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Articles

Spatial and seasonal distribution of pesticides and clustering contamination status in a reservoir (Northeastern Mexico): Spatial analysis and multivariate approach

Distribución espacio-temporal de plaguicidas y clasificación de áreas de contaminación en un embalse al noreste de México: análisis espacial y multivariante

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Abstract

This study focused on the analysis of the spatial and temporal distribution of 13 pesticides in sediment and largemouth bass (*Micropterus* spp.) tissue, by spatial and multivariate analysis techniques in the "Vicente Guerrero" dam (Tamaulipas, Mexico). The concentration of the compounds was obtained by HPLC-MS/MS using the QuEChERS extraction procedure. The mean pesticide concentration varied in sediment from 0.37 to 8.33 µg/kg, and in largemouth bass from 0.05 to 2.88 µg/kg. Spatial variation was significant at the five sampled sites, both in sediment and fish. The highest concentration and number of pesticides was recorded in the center and east of the reservoir and declined towards

the landfill. The concentration of pesticides in sediment was significant ($p < 0.05$) throughout the evaluated period, while differences in the concentration of largemouth bass were only significant in December and May. The most frequent pesticides in sediment and tissue were amitraz, ethion, parathion, pyriproxyfen and propargite, the latter present only in the center of the dam. The results obtained suggest bioaccumulation of five pesticides from sediment to fish. Parathion is an extremely dangerous pesticide for human health and together with ethion and propargite are highly toxic to aquatic life. The results suggest carrying out frequent monitoring of the dam to detect the presence of high-risk pesticides and preserve the ecosystem health.

Keywords: Vicente Guerrero dam, high risk pesticides, sediment, *Micropterus* spp., HPLC-MS/MS.

Resumen

Este estudio analizó la distribución espacial y temporal de 13 plaguicidas en sedimento y tejido de lobina (*Micropterus* spp.), por técnicas de análisis espacial y multivariantes en la presa "Vicente Guerrero" (Tamaulipas, México). Los compuestos fueron detectados por HPLC-MS/MS siguiendo el procedimiento de extracción QuEChERS. La concentración media de plaguicidas varió en sedimento de 0.37 a 8.33 µg/kg y en lobina de 0.05 a 2.88 µg/kg. La variación espacial fue significativa en los cinco sitios muestreados tanto en sedimento como en pescado. La mayor concentración y diversidad de plaguicidas se dio en la zona de confluencia (centro y zona este) en el embalse y declinó hacia el vertedero. La variación temporal en sedimento fue significativa ($p < 0.05$)

en todo el periodo muestreado, mientras que en lobina solo en diciembre y mayo. Los plaguicidas más frecuentes en los dos tipos de muestras fueron amitraz, etión, paratión, piriproxifen y propargita, este último con la mayor variación y presente solo en el centro de la presa. Los resultados sugieren bioacumulación de al menos cinco plaguicidas desde el sedimento hacia el pescado. El paratión ha sido señalado como extremadamente peligroso para la salud humana; junto con etión y propargita son altamente tóxicos para la vida acuática, por lo que se sugiere realizar monitoreo frecuente de la presa, a fin de detectar la presencia de plaguicidas de alto riesgo y conservar la sanidad del ecosistema.

Palabras clave: presa Vicente Guerrero, plaguicidas de alto riesgo, sedimento, *Micropterus* spp., HPLC-MS/MS.

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Introduction

Lentic aquatic ecosystems are highly valued for the complex structures they develop inside (Cervantes, 2007), and are in turn vulnerable to anthropogenic pressures (Semarnat, 2016). Urban, industrial (Mateo-Sagasta, Zadeh, & Turral, 2017), agricultural and livestock activities are the main causes of deterioration and contamination of this type of

ecosystems (Ongley, 1996). Compounds that are deposited directly or indirectly in aquatic systems include pesticides and veterinary drugs. In Mexico, the use of pesticides per unit of cultivated area increased more than 50 % in the last two decades; in 2017 alone, more than 47 000 t were applied (USEPA, 2017; FAO, 2020).

Pesticides are used in production chains, health systems and domestically to control or eradicate harmful or unwanted species of organisms (Damalas & Eleftherohorinos, 2011). Commerce and use of these substances in Mexico occur in scenarios with little regulation and minimal institutional surveillance (CNDH, 2018). Currently, there are about 7 700 products in the country with valid registration according to Comisión Federal de Protección contra Riesgos Sanitarios (Cofepris, 2020). Of these, 4 000 are prohibited or restricted in other countries by international organizations or treaties (Bejarano-González, 2017) due to their high persistence, bioaccumulation capacity and negative effects on the environment and human health (Zijian & Jennings, 2018; Albert & Viveros, 2019; FAO & WHO, 2019). The introduction of chemical compounds into water bodies represents a threat to organisms, puts the ecosystem balance at risk (Whitmore, Künast, & De-Graeff, 2015) and its effects can extend to terrestrial environments along food webs (Tsaboula *et al*., 2016).

Primary activities in northeastern Mexico are focused on the agricultural, livestock and fishing sectors (Banco de México, 2020). In the state of Tamaulipas, 1.3 million hectares are cultivated mainly with sorghum and corn (SIAP, 2020), under cycles of rainstorm and irrigation. The area for livestock exploitation, mostly bovines, is 5 million hectares

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(Secretaría de Desarrollo Rural, 2019). Both types of activity use chemicals to control pests and ectoparasites. The second most important citrus growing area in the country is located in the center of the state of Tamaulipas, made up of 32 thousand hectares (SIAP, 2020). The irrigation water that supplies the citrus fruit comes from three tributaries, the "Corona", "Purificación" and "Pilón" rivers, contained by the "Vicente Guerrero" dam (VGD). This reservoir discharges its waters to the "Soto La Marina" river and provides water to cities and communities, among which Ciudad Victoria stands out.

The distribution, destination and environmental impact of the pesticides used in the central zone of the state of Tamaulipas is uncertain. Recent studies indicate the presence of organochlorine compounds in water (Heyer, Ramos, De-la-Garza, Rivera, & Castro, 2008) and fauna (Uresti *et al*., 2008) of the VGD. However, there is currently a wide catalog of pesticides available on the market, which could be incorporated into the reservoir by agricultural activity without knowing their distribution and possible impact on the water ecosystem. Therefore, monitoring is required to know the identification and distribution of pesticides, and the areas where they pose the highest risk.

Monitoring studies are expensive and generate large data matrices (Schenone, Moscuzza, Avigliano, Rosso, & Mabragaña, 2014), which need to be organized and explored to obtain the highest quantity and quality of information. On this account, multivariate statistical (James & McCulloch, 1990; Mangeaud, 2004) and geospatial tools represent an alternative for the management and processing of a significant amount of data (Drake & Bauder, 2005). The integration of these techniques makes

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it possible to analyze the distribution patterns of pesticides in the different components of the ecosystem, determine spatio-temporal variations and identify the regions with the highest number and concentration of compounds (Chaudhry, Kumar, & Alam, 2019).

The objectives of this study were to identify the presence and spatio-temporal distribution of pesticides in sediment and muscle of largemouth bass (*Micropterus* spp.), as well as to classify the variety and concentration of pesticides at the sampling sites.

