Use of chemometric and geostatistical methods to evaluate pesticide pollution in the irrigation and drainage channels of the Ebro river delta during the rice-growing season

**Marta Terrado · Marina Kuster · Demetrio Raldúa ·
Miren Lopez de Alda · Damià Barceló · Romà Tauler**

Abstract Data sets obtained from quantitative analysis of seventeen pesticides in water samples from a network of irrigation and drainage channels in the Ebro river delta (Catalonia, NE Spain) have been analysed by chemometric and geostatistical methods. Samples were taken at fourteen locations during the main rice-growing season, from May to August 2005. Principal-component analysis enabled investigation of the spatial and temporal distribution of the main pollution patterns caused by application of pesticides in the region under study. A first pesticide-contamination pattern from the Ebro river was differentiated from a second more specific pattern from the water-drainage channels of the delta, collected from the rice fields. The seasonal peak in this more specific rice pesticide source was observed in July. Coupling the results from chemometric data analysis with use of geostatistical methods was shown to be a useful procedure for discovery of the most significant spatial and monthly variations of the main pesticide-contamination patterns, taking into account the particular geographical structure of the area under study.

Keywords Pesticides · Chemometrics · PCA · GIS · Ebro river delta

M. Terrado · M. Kuster · M. Lopez de Alda · D. Barceló ·
R. Tauler (✉)
Department of Environmental Chemistry, IIQAB-CSIC,
Jordi Girona 18-26,
08034 Barcelona, Spain
e-mail: rtaqam@iiqab.csic.es

D. Raldúa
Laboratory of Environmental Toxicology, UPC,
CN 150 Km 14.5,
08220 Terrassa, Spain

Introduction

Diffuse pollution by pesticides from agriculture is an issue of great concern, because of their presence in water, sediments, and soils and their potential adverse effects on human health, wildlife, and the environment [1]. Non-point-source pollutants (which include pesticides) are usually detected at medium or low concentrations in the different environmental compartments (air, water, sediments, and biota), but their extensive use and behaviour makes them widely distributed, making it difficult to trace a specific and localized source. Pesticides are intentionally introduced into the agricultural ecosystem to control pests or weeds. Their application reduces crop losses by an important percentage, so their valuable function is generally accepted, but their movement toward environmental compartments may affect non-target ecosystems [2]. Despite increasing knowledge and concern in relation to the potentially harmful effects of pesticide pollution, large amounts of human-produced chemicals are still entering in ecosystems and, in particular, the Ebro river delta, every year.

The Ebro delta (Catalonia, NE Spain) is a geographical area of 20,600 ha mainly used for rice cultivation but also for other crops, such as orchard and fruit trees (at the sides of the river, because they need sweet water to subsist). The area contains a network of irrigation and drainage channels devoted to rice farming. The irrigation channels bring water to the fields and it is later collected by the drainage channels. The whole hydrological cycle of the delta is man-controlled by means of upstream barrages and water canalisation. Until 1981, water leaving the fields was collected by a network of drainage channels and driven to littoral lagoons. Between 1981 and 1990, circular channels were built around the lagoons to collect drainage water and

direct it straight to the sea [3]. Two main channels (Fig. 1), one on each side of the river, bring the water from Xerta, 25 km upstream, to the rice cultivation system of the delta. This area receives large amounts of pesticides, especially during the main rice-growing season (from May to August).

In this work, sampling was conducted monthly from May to August 2005 at 14 locations (Fig. 1). The first sampling site, ERT, was located upstream of the entrance to the left-hand channel of the Ebro river, near Tivenys. It consisted of river water before running through the delta system. The right-hand channel is the main irrigation channel of the right hemi-delta. It leads to a network of secondary channels. A second sampling site, CE1, was at the beginning of the Sèquia de l'Agulla, a secondary irrigation channel, where water is not affected by the pollution of the delta because it comes directly from the Ebro river through the right-hand channel without any

additional input. A series of drainage channels belonging to the drainage system of the Sèquia de l'Ala, were also sampled, from small channels (CD1–CD3) that collect water from some land fields and from larger drainage channels (CD4–CD6) which collect water from larger land extensions. Samples were also taken from the other two main drainage channels in the right hemi-delta (CD7 and CD8), which together with the Sèquia de l'Ala, lead the water to the Badia d'Alfacs, where another sampling site, BA, is located. Irrigation channels play a key factor in the transport of pesticides from the rice crop fields to the bays (in this instance the Badia d'Alfacs), where important mussel farms are located. The effects of pesticides or their degradation products on these organisms is a matter of ecological concern [4]. Samples were also taken from the Llacuna de l'Encanyissada (EL) and from two irrigation channels (CE2 and CE3) which were selected to check the

