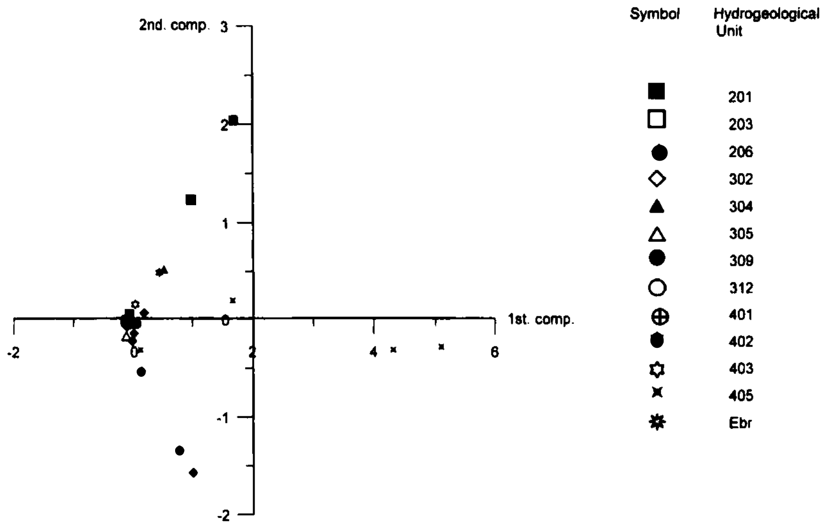


FIGURE 7 Scores plot of the first two principal components for organophosphorus insecticides

CONCLUSIONS

In connection with the application of the recently approved Directive 98/83/EC[4], we have accomplished for the first time a systematic survey of the quality status of the main aquifers of Catalonia (Spain) placed in rural areas, concerning pesticide pollution. A total of 44 compounds, selected among triazine herbicides (7), organophosphorus (19) and organochlorine insecticides (18) have been monitored, their selection based on the extension of their use, their environmental harmful and/or legislation criteria (Directive 76/464/EEC)[9].

The results obtained in the areas prospected indicate the presence of pesticides in a substantial number of the sites analyzed (84.2%), thus evidencing the effect of an intensive agricultural practice in the underlying groundwater. However, under the provisions of the foregoing EC Directive 98/83/EC[4], only 23.7% of the sites examined exceeded the maximum level requirements for drinking waters.

The work presented will provide the basis for the implementation of a groundwater monitoring network for routine pesticide pollution control.

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