Materials and methods

Study area

The Vicente Guerrero dam (VGD) or Las Adjuntas is located in Padilla, Tamaulipas, between the geographical coordinates 23° 57’ 34” N and 98° 39’ 57” W (Figure 1). The VGD is the reservoir with the highest capacity in the northeast of Mexico, with 3 910 million m^3 at the Normal Pool Elevation (NPE) (Conagua, 2015). The main uses of the dam water are flood control, domestic supply, irrigation, aquaculture in floating cages, commercial and recreational sport fishing (Semarnap, 1999).

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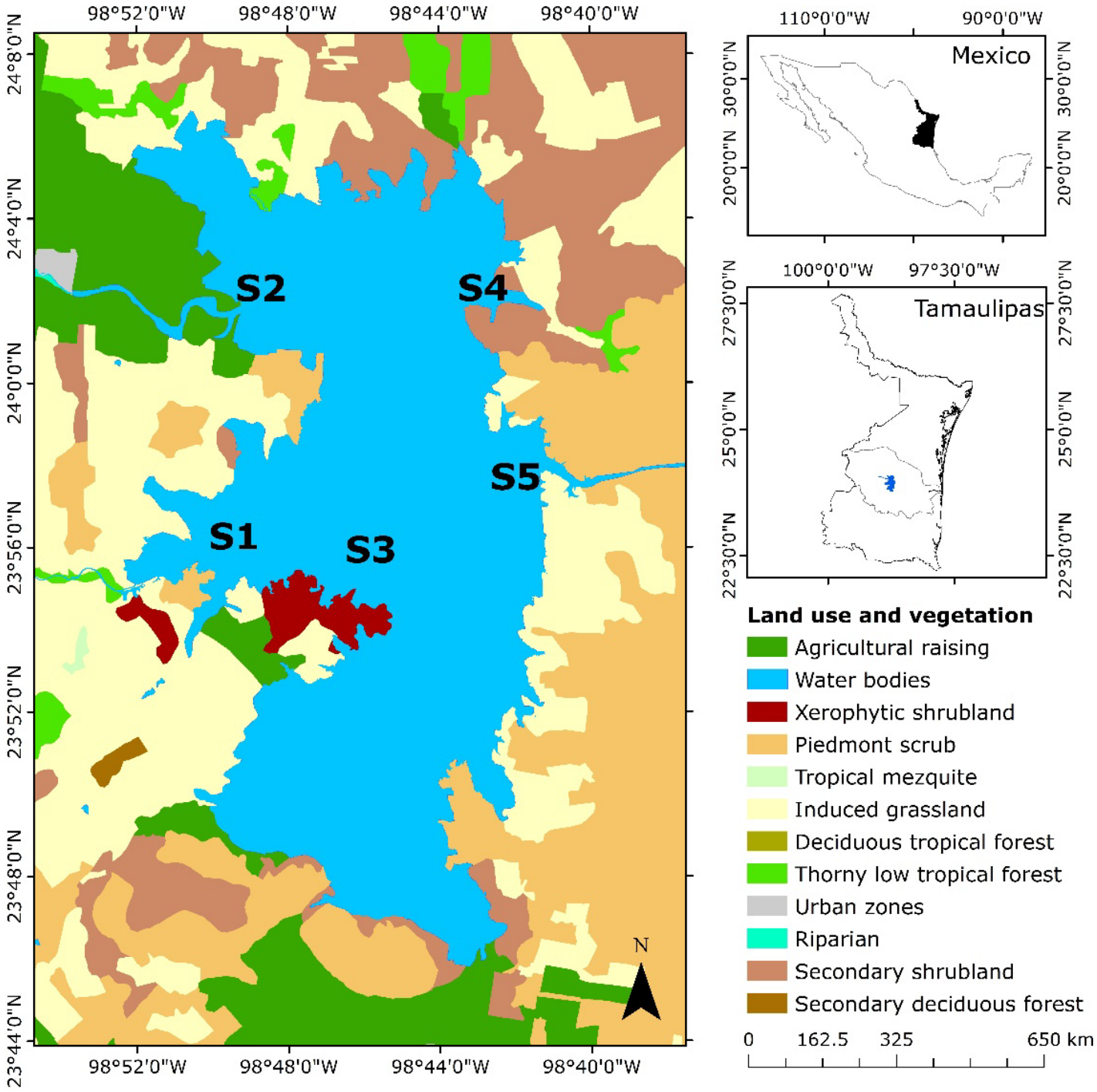

Figure 1. Study area of sediment and largemouth bass muscle sampling sites. Vicente Guerrero Dam, Tamaulipas, Mexico.

Sampling

We obtained the concentration of pesticides from sediment and tissue samples of largemouth bass (*Micropterus* spp.), which were collected monthly (in triplicate) at five sampling sites (Figure 1) from December 2016 to May 2017. Table 1 shows the description of the sampling sites. The sediment sample (500 g) was obtained from the first 15 cm of the bottom surface at 1.5 m depth, using a polyvinyl chloride (PVC) tube, and placed in sealed polyethylene bags (Vázquez-Sauceda, Pérez-Castañeda, Sánchez-Martínez, & Rábago-Castro, 2015), transferred to the laboratory on ice and frozen at -20 °C.

Table 1. Description of the sediment and largemouth bass muscle sampling sites, Vicente Guerrero dam, Tamaulipas, Mexico.

Site	Latitude	Longitude	Site description	General characteristics
S1	23º 54´ 967	98º 52´ 372	Río Corona mouth	Discharge of water with agrochemical residues in crops (citrus, corn and sorghum) and livestock (cattle and pigs), domestic and industrial wastewater.
S2	24º 49´ 737	98º 49´ 597	Río Purificación mouth	Chemical load contribution area for citrus, corn and sorghum cultivation. Livestock production (bovines, sheep and pigs).
S3	23º 56´ 880	98º 45´884	Confluence of rivers Corona and Purificación	Receiving area for the waters of both tributaries. It presents three islets with rural human settlements.
S4	24º 2´ 153	98º 42´294	Far Northeast of the VGD	Receiving area for the flow of Río Purificación and part of Río Corona. Presence of tilapia aquaculture farms.
S5	23º 57´ 884	98º 41´303	Spillway	VGD dump zone. It flows into the Soto La Marina River; later, in the Gulf of Mexico.

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The fishing method was by lure and then the specimens were marked and preserved on ice for transport to the laboratory. Subsequently, a 500 g sample composed of skin, subdermal fat and edible muscle fraction from each fish was kept in a polyethylene bag and frozen at -20 ºC in the laboratory.

Materials, reagents, and solutions

Pesticide standards were purchased from Dr. Ehrenstorfer Laboratory (Augsburg, Germany), the purity of all standards was > 95 %. Stock solutions (concentrated) were prepared for each pesticide by dissolving the standards in methanol or acetronitrile at a concentration of 10 mg/l and the diluted pesticide solutions at 0.01 mg/l, both stored at -20 ºC. The HPLC grade solvents were purchased in JT Baker (Phillipsburg, NJ, USA). The multi-residual extraction and dispersion kits for the quick, easy, cheap, effective, rugged and safe (QuEChERS) method (BSI, 2008) were supplied by Agilent (Agilent Technologies, Santa Clara, CA, USA). Triphenyl phosphate (TTP) was used as surrogate standard and bromophos methyl as internal standard.