Fig. 1 Location and identification of sampling sites in the irrigation and drainage network of the Ebro delta: *ERT*, Ebro river at Tivenys; *CD1*, drainage channel 1; *CD2*, drainage channel 2; *CD3*, drainage channel 3; *CD4*, drainage channel 4; *CD5*, Sèquia de l'Ala-Before Gates; *CD6*, Sèquia de l'Ala-After Gates; *CD7*, Sèquia de Campredó; *CD8*, Sèquia de Baladres; *CE1*, irrigation channel 1; *CE2*, irrigation channel 2; *CE3*, irrigation channel 3; *EL*, Llac de l'Encanyissada; *BA*, Badia d'Alfacs
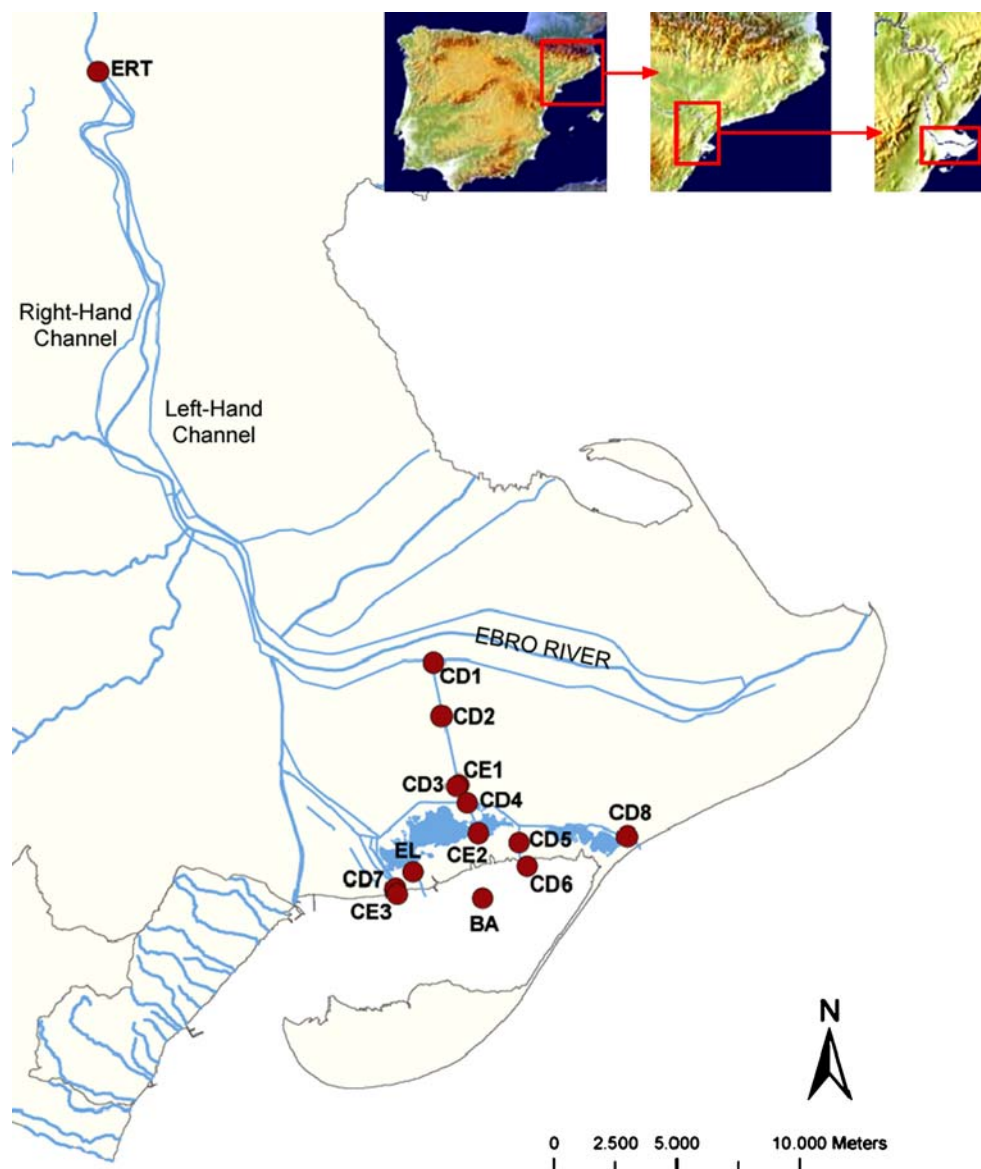
effects of the water-repumping system. When the level of water decreases in the irrigation channels, water from the drainage channels (containing larger amounts of pesticides) is repumped to them. This water is then reused to irrigate the fields.

Contamination as a result of pesticide use in the Ebro river delta, and its relationship with the main growing season of the rice cycle, were investigated in this study. Chemometric methods based on multivariate factor-analysis tools [5], for example principal-component analysis (PCA), were used to extract useful environmental information from the data (contribution and composition profiles of the main contamination sources), and geostatistical interpolation techniques [6–8], using geographical information systems (GIS) [9, 10], were used to predict geographical and spatial distribution of the identified contamination patterns throughout the area under study.

Description of data sets

Four sampling campaigns were performed monthly from May to August 2005. In each campaign, the number of water samples collected at the selected locations (Fig. 1) varied from 12 to 14. Sampling sites CE2 and CE3 were sampled in June and July only (when water was repumped from the drainage channels) and ERT was not sampled in July.

The concentrations of the pesticides in the water from the Ebro delta channels were arranged in four data matrices (each one corresponding to a sampling month, with 12 or 14 sampling sites and 17 pesticides). Rows (samples) corresponded to the sampling sites and columns (variables) were the seventeen pesticides analysed in the water samples. Each entry of the data matrix therefore gave the concentration (ng L^{-1}) of a particular pesticide in a particular sample. Pesticides included in this study were organophosphates (fenitrothion, malathion, and diazinon), triazines (simazine, atrazine, and cyanazine), phenylureas (chlortoluron, isoproturon, and diuron), anilides (propanil), chloroacetanilides (alachlor and metolachlor), acidic herbicides (bentazone, MCPA, 2,4-D, and mecoprop) and thiocarbamates (molinate). Bentazone, molinate, MCPA, fenitrothion, and propanil are specifically used for cultivation of rice in Spain. Pesticides were analysed by on-line solid-phase extraction–liquid chromatography–tandem mass spectrometry (SPE–LC–MS–MS) with an electrospray ionization source. The analytical procedures are described in detail elsewhere [11]. Detection limits achieved were below 0.0015 μg L^{-1} for all the compounds except for bentazone, cyanazine, atrazine, and molinate (0.01 μg L^{-1}), and alachlor, metolachlor, and malathion (0.1 μg L^{-1}). The uncertainty of the analytical method,

obtained by analysis of eight replicates of a standard solution and expressed as the relative standard deviation (RSD), was always below 15% for all the pesticides except isoproturon, for which it was slightly higher (16.4%).