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Sample preparation

The sediment and tissue samples underwent analysis to detect and estimate the concentration of ametrine (AME), amitraz (AMZ), ethion (ETN), malathion (MAL), methamidophos (MPS), parathion (PAR), methyl parathion (P- MET), pyrimethanil (PML), pyriproxyphen (PFN), propargite (PRO), propiconazole (PZL), thiabendazole (TZL), and trifloxystrobin (TBN). The frozen sediment and fish samples were milled and homogenized with blender separately to avoid defrosting (Ernst *et al*., 2018). We carried out extraction by solid phase dispersion (dSPE) – QuEChERS using salts and acetronitrile according to the European Standard EN 15662 (BSI, 2008) for 10 g of sample. A 1 ml aliquot of extract was transferred in a vial and acidified with 10 µL of 5 % formic acid solution in acetronitrile. The supernatant was transferred for HPLC-MS/MS analysis.

High performance liquid chromatography/tandem mass spectrometry

Detection and quantification of pesticides were performed on an Agilent 1200 SL binary liquid chromatograph coupled to 6430 triple quadrupole (QqQ) mass spectrometer, both from Agilent Technologies (Santa Clara, CA, USA). The extract was inyected in an Agilent Technologies Zorbax Eclipse XDB-C18 column (150 mm x 4.6 mm, 5 µm). The chromatographic separation was carried out with a linear gradient with 0.1 % formic acid in ultrapure water as mobile phase (A) and acetronitrile as organic phase

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(B). The gradient elution program started at 70 % (A) and 1 % (B) and was held for 3 min; gradually, A reached 0 % and B 100 % after nearly 22 min and was upheld for 5 min. Subsequently, A increased to 30 % and B to 70 % in 5 min, and sustained for 5 min. We performed the MS/MS detection under the following conditions: 11 l/min drying gas flow, gas nebulizer at 15, gas temperature at 300 °C. Data collection and processing was done using Agilent Mass Hunter and dynamic multiple reaction monitoring (DMRM) mode. Table 2 shows the recovery percentages, standard deviation, and the detection limits of pesticides by type of sample analyzed.

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Table 2. Percentage of recovery, standard deviation and limit of detection of pesticides by type of sample.

Compound	Recovery (%)		Detection limit (µg/kg)	
	S	F	S	F
AME	92 ± 0.0012	92 ± 0.0014	0.0040	0.0047
AMZ	79 ± 0.0011	91 ± 0.0015	0.0039	0.0051
ETN	86 ± 0.0013	93 ± 0.0014	0.0043	0.0049
MAL	72 ± 0.0013	81 ± 0.0013	0.0043	0.0045
MFS	91 ± 0.0012	84 ± 0.0014	0.0042	0.0047
P-MET	75 ± 0.0011	78 ± 0.0014	0.0038	0.0047
PAR	94 ± 0.0011	96 ± 0.0014	0.0039	0.0048
PML	91 ± 0.0012	91 ± 0.0015	0.0040	0.0051
PFN	89 ± 0.0011	84 ± 0.0015	0.0036	0.0050
PRO	86 ± 0.0013	91 ± 0.0015	0.0044	0.0050
PZL	92 ± 0.0011	85 ± 0.0014	0.0038	0.0048
TZL	95 ± 0.0013	81 ± 0.0015	0.0044	0.0051
TBN	86 ± 0.0012	77 ± 0.0015	0.0041	0.0050

S = Sediment
F = Fish
AME = Ametryn
AMZ = Amitraz
ETN = Ethion
MAL = Malathion
MPS = Methamidophos
PAR = Parathion
P-MET = Parathion-methyl
PML = Pyrimethanil
PFN = Pyriproxyfen
PRO = Propargite
PZL = Propiconazole
TZL = Thiabendazole
TBN = Trifloxystrobin

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Exploratory data analysis

Sediment and tissue independent data were tested for normality with the Royston statistics, and homogeneity of variances by the Levene test (Porras-Cerrón, 2016). The original data in the two types of samples presented non normal distributions, so we performed their logarithmic transformation to examine them again.

Tests for normality and homoscedasticity in the transformed data showed non normal distributions, again; therefore, subsequent multivariate analyses were conducted using original data set. Distribution and spatial structure of data were analyzed during selection of the interpolation method.

Spatial-temporal analysis of pesticides

Spatial and temporal distribution of pesticides in sediment and tissue were analyzed by Discriminant Function Analysis (DFA). The DFA is a multivariate statistical test that uses linear combinations from a set of variables to find the one that contributes the most to discrimination between groups (James & McCulloch, 1990). The discriminant function is constructed from the following formula:

$$f(G_i) = K_i + \sum_{j=1}^{n} w_{ij} p_{ij} \quad (1)$$

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where:

i = number of groups (Singh, Malik, Mohan, & Sinha, 2004)

K_i = constant inherent to each group

n = number of parameters used to classify a set of data into a given group

w_j = weight coefficient assigned by the DFA for a given selected parameter (p_j)

The DFA was operated using standard mode and the original sediment and tissue databases. The groups to be compared were the combination of the categories of five sites (spatial) and six months (temporal). The first two functions (roots) were retained by providing a variance > 70 %. Wilks-Lambda test was used to determine the discriminatory ability of the function.

Clustering of pollution degree

Monthly pesticide concentrations in sediments and tissues were converted into individual point shapefiles. Subsequently, these shapefiles layers led to the generation of interpolation surfaces for each pesticide, by type of sample and month. The files were projected in the UTM coordinate system (datum WGS84) zone 14 N. We performed the selection of the interpolation method by comparing the results of three Kriging geostatistical models (Ordinary, Simple and Universal) and the Inverse-distance weighting method (IDW). The Kriging methods require statistically homogeneous spatial variation at all sites along the analysis surface (ESRI, 2016). In this study, samples were concentrated in five

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regions of the VGD, which generated a high correlation between the data from the same site and little or no correlation between sites. Therefore, the structural analysis showed a weak spatial homogeneity or stationarity in the distribution of the data on the VGD surface, this is a fundamental characteristic for the regionalized variable theory (Matheron, 1965). Additionally, Juang, Lee and Ellsworth (2001), and Drake and Bauder (2005) point out that pollutants of anthropogenic origin frequently present non-normal distribution and wide variations, so that the choice of the interpolation method depends on the structural analysis of the data. Considering the former, geostatistical methods were discarded as viable.