Data treatment

Alpha-numerical data were arranged in four data matrices (see the section Description of data sets) and geographical information for the studied area was selected and arranged in different graphical layers (hydrology, sampling sites, and delimitation of the deltaic area, among others). Preliminary description of the data was performed using the software Excel (2002; Microsoft, Redmond, WA, USA), including descriptive statistics, boxplot representation, and correlation maps between variables. The data set was then transferred to Matlab (v.7.0, 2004; The Mathworks, MA, USA) computer and visualization environment to perform more exhaustive data analysis using chemometric methods.

Data pretreatment

First, preliminary pretreatment was performed before applying principal-component analysis (PCA) to the data. When a particular compound was not detected its concentration was set to half its detection limit (LOD) except for fenitrothion, for which half of the minimum measured concentration was used. In PCA studies it has been shown that substitution of BLD (below detection limit) values by LOD/2 values gives superior results than substitution by LOD or zero [12]. Pesticides with very few concentrations above the detection limit, for example cyanazine and malathion, were eventually removed from the data matrix before further analysis. The next data-pretreatment method was autoscaling, which consists in data column mean centring and then scaling (dividing each value by the standard deviation of its column) [13], except for chlortoluron and metolachlor—for these many concentrations were below the detection limit and the concentrations were divided by 20 (after mean centring) instead of scaling. In this way, they could still be used for data analysis but their values were not overweighted when they were divided by their very small standard deviations. In this work, two different analyses were performed depending on the way autoscaling was applied. In the first type of data scaling (j-scaling, [5]), each individual data matrix corresponding to the four different months was first autoscaled and then concatenated to give a new augmented data matrix for further chemometric analysis. In the second type of data scaling the four data matrices corresponding to the four months of the sampling campaign were concatenated first in the new column-wise augmented data matrix and then

autoscaled. As will be shown below, information obtained from the results after data analysis by these two different data-scaling pretreatments is not equivalent and it can be used to distinguish temporal from geographical contamination trends.

Chemometric analysis

Principal-component analysis was used to investigate multivariate correlations between the concentrations of the different pesticides, identify their main contamination patterns, and deduce their geographical and temporal distributions [14]. This method uses a bilinear model to explain the observed data variance using a reduced number of components. Using the combination of the original variables (loadings), a new group of non-correlated orthogonal variables (principal components) is deduced; this enables calculation of new orthogonal axes where the samples are represented (scores) and in which the explained data variance is given in a decreasing order. The loadings identify the chemical composition of the main sources of data variance, and the scores describe the contribution of these sources in the samples, enabling sample mapping of these sources and description of the distribution of possible contamination patterns in geographical and temporal terms.

Geostatistics

PCA results (scores matrix) were transferred to an Access (2002; Microsoft, Redmond, WA, USA) geodatabase for analysis in a Geographical Information System (GIS) environment. By use of the ArcGis software (v.9.0, 2005; ESRI, Redlands, CA, USA) extension Geostatistical Analyst [15], prediction maps of the different contamination patterns were created. Geostatistical techniques [6–8] were selected because they may interpolate continuous surfaces from sample points taken at different locations, giving an indication of how good predictions are (uncertainty). The geostatistical interpolator used was ordinary kriging [16–19], which follows the steps:

1. calculation of the empirical semivariogram built on the basis that objects that are closer are more alike than those further away;
2. model fitting, defining the function that provides the best fit through the points;
3. creation of weight matrices, determining the kriging weights assigned to each measured value; and
4. prediction.

The combined use of chemometric and geostatistical analysis tools to assess water quality has been reported elsewhere [20, 21].

The kriging geostatistical tool was applied only to PCA results obtained using the second data pretreatment (j-scaling) for the four data matrices scaled together after column-wise concatenation. Sampling sites ERT and CE1 were omitted from the mapping interpolation; ERT was not considered because of its long distance from the irrigation channels system and CE1 was not considered because its water comes directly from the river, which would cause significant distortion in the interpolation results.

Results

Results obtained in preliminary statistical description of data (Table 1) revealed pesticide concentrations were very high compared with those measured in previous studies

Table 1 Descriptive statistics of pesticide concentrations in water

Pesticide	Mean (ng L^{-1})	Median (ng L^{-1})	Minimum (ng L^{-1})	Maximum (ng L^{-1})	Standard deviation (ng L^{-1})	Kurtosis	Asymmetry coefficient
MCPA	1.9×10^3	6.9×10^2	5.6	1.4×10^4	3.0×10^3	6.7	2.6
Mecoprop	7.6	5.4	0.75	26	6.1	1.4	1.3
2,4-D	22	15	0.75	1.7×10^2	27	19.0	3.8
Bentazone	3.1×10^4	1.2×10^4	10	1.3×10^5	3.4×10^4	0.4	1.1
Simazine	44	28	0.75	3.8×10^2	54	29.1	4.8
Isoproturon	2.3	1.8	0.21	7	1.6	1.8	1.4
Chlortoluron	0.83	0.75	0.75	2.7	0.32	24.5	4.7
Atrazine	3.1×10^2	2.7×10^2	22	9.0×10^2	1.8×10^2	1.0	0.9
Diuron	13	13	0.75	36	8.6	−0.5	0.5
Propanil	8.5×10^2	14.4	0.75	16.8×10^3	2.5×10^3	33.9	5.5
Molinate	1.9×10^2	1.3×10^2	2.9	8.5×10^2	2.1×10^2	2.1	1.6
Alachlor	2.5×10^3	50	0	6.3×10^4	1.2×10^4	22.9	4.9
Metolachlor	2.0	0.75	0.75	27	4.7	19.2	4.3
Fenitrothion	84	14	14	6.8×10^2	1.6×10^2	5.1	2.4
Diazinon	4.7	0.57	0.04	44	9.9	7.2	2.7