On the contrary, some studies recommend the IDW method when the number of samples is reduced and the distribution is not uniform (Cely-Pulido, Siabato-Vaca, Sánchez-Ipia, & Rangel-Sotter, 2002; Drake & Bauder, 2005), or there are large distances between sampling sites (Villatoro, Henríquez, & Sancho, 2008). Consequently, the IDW model was chosen to perform the interpolations. The IDW estimates the value of unsampled points by considering that the nearest neighbor to the observed point will have similar characteristics and their influence or weight will be greater (Wong, 2017). The estimated values were calculated according to:

$$Z=[\sum_{i=1}^{n}(Z_i/d_i^m)/\sum_{i=1}^{n}(1/d_i^m)] \quad (2)$$

where:

Z = estimated value

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Z_i = measured sample value at point *i*

d_i = distance between Z and Z_i

m = weighting power to d_i (Arslan & Turan, 2015)

Weighting factors were assigned in proportion to the second power and we use the default value of 12 close neighbors to perform the interpolations in ArcMap 10.3 - Spatial Analyst Tools - IDW. Individual IDW raster layers were generated for each variable, on a monthly basis (78 layers for each type of sample). The shapefiles layers obtained were converted into polygon vector format in QGIS 3.8.1-1. The vector layers were geometrically intersected in ArcMap Geoprocessing - Intersect, which projects a common spatial reference system (input and output) to calculate the geometric relationships and intersection vertices between the different feature layers, whose data are identified by a new digital number (ESRI, 2016). With these digital numbers for each variable, we built the clusters through the generalized k-means analysis in Statistica 13.0. This analysis is a non-hierarchical method that seeks the optimal number of k groups, into which a set of objects can be divided to minimize the variance within the group (David, 2017) and maximize the differences between groups (Arriaga-Flores *et al*., 2018). The analysis generates the centroid in an initial cluster, performs iterations by calculating the Euclidean distance between each data point and the centroid, and groups the closest data (Zubaidah, Karnaningroem, & Slamet, 2018). The centroids of each pesticide were weighted on an ascending scale and after we calculated the average of the weights per cluster, the pollution degree was obtained. The classification was linked to the intersection maps to

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visualize the spatial and temporal patterns of contamination in the reservoir.

Results

In the sediment and largemouth bass samples from VGD we identified 13 pesticide residues. The mean value and standard deviation of the concentration by type of sample are presented monthly (Annex A and B).

The highest mean concentration in sediment was pyrimethanil, PML (8.33 µg/kg) in S4 (Table 1) during March, while the lowest in S3 in February (0.37 µg/kg). The highest mean concentration in tissue was pyriproxyfen, PFN (2.88 µg/kg) in S2 in May, and the lowest thiabendazole TZL (0.05 µg/mg) in December. Parathion (PAR) was present in 100 % of the sediment and bass tissue samples (Figure 2). Amitraz (AMZ) was detected in all sediment samples, and ethion (ETN) in all tissue samples.

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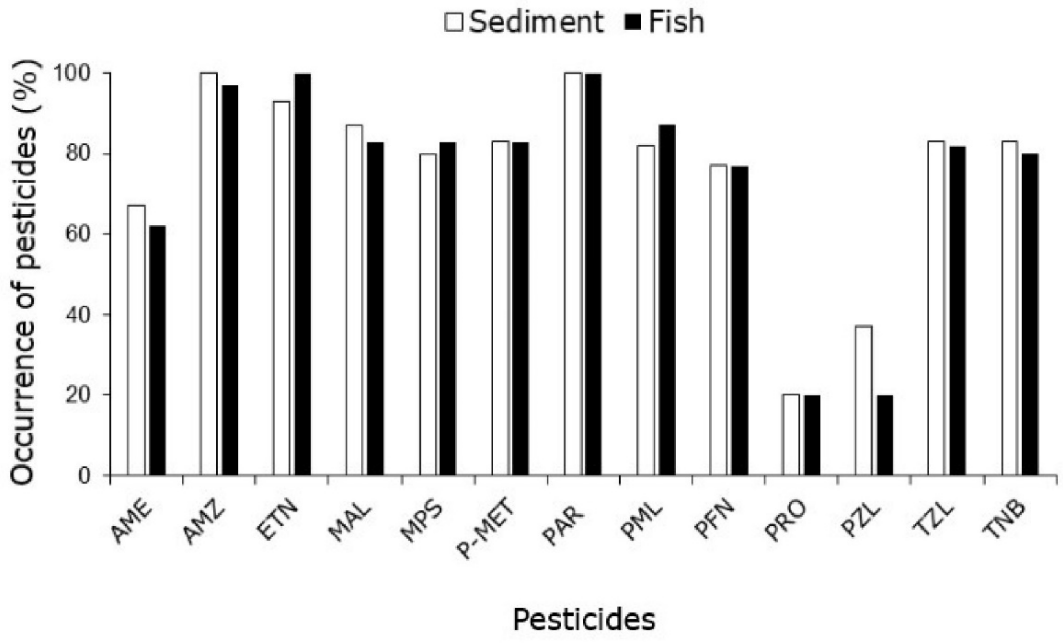

Figure 2. Frequency of pesticide residues in sediment and bass muscle.

Spatio-temporal distribution of pesticides

Sediment

Five sampling sites presented significant spatial differences (*Wilks lambda* = 0.0097; *F* (52.26) = 11. 964; $p < 0.001$; Annex C) explained by the sum of the eigenvalues of the first two roots (90.34 %). The Wilks lambda estimator value showed discrimination between groups. The pesticide presenting the greatest variation associated with the first root was propargite, PRO (Figure 3), which was registered only in S3 during six months of sampling (Annex A). Likewise, this compound was negatively

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correlated with ametrin AME and PFN, which were associated with the rest of the sites. Pesticide methamidophos (MPS) registered the greatest variation on the second root. The MPS concentration was related to S3 in January, February and April, and to S4 in March and May (Figure 3). The AMZ and PAR were recorded at all sites during the time of the study (Annex A).

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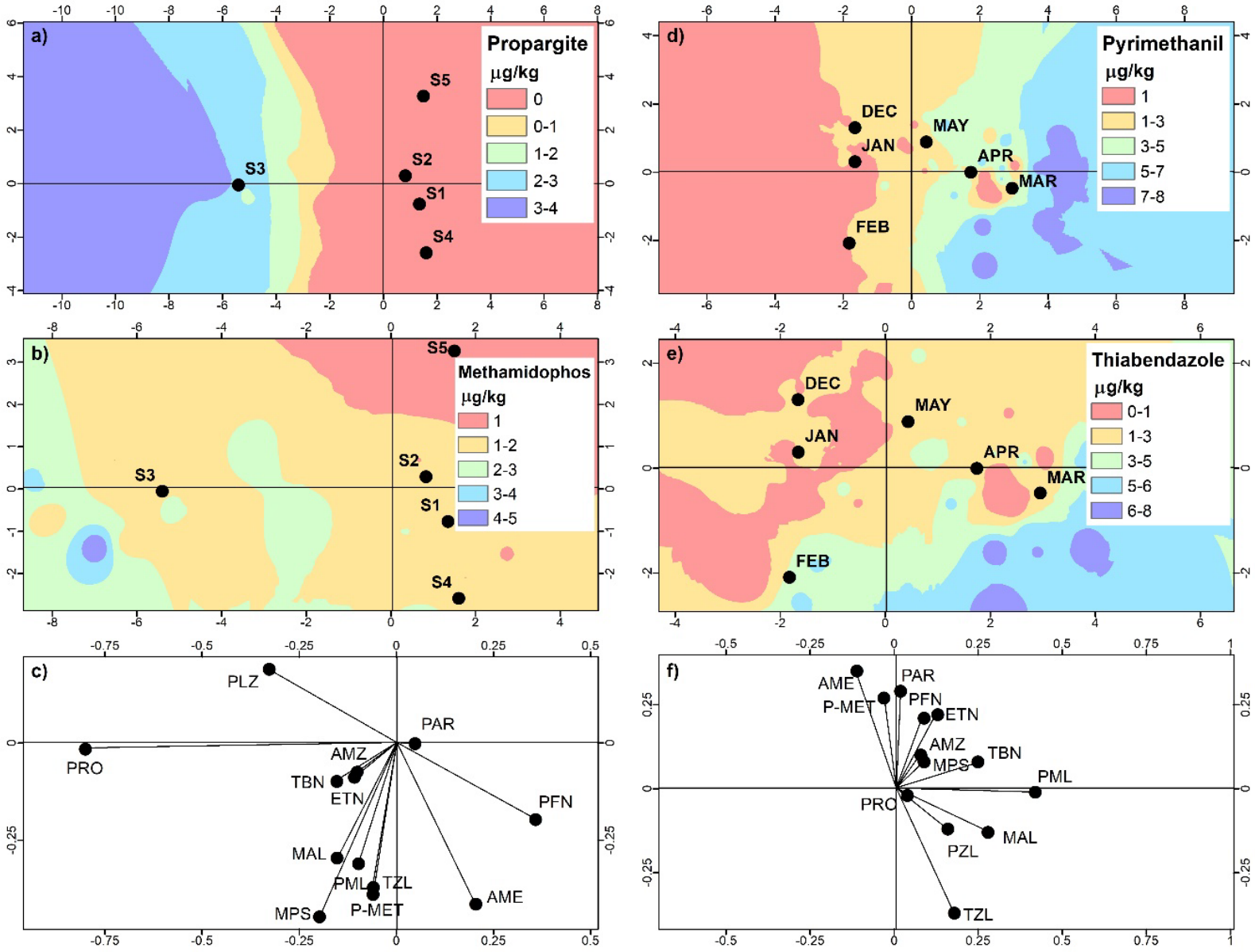