[22]. The most abundant organophosphate pesticide was fenitrothion, for which the peak value was 0.68 $\mu g\ L^{-1}$. Bentazone was also present at high concentrations in the area under study; the maximum concentration, 127 $\mu g\ L^{-1}$ in June, was 474 times the average concentration of this pesticide in Ebro river water. Peak concentrations of alachlor, propanil and MCPA were 62.9, 16.8, and 13.9 $\mu g\ L^{-1}$, respectively. These values are rather high if we take into account the Water Framework Directive (60/2000/CE), in which draft with the proposal of substances that shall be identified as prioritary, establishes maximum allowable concentration quality standards (MAC-QES) for some of the pesticides studied in this work. The MAC-QES is a concentration established to ensure protection against short-term exposure. For alachlor, a concentration of 0.7 μg L^{-1} is recommended in inland and other surface waters. Levels of 4, 2, 1.8 and 1 are recommended for simazine, atrazine, diuron and isoproturon, respectively [23]. All variable distributions were positively skewed (with positive asymmetry coefficients), especially for propanil, alachlor, simazine, and chlortoluron (Table 1). Positively skewed distributions have a long right tail and the median of the data falls well below the mean value. This characterizes a distribution of concentration values containing a larger proportion of small values and only a few high concentrations. Nothing can be confirmed about alachlor or chlortoluron, because levels of these were usually below their detection limits. From pairwise correlations between concentrations of the different variables, groups of positively correlated specific rice-crop pesticides (MCPA, fenitrothion, molinate, bentazone, and propanil) were detected in preliminary work:

1. MCPA was in a first group containing two other acidic herbicides (mecoprop and 2,4-D) and diazinon;
2. fenitrothion and molinate, with diuron, constituted a second group;
3. bentazone was not correlated with any other pesticide; and
4. propanil was positively correlated with chlortoluron.

Results from PCA are discussed in two different sections to enable better interpretation of the data. In the section Spatial variation of pesticide pollution, PCA results from data analysis using the first type of data pretreatment (first separate autoscaling of the data matrices of the four months and then column-wise concatenation) are reported. In this analysis possible scale variations among different months are removed and major variations in the concentrations of the pesticides among the different sampling sites of the Ebro delta area (study of the distribution of pesticide pollution over the territory) are emphasized. In the section Temporal patterns of pesticide pollution in the Ebro delta,

PCA and GIS results from data analysis using the second type of data pretreatment (column-wise concatenation of the data matrices for the four months then column autoscaling) are presented. In this section, interpretation of temporal changes in the application of pesticides in the Ebro delta (study of pesticide pollution over the rice cultivation temporal cycle) is discussed. Some spatial distribution trends of the major contamination patterns will be also inferred, however, although they are discussed in more detail in the previous section. PCA loadings obtained in these sections are summarized in Fig. 2a and b, which enable characterization of the main identified patterns of contamination by pesticides in the Ebro delta region.

Spatial variation of pesticide pollution

Four principal components (PCs) explaining 72.9% of the total data variance were selected describing the main spatial variation trends of pesticide concentrations in the Ebro delta during the main rice-growing season (Fig. 2a), after applying the first proposed data pretreatment (previous section). Whenever possible, these PCs were related to pesticide pollution patterns. PC1 explained the 31.6% of the data variance and described the contrast between two main patterns of contamination occurring in the region under study, one related to pesticide contamination from the Ebro river and another, more specific, related to pesticide contamination from rice cultivation. The contamination pattern from the Ebro river, described by pesticides giving positive loadings for PC1, includes mecoprop, 2,4-D, isoproturon, atrazine, and diazinon. Water samples collected directly from the river (sampling sites ERT, CE1, and CD1) and samples collected from the entrances of the irrigation channels, CE2 and CE3 (sampled in June and July), were mostly characterized by the presence of this river contamination pattern (Fig. 3). Another source of pesticides contamination, from the rice fields (inversely correlated with the previous source), was identified with high negative PC1 loadings for bentazone, propanil, molinate, and, to a lesser extent, fenitrothion and MCPA (pesticides typically applied to rice crops). Contamination from this source increased (Fig. 3; sampling sites with higher negative scores) throughout the irrigation system, from drainage channel CD2 (at the beginning of the drainage channels system) to CD8 and to the Badia d'Alfacs (BA) (at the end of the drainage channels system), having an accumulative effect which indicates clear and steady application of these products over the rice fields during the sampling period. Therefore, and according to this first PC, a contamination pattern from the rice-irrigation system is clearly distinguished from pesticide contamination from the Ebro river. Although temporal variations were minimized by the pretreatment method

Fig. 2 Loading plots of the main contamination patterns identified by PCA for pesticides in the Ebro river delta and explained variances for each PC. (a) PCA performed over separate autoscaling of the four data matrices (section Spatial variation of pesticide pollution); (b) PCA performed over concatenation of the four data matrices followed by column autoscaling (section Temporal patterns of pesticides pollution in the Ebro delta). Variables: *1*, MCPA; *2*, mecoprop; *3*, 2,4-D; *4*, bentazone; *5*, simazine; *6*, isoproturon; *7*, chlortoluron; *8*, atrazine; *9*, diuron; *10*, propanil; *11*, molinate; *12*, alachlor; *13*, metolachlor; *14*, fenitrothion; *15*, diazinon
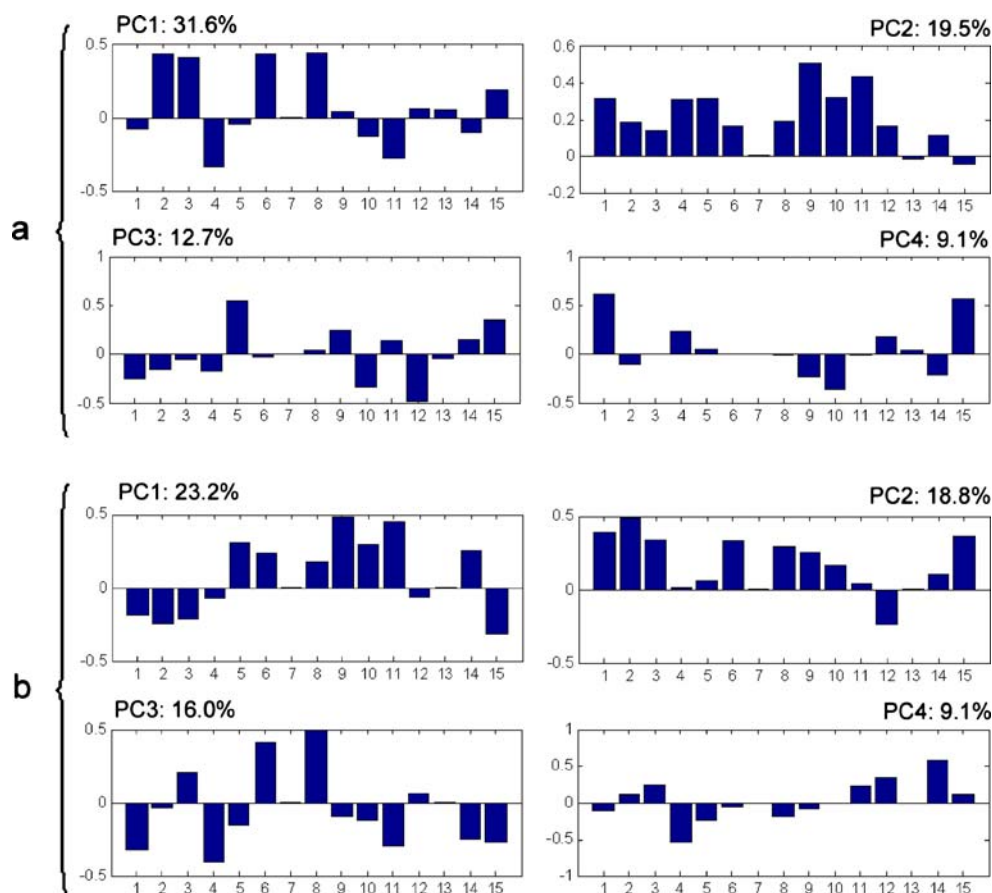
used in this work (see above), July seemed to be the month in which the contribution of pesticide contamination related to rice farming was at its maximum, especially at sampling sites CD8 and BA, located at the end of the irrigation system (Fig. 3). Summarizing, a steady decrease of contamination from the Ebro river and an increase of

contamination from the irrigation–drainage-water system, running through the rice fields, were clearly distinguished from PC1. Estimation of the relative contribution and distribution profiles of these two sources of pesticide contamination was possible for the samples analysed during all the months in which monitoring was performed.

Fig. 3 Scores plot of the first contamination pattern showing the spatial distribution of pesticide pollution. Comparison of the contamination pattern contributing to the upper part of the irrigation system with the contamination profile in the drainage channels in the lower part of the system
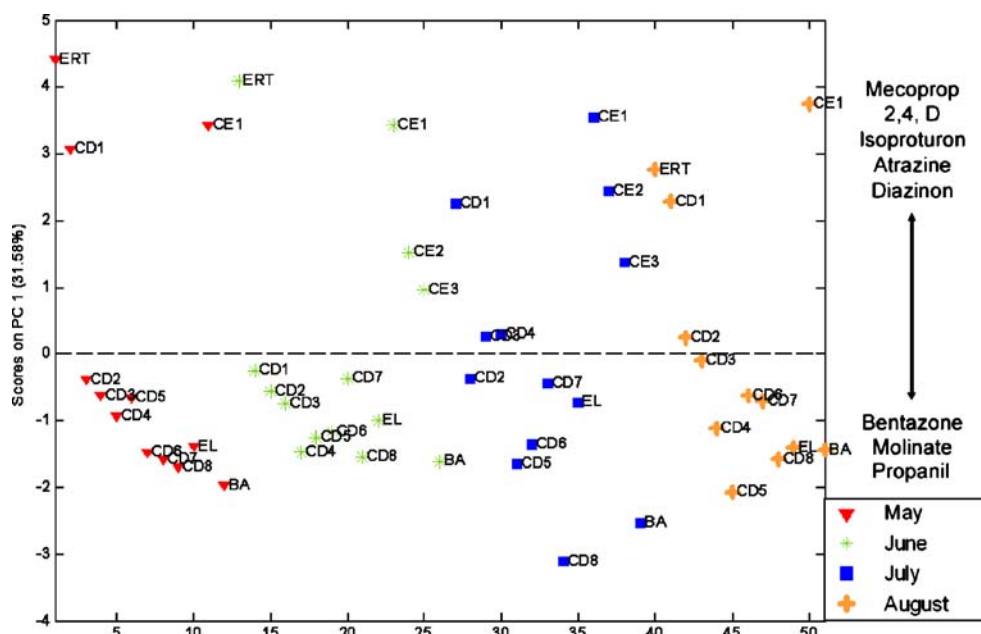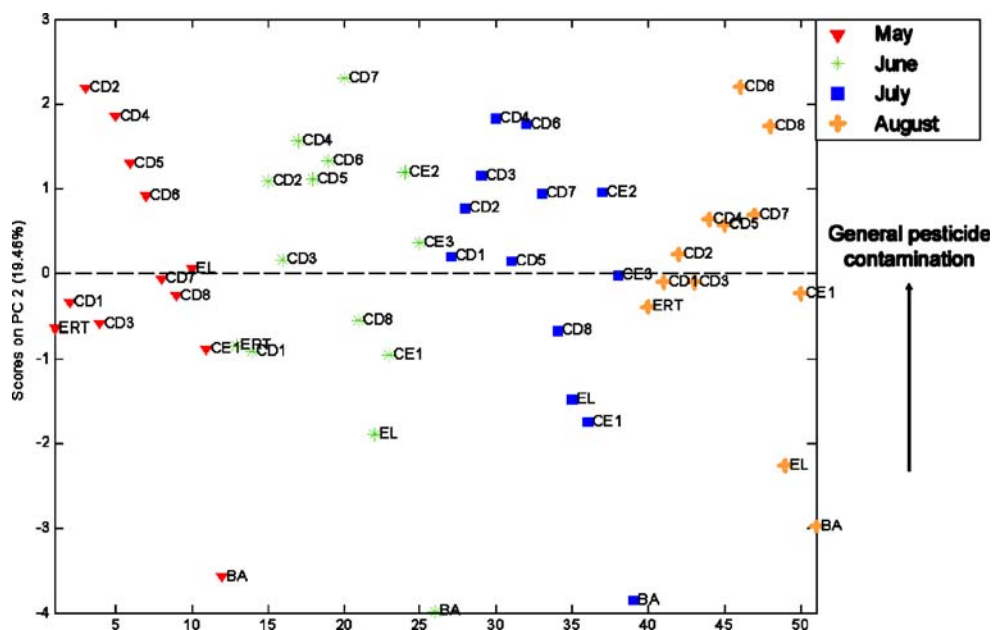
Fig. 4 Scores plot of the second contamination pattern showing spatial distribution of pesticide pollution