Figure 3. Discriminant functions in sediment. Spatial analysis, distribution of the most significant variables a) PRO and b) MPS, c) factor structure graph. Temporal analysis, most significant variables d) PML, and e) TZL, f) factor structure graph.

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The temporal variations were significant in the six months of sampling. The DFA presented the following *Wilks lambda* values = 0.0331; F (65.32) = 5.2837; $p < 0.001$ (Annex C), while the accumulated variance explained by the first two roots was 78.11 %. The variable that registered the greatest difference over the first root was PML, associated with the month of March. The TZL presented greater variation on the second root, associated with February, although it was negatively correlated with AME (Figure 3).

The k-means clustering analysis identified several groups for each month of sampling (Annex D). The pollution degree was represented on maps (Figure 4). The sediment in S3 registered the highest pollution values during four months, represented through the clusters (centroids): February (C3), March (C3), April (C8), and May (C4), with presence of malathion (MAL) and PRO on these clusters. The S4 registered the highest pollution in January (C2) and May (C1), with the presence of AMZ and PFN. The concentration of AMZ in the sediment of S3 and S4 was high in all months, except April. S1 registered higher contamination in December (C2) with a predominance of AME, AMZ, MAL, MPS, methyl parathion (P-MET) and PAR. The S5 sediment presented a lower concentration and variety of pollutants during the six-month period; however, some months registered increases in PFN (December), PAR (February), propiconazole (PZL, April and March) and trifloxystrobin, (TBN, April). The monthly analysis of variance of the clusters showed significant differences ($p < 0.05$) with respect to the 13 variables (Annex D).

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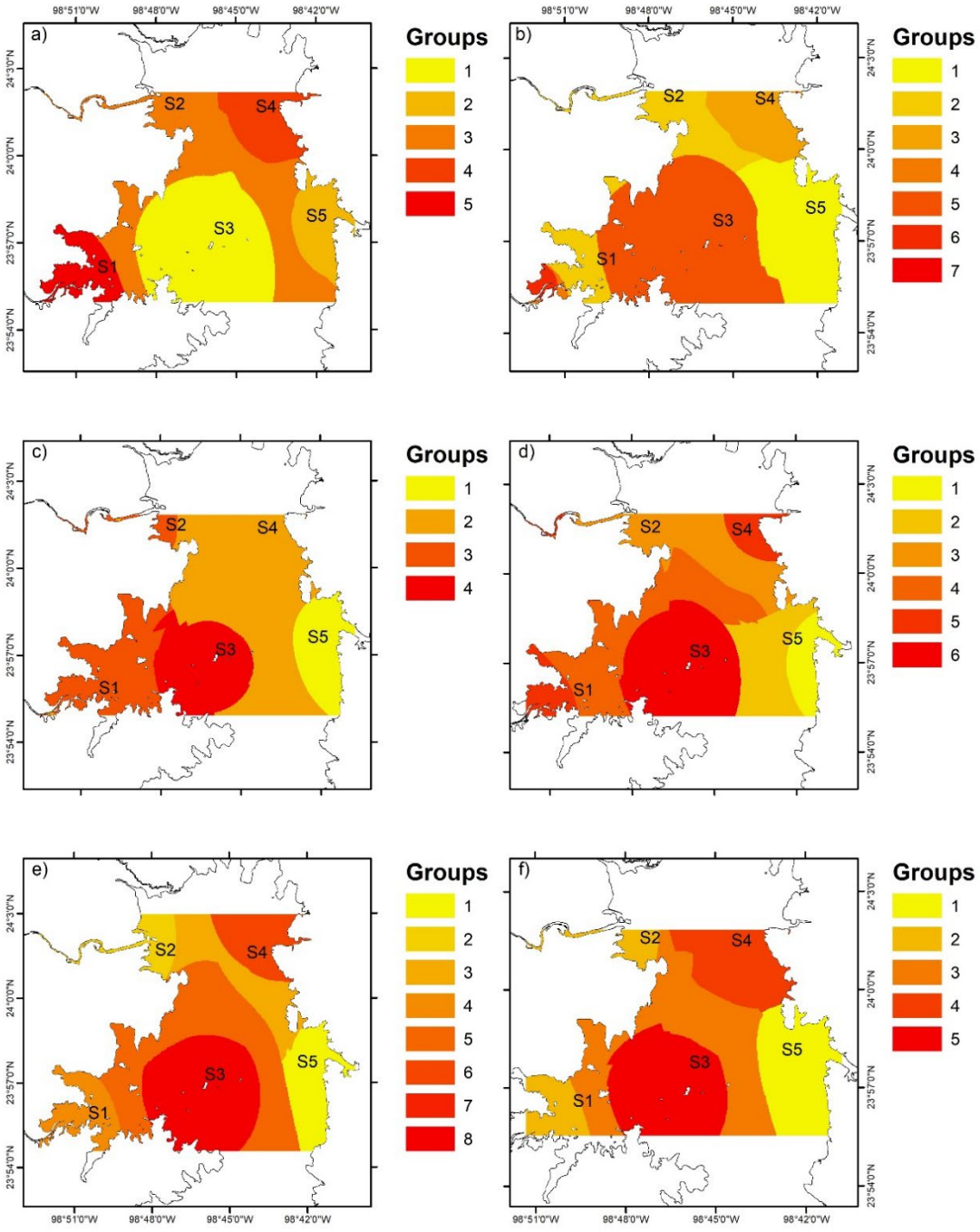

Figure 4. Classification of sites by degree of sediment pollution: a) December, b) January, c) February, d) March, e) April, f) May. S1, S2, S3, S4, S5 described in Table 1.

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Tissue

The spatial differences of the bass samples were significant between the sites (*Wilks lambda* = 0.0039; *F* (52.26) = 16. 503; *p* < 0.001; Annex C). The first two roots presented a cumulative variance of 84.52 %. The compounds that showed the greatest variation on the first root were PRO and PZL associated with S3 during the six months (Annex B) and negatively correlated with AME (Figure 5). The greatest variation associated with the second root was represented by the MPS linked to S4. The pesticides AMZ, ETN and PAR were detected in the bass specimens from the five sites during the six months (Annex B).

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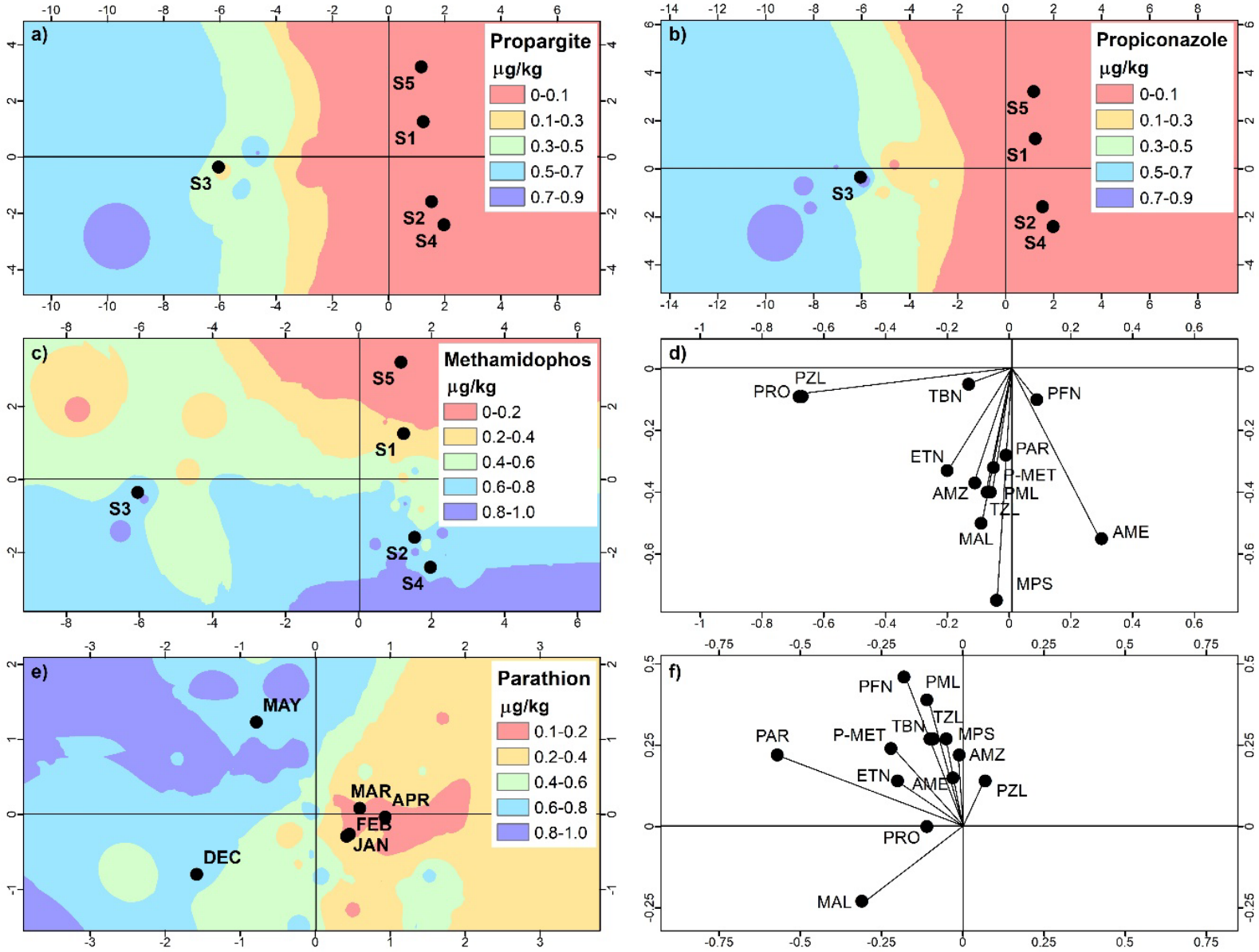

Figure 5. Discriminant functions in bass tissue. Spatial analysis, distribution of the most significant variables a) PRO b) PZL c) MPS, d) factor structure graph. Temporal analysis, most significant variables e) PAR and f) factor structure graph.

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December and May showed significant variations in the concentration of pesticides [*Wilks lambda* = 0.2971; *F* (65.32) = 1.4653; $p < 0.0174$; Annex C]. The first two roots recorded 82.25 % of the data variation. Wilks's lambda estimator only discriminated the groups on the first root; therefore, an overlap between groups occurred on the second root. The most significant variable related to the first root was PAR in December and May, but it was negatively correlated with PZL (Figure 5).

The k-means analysis recognized various groups per month of sampling (Annex E), and the pollution degree was represented on maps (Figure 6). For the construction of the clusters, some compounds were removed as variables during the k-means analyses, as they provided little or no information. The largemouth bass collected in S4 presented the highest pollution degree during the sampling period (Figure 6), and the associated clusters were December (C3), January (C3), February (C2), March (C2), April (C2) and May (C3), all with AMZ presence. Sites S4 and S5 registered a higher concentration in December with a predominance of MAL, P-MET and PAR. The S3 presented two contamination peaks: March and April, both with high concentrations of AME, AMZ, ETN, MPS, P-MET, PAR, PFN, and TZL. S5 registered higher contamination in December, but the remaining months had the lowest concentration and the least variety of contaminants. S1 exhibited a low degree of bass contamination from January to April, although with contamination peaks in May by ETN, P-MET, PML, TZL, and TBN.