PC2 explained the 19.5% of the data variance (Fig. 2a) and described a rather general and diffuse pesticide-contamination pattern loaded by most of the pesticides except for chlortoluron, metolachlor, and diazinon (with very low loadings in this second PC). According to PC2 scores (Fig. 4), this general pesticide pollution was greater in the drainage channels (positive scores in Fig. 4) than in water coming directly from the river and from sampling sites located at the Badia d'Alfacs (BA) and Llac de l'Encanyissada (EL) (negative scores in Fig. 4). Sampling site BA was less affected by this PC2 contamination

pattern, possibly because of dilution by the sea water nearby. The sites with a higher contribution of this pesticide pollution pattern were, on the other hand, drainage channels from CD2 to CD7.

PC3 explained 12.7% of the data variance; its loadings profile (Fig. 2a) has a composition in which propanil, alachlor, and the acidic herbicides (negative loadings) were inversely correlated with simazine, diuron, diazinon, molinate, and fenitrothion (positive loadings), probably indicating different use of these pesticides in some sampling locations. PC4 explained only the 9.1% of the data variance

Fig. 5 Geostatistical interpolation using kriging for the distribution of the first contamination pattern of pesticides in the Ebro delta during the different months: (**a**) May, (**b**) June, (**c**) July, and (**d**) August
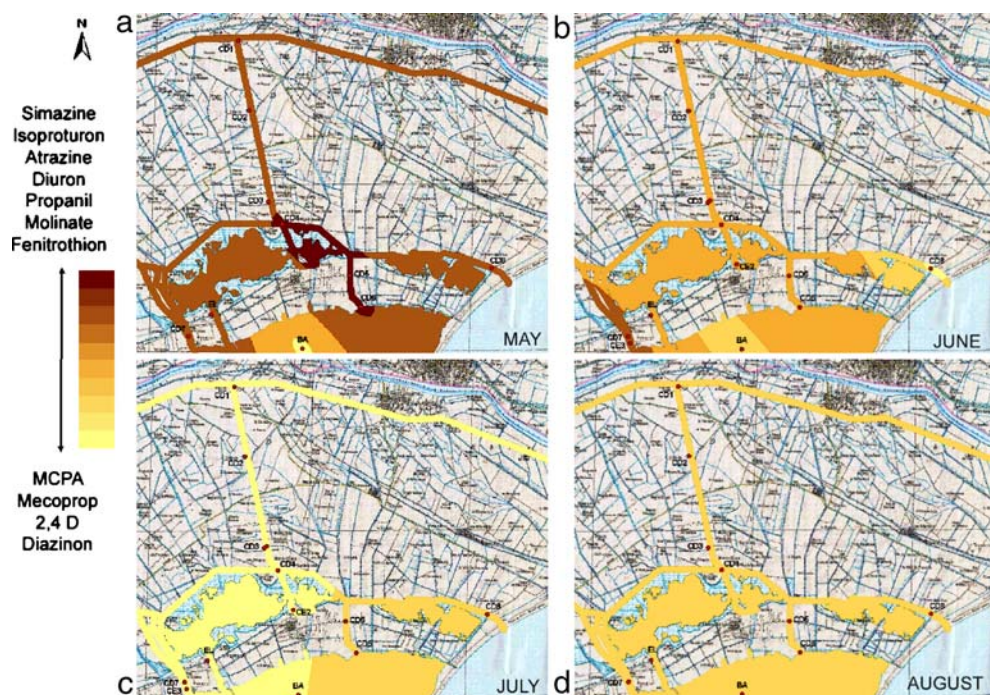
and also described the contrast between MCPA, diazinon, bentazone, and alachlor (positive loadings) and propanil, diuron, and fenitrothion (negative loadings). Interpretation of spatial distribution tendencies for PC3 and PC4 scores was not attempted and they probably refer only to small local changes in the concentrations of these pesticides. Better interpretation of these local changes would need a more detailed study.