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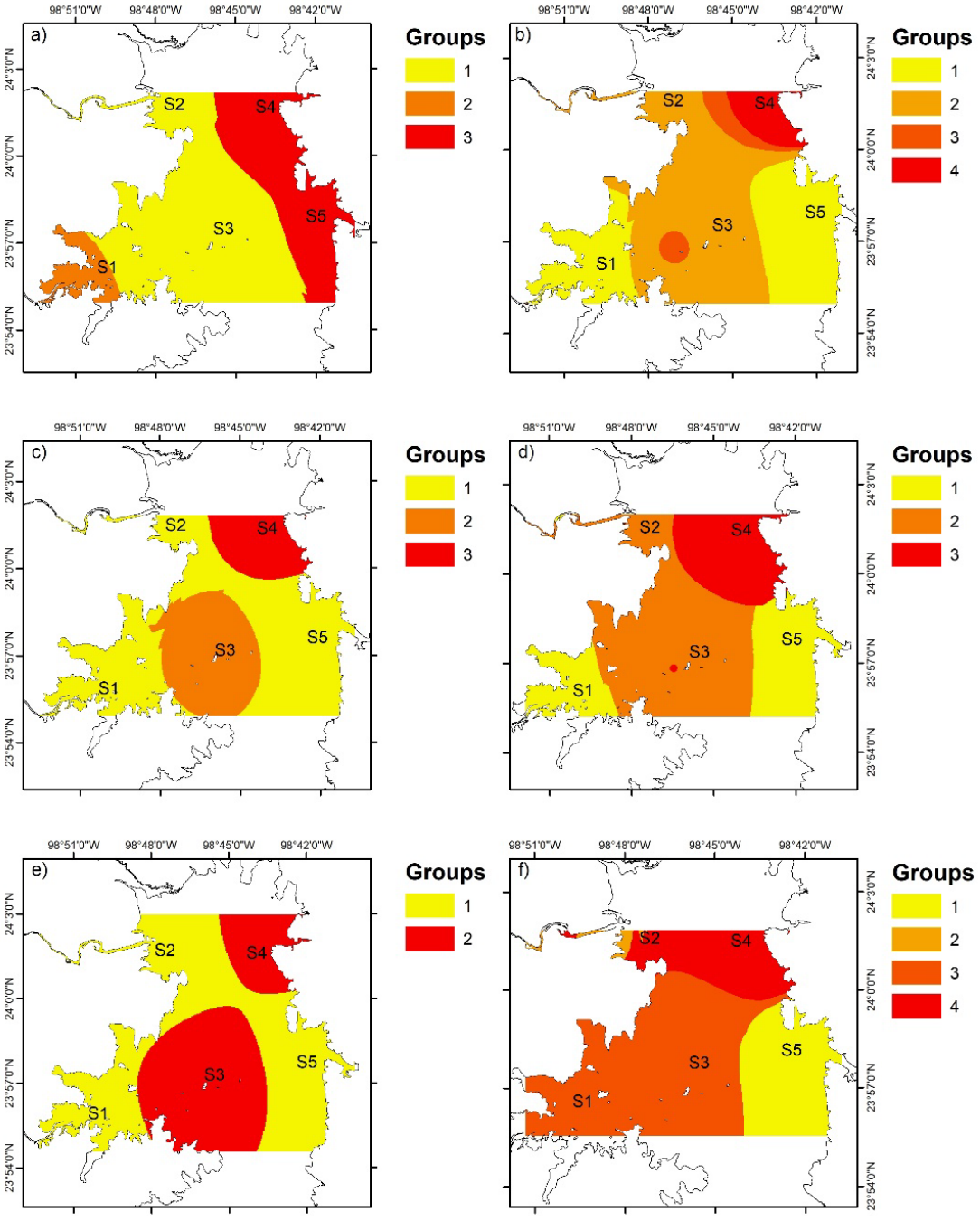

Figure 6. Classification of sites by degree of contamination of bass tissue: a) December, b) January, c) February, d) March, e) April, f) May. S1, S2, S3, S4, S5 as described in Table 1.

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Discussion

The study generated a prospective scenario on the spatial and temporal distribution of the pesticides contained in sediment and bass in the VGD. The presence of pesticides in aquatic ecosystems is usually linked to non-point sources of pollution of anthropogenic origin, such as runoff or leachate (Manahan, 2007). The residues found in sediment and tissue in the present study possibly come from pesticide products used in the agricultural and livestock areas within the hydrological basin. The main crops planted in 2019 in the basin (SIAP, 2020) were sorghum, citrus, grasslands, and corn; while bovine breeding is predominant (SIAP & Sader, 2020). The compounds AME, ETN, MAL, PAR, P-MET, and PRO registered in sediment and tissue are used as pesticides in citrus, sorghum, and corn (Cicoplafest, 1991; López-Arroyo & Loera-Gallardo, 2009). PML and TBZ are used for fungicidal control in citrus (De Liñán, 2009; Rocha-Peña & Peña-del-Río, 2009). AMZ has application in veterinary medicine in the control of ticks in bovines, sheep, and pigs (Cicoplafest, 1991).

The active ingredients of the pesticides detected have an active or indefinite registration in Mexico (Cofepris, 2020). In contrast, AME, AMZ, ETN, MPS, PAR, P-MET, PRO, and PZL are prohibited or restricted in the United States and the European Community (AERU, 2017; NIH, 2019); ECOTOX, 2020) due to their toxicological relevance, in terms of human and environmental health. The World Health Organization (WHO, 2009) classifies PAR and P-MET as extremely hazardous (Ia), and MPS as highly

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hazardous (Ib). Additionally, MAL, MPS, PAR, P-MET, and PZL are listed as Highly Hazardous Pesticides (FAO & WHO, 2019; PAN International, 2020).

The list of authorized pesticides in Mexico needs to be reviewed and updated in order to prohibit or restrict the trade and use of compounds that cause damage or environmental risk and may affect public health, according to international standards.

Spatio-temporal distribution of pesticides in sediments

Sediments play an important role in the transport of various pollutants from water bodies, in suspension or as a bed load; the latter defined by Hernández-Azúnaga (2005) as the transport of particles due to rolling or sliding. The mobility of the pesticide with the sediment occurs by a physicochemical affinity process between the chemical structure of the compound and the charge on the substrate surface (Hanningan, Genest, & Robinson, 2018; AERU, 2019), known as adsorption (K_{oc}) (Adams, 1973). The K_{oc} or adsorption coefficient is directly related to the lipophilicity of the compound (Delle-Site, 2001), and the organic matter content of the substrate (Nicholls, 1988). The K_{oc} reference values of the detected pesticides suggest that 11 pesticides present in sediment could show slight or no mobility (K_{oc} = 835 – 1.2x105). ETN, PAR, PFN, and PRO registered the highest K_{oc} values, theoretical half-life values (DT50) of 146 to 206 d by hydrolysis in the aqueous phase (at 20 ºC and pH 7), and little susceptibility to photolysis (AERU, 2017; NIH, 2019; ECOTOX, 2020).

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The possible stability, persistence and low solubility (0.21-2.00 mg/l) may be related to the frequency and high concentration in sediment of the four pesticides described. Sharom, Miles, Harris and McEwen (1980) analyzed the adsorption capacity of ETN and PAR on three types of substrate, and found that ETN was more strongly adsorbed than PAR (K_{oc} = 2 818 and 741, respectively) on sedimentary substrates. In addition, the authors highlighted the correlation between the desorption capacity of the compounds and their solubility, so that the insolubility of both pesticides facilitated their persistence in sediments and increased the toxicological potential in the aquatic ecosystem.

The spatial differences observed in sediment pesticides could be related to the agricultural and livestock land uses developed within the hydrological basin. The continuous presence of AME, AMZ, MAL, P-MET, PAR, and PRO in the sediments from agricultural sites that drain through the Corona River (S1) suggests influencing the contribution of pollutants from the dam. This sediment dynamics was observed by Hernández-Antonio and Hansen (2011), when noting the correspondence between pesticides used in agricultural areas near tributaries and those found in permanent runoff sediments.

The mobility and variation in the concentration of compounds in the VGD sediments presented similar conditions to those observed in other lentic bodies. Murdoch and Azcue (1995) pointed out that the deposition of particles with high adsorption capacity tends to occur in deep areas of reservoirs with slow currents, as observed in the center of the VGD (S3). In the depths of the reservoir, low luminosity reduces biomass and microbial activity, which diminishes its capacity and rate of compounds

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degradation (Nicholls, 1988). Additionally, in S3 the avenues of S1 and S2 converge, which could lead to greater complexity in the composition of pesticides, as suggested by Agudelo, Flóres, López and Palacio (2013) by relating the increase of pesticides in clay sediments with a high content of organic matter, deposited in areas of stream confluence.