Temporal patterns of pesticides pollution in the Ebro delta

Four principal components explaining 66.5% of the total data variance were selected to describe the temporal variation of pesticide concentrations in the Ebro delta during the main rice-growing season (Fig. 2b), deduced after applying the second proposed data pretreatment (column-wise concatenation of matrices of the four months then column autoscaling). PC1 explained the 23.2% of the total data variance and distinguished the different use of two groups of pesticides with inverse covariance, one with positive loadings for simazine, isoproturon, atrazine, diuron, propanil, molinate, and fenitrothion, and the other with negative loadings for the three acidic herbicides (MCPA, mecoprop, and 2,4-D) and for diazinon. The temporal trend in the use of these two groups of compounds changed during the different sampling months according to the prediction maps of PC1 scores obtained using GIS (Fig. 5). In May and June the contribution to the contamination profile, defined by positive loadings of PC1, was higher, with some pesticides characteristic of rice farming and

some that are not (Fig. 5a,b). Input of this contamination pattern was highest in May and decreased with time (displayed using dark colours in the GIS prediction map), especially at sampling sites CD4, CD5 and CD6 (Fig. 5a). Pesticides analysed in this study are moderately persistent (characterized by a low half-life) [24] and their concentrations are expected to decrease with time. Use of pesticides for sowing, soil preparation, and during the early tilling (20–35 days after sowing) but not after the panicle initiation must be taken into account to interpret the decreasing concentrations of typical rice crop pesticides, for example molinate or propanil. For fenitrothion the explanation is possibly different, because it is only applied when specific problems occur. In July and August, in contrast, there was more contamination by pesticides with negative loadings for PC1 (clearer colours in Fig. 5c,d). These are acidic herbicides typically used to control weeds, and diazinon, an insecticide very widely used in agriculture. July was the month most affected by the pollution pattern defined by negative PC1 loadings.

PC2 explained 18.8% of the data variance (Fig. 2b) and described more general diffuse contamination by pesticides with high positive PC2 loadings (pesticides used on the rice crop in the delta and other, non-specific, pesticides from the Ebro river; see the section Spatial variation of pesticide pollution), all of them covarying negatively with alachlor. The contamination pattern described by this PC was similar for sampling in May and July (Fig. 6a,c). This contamination pattern made greater contribution at sampling site CD2 in May whereas in July it was observed at the three

Fig. 6 Geostatistical interpolation using kriging for the distribution of the second contamination pattern of pesticides in the Ebro delta during the different months: (a) May, (b) June, (c) July, and (d) August
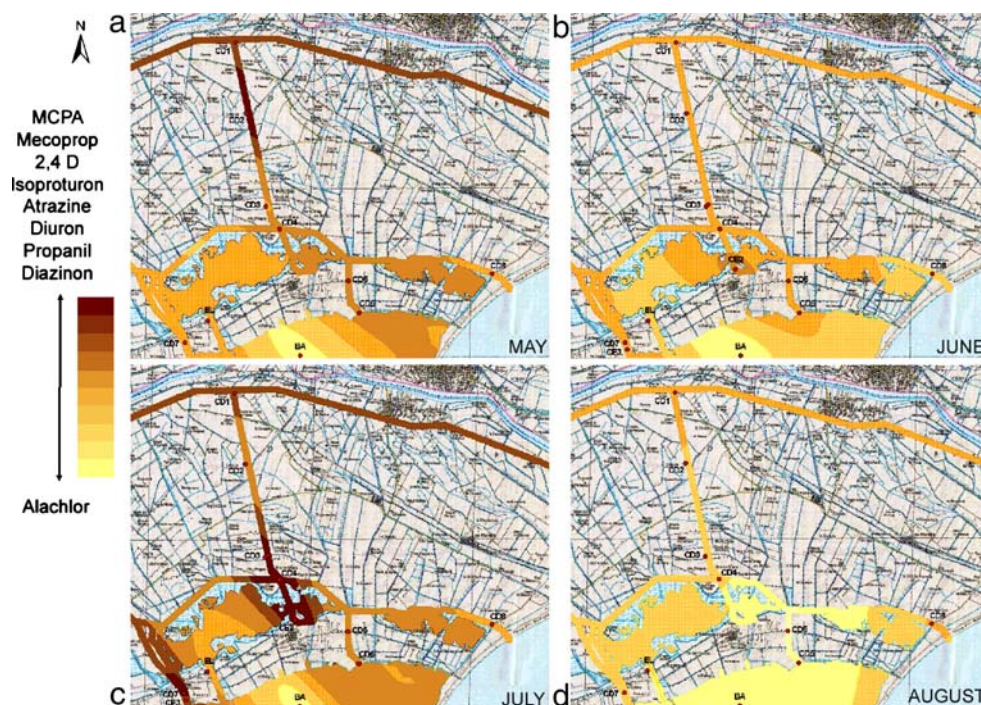
entrance channels (CE1, CE2, and CE3) and at CD3, CD4, and CD7. The last three sites were affected by the water repumping which occurred during June and July in particular, when the amount of water in the irrigation channels decreased and water from the drainage channels (already polluted with pesticides) was repumped. The effect of this water repumping had a clear environmental impact with a significant increase in the levels of pesticide pollution measured during the month of July (Fig. 6c). June was less affected by this pesticide contamination, as also was August (Fig. 6b,d).

PC3 explained the 16.0% of the data variance (Fig. 2b) and distinguished contamination from two groups of compounds covarying inversely. Pesticides with positive loadings were isoproturon, atrazine, and 2,4-D. In contrast, MCPA, bentazone, molinate, fenitrothion, and diazinon had higher negative loadings for this third PC. It described the behaviour of bentazone (with high negative PC3 loadings), which was found at high concentrations and was not described by the previous PCs. PC3 positive loadings again described pollution from the Ebro river (affecting mainly ERT, CD1, and CE1 sampling sites). Conversely, the lowest part of the irrigation system is characterized by the pollution, mostly from rice crop-specific pesticides, defined by negative loadings. PC4 explained only the 8.5% of the data variance (Fig. 2b) and described a contrast between contamination from fenitrothion and alachlor on one side (positive loadings) and that from bentazone on the other side (negative loadings). Investigation of the PC3 and PC4 scores enabled preliminary description of the use of

bentazone [3], especially during June and July. Whereas PC4 negative scores showed bentazone was applied to the rice fields during June (measured in the drainage channels), PC3 showed bentazone was applied during July in particular and was enriched (positive correlation) by simultaneous use and presence of molinate, MCPA, fenitrothion, and diazinon during the rice panicle period (Fig. 7a–d). Diazinon is not a rice crop-specific pesticide, as has already been remarked; it did, however, correlate positively with this group of pesticides in PC1 and PC3. It should, however, be borne in mind that diazinon occurred at rather low concentrations in all the delta samples investigated (Table 1).

Conclusions

From chemometric results obtained during analysis of pesticide concentrations in the four sampling campaigns performed in the Ebro delta during the main rice-growing season, two general interrelated trends, spatial and temporal, were discerned. First, a spatial distribution of pesticide pollution was identified which depended on the origin of the water contamination and distinguished pollution by pesticides from the Ebro river (in the upper part of the irrigation system, mostly detected at sampling sites CE1, ERT, and CD1) from another pollution pattern with its origin in the delta rice crops (measured in the drainage channels which collect water after it has passed through the fields). A decrease in the contribution of contamination

Fig. 7 Geostatistical interpolation using kriging for the distribution of the fourth contamination pattern of pesticides in the Ebro delta during the different months: (a) May, (b) June, (c) July, and (d) August
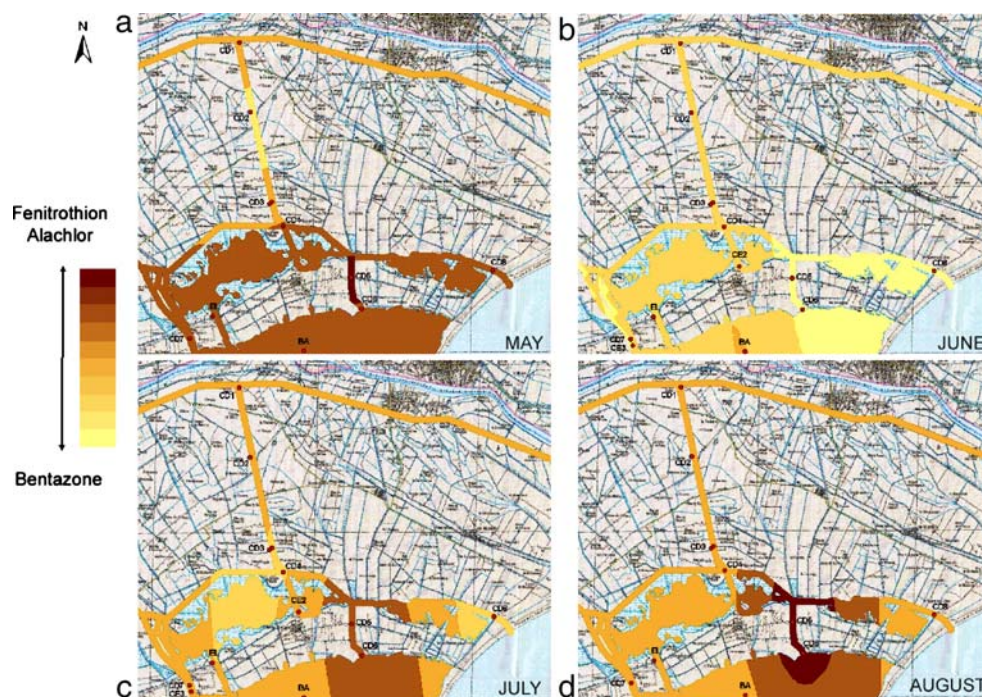
from the river was observed as water running through the delta rice fields was enriched with the new contamination pattern. This contamination was characterized by pesticides widely used in agriculture, especially for cereal crops, but not specific for rice. A contamination profile characterized by rice-specific pesticides (molinate, bentazone, propanil, MCPA, and fenitrothion) was identified in the drainage channels during July. At sampling sites BA and EL, contamination from the products from rice farming was also detected at lower levels than at the drainage channels, possibly because of a dilution effect.

A temporal distribution tendency, closely related to the rice crop cycle, was markedly different for May and July. In May some rice-specific pesticides were applied to the fields but the main origin of pesticide contamination was Ebro river water. Application of the pesticides propanil and molinate to prepare soil for sowing and for early tilling of the rice crop was identified, however. July, in contrast, was characterized by release of large amounts of pesticides into the irrigation channels and contamination from this source increased substantially. In June, a pollution profile in which bentazone contributed substantially was clearly identified in the drainage channels; during this month bentazone was used for post-emergence treatments of weeds, when the rice leaves were developing. Another possible source of contamination was identified in July, when insecticide treatments were applied, with other rice crop-specific pesticides, indicating that bentazone continued to be used with molinate, MCPA, fenitrothion, and diazinon. During July the effect of repumping was clearly apparent from the high input levels of pesticides; during this time there was not enough water in the irrigation channels and already polluted water was reused to irrigate the fields.

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