The drainage zone of the dam or curtain (S5) registered the lowest degree of contamination by pesticides, possibly due to the time passed and the decrease of organic matter content in the sediments of this zone, which contributed to the desorption of pesticides. Hanningan *et al*. (2018) showed that with the passage of time the chemical structure of compounds changes and modifies the solubility and stability of pesticides. Carreño, Zarazúa, Fall, Ávila-Pérez and Tejeda (2018) observed the degradation of the total organic carbon content (TOC) in sediments exiting a reservoir in relation to those entering (0.8 % *vs*. 6.2 %, respectively). The adsorption capacity of the compounds decreased and the sediments' quality at the site improved. These principles have influenced the processes that accompany wastewater treatment, mainly the degradation of pesticides and other organic compounds (Garrido-Cárdenas, Esteban-García, Agüera, Sánchez-Pérez, & Manzano-Agugliaro, 2019).

The temporal variation of pesticides in sediment can be related to the phenology of the crops and the periodicity with which the chemical control of agricultural pests is carried out. The presence of PRO during the six months of sampling is possibly associated with the chemical control of mites in various phenological stages of citrus (López-Arroyo & Loera-Gallardo, 2009) and corn (De Liñán, 2009). Some varieties of citrus fruits grown in the region, such as the "Valencia" orange, present continuous

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fruiting throughout the year (Mata-Vázquez, 2013); therefore, the use of agrochemicals could be permanent. Sorghum occupies the largest area within the basin and presents two cycles in the year, spring-summer and autumn-winter (SIAP, 2020), so that the application of AME, ETN, MAL, PAR, P-MET, and PRO could cover a large area in both growing cycles. However, the variation in pesticide use between the two sowing periods is unknown.

Spatio-temporal distribution of pesticides in largemouth bass tissue

Fish muscle tissue is identified as a reservoir of contaminants of organic origin (Kolanczyk, Serrano, Tapper, & Schmieder, 2018; Arisekar, Shakila, Jeyasekaran, Shalini, & Kumar, 2019), and heavy metals (Foster, Drake, & DiDomenico, 2000). The presence of pesticides in aquatic organisms of the VGD requires further study. The analysis carried out by Uresti *et al*. (2008) discovered the presence of organochlorine pesticides (aldrin, endrin, chlordane, mirex, heptachlor, DDT, DDE, and DDD) in four species of fish from this reservoir. The highest concentration of pesticides was recorded in largemouth bass (*Micropterus salmoides*) and catfish (*Ictalurus punctatus*), with mean values of 0.97 to 41.40 ng/g, and 0.93 to 212.31 ng/g, respectively.

The S4 registered the highest degree of contamination in bass during the six months contemplated. The temporal variations in the concentration of pesticides were only significant in December and May, which could be related to the seasonal variation in the feeding habits of

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bass. Studies affirm that bass is an opportunistic predator, with marked variations in its diet throughout the year (Cochran & Adelman, 1982; Rodríguez-Jiménez, 1989). Aloo and Dadzie (1995) observed the ingestion of insects, small fish and aquatic vegetation during winter; while in spring the consumption of fish of various sizes, insects and frogs increased. These changes in the feeding patterns of the bass are commonly influenced by the migratory habits of prey occurring in the dams, originated by the seasonal differences in the water levels and temperature of the reservoirs (Torres-Morales, 2000).

All the compounds detected in largemouth bass tissue were also found in the VGD sediments in higher concentrations. The sites sampled at the center (S3) and East (S4) of the reservoir recorded the highest variety and concentration of pesticides, both in sediments (Annex D), and in bass tissue (Annex E). Additionally, the predominant compounds in sediments (AMZ, ETN, PAR, PFN, and PRO), were also predominant in bass. The lipophilic properties of these compounds, associated with stability and persistence in the case of sediments, could be related to their presence in bass tissues. Compounds AMZ, ETN, PAR, PFN, and PRO present high theoretical values with respect to Bioconcentration Factors (*BCF* = 1 838, 1 600, 462, 1 620, and 4 890, respectively) and Bioaccumulation (*BAF* = 5.5, 5.07, 3.83, 5.37, and 5.7), which suggest great potential to be bioaccumulated in bass tissues (AERU, 2017; NIH, 2019; ECOTOX, 2020).

The *BCF* estimates the ability of a compound to concentrate in tissues of aquatic organisms, from water (Larisch & Goss, 2018). The *BAF* is determined by the lipophilicity of the compound, expressed by the log10

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of the n-octanol/water Partition Coefficient (*Log* K_{ow}) (Hanningan *et al*., 2018), which considers the sum of the bioconcentration and the chemicals ingested in food (Dodds & Whiles, 2020). Compounds with high *Log* K_{ow} are regularly bioaccumulated in tissues of lipid constitution in fish, such as viscera, subdermal fat and edible muscle (Kolanczyk *et al*., 2018). Therefore, the chemical structure and lipophilic properties of pesticides could be considered as the most important factors in the bioaccumulation process (Maund *et al*., 1997). The bioaccumulation of pesticides in aquatic organisms is associated with the presence of these compounds in some of the environmental compartments (Arisekar *et al*., 2019) and their possible translocation in food webs (Tsaboula *et al*., 2016). Some studies indicate the bioaccumulation of compounds from sediments at higher trophic levels through the consumption of benthic organisms (Burgess, Berry, Mount, & Di Toro, 2013; Ccanccapa, Navarro-Ortega, Picó, & Barceló, 2016), which could generate ecotoxicity within the VGD aquatic ecosystem (Maund *et al*., 1997).

The effects and impacts of pesticides transported to water bodies are documented in various studies, which confirm the lethal and sublethal effects on aquatic life (Hua & Relyea 2014; Whitmore *et al*., 2015; Rahman, Majharul-Islam, Haque, & Shahjahan, 2020) and human health (Goldman, Musgrove, Jewell, & Di Monte, 2017; Sabarwal, Kumar, & Singh, 2018). In particular, *Micropterus salmoides* reported mortality to ETN and PAR exposure with LC50 ranging from 0.5 to 173 mg/l and 0.5 to 620 mg/l, respectively (Weiss, 1961; Munn, Gilliom, Moran, & Nowell, 2006). Additionally, *M. salmoides* presented sublethal effects at the hormonal and reproductive levels due to exposure to organochlorine

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pesticides (Johnson, 2005); as well as physiological and behavioral changes due to the inhibition of brain acelicolinesterase by exposure to organophosphate pesticides (Pan & Dutta, 1998).

Conclusions

The study of sediment and largemouth bass tissue in the VGD detected the presence of 13 pesticides, five of them related to ecotoxicological effects. The spatial and temporal variations of the pesticides in sediment were significant for all sites and months of the study. These variations seem to be associated with the chemical control applied by the agricultural and livestock activities developed within the hydrological basin. The spatio-temporal variations of pesticides in bass tissue may be related to seasonal variation in bass feeding habits, which were significant only in December and May. The areas of the reservoir that registered the greatest variety and concentration of pesticides in sediments and bass tissue were located in the central and eastern areas of the dam. The curtain or spillway presented the lowest pollution degree, both in sediments and bass. The pesticides AME, ETN, MAL, PAR, PFN, and PRO were predominant in both types of sample; this could be related to its lipophilic properties that enhance sediment adsorption and bioaccumulation in bass tissue through the VGD trophic structure.

Results also represent an alert for health authorities, since fish products and water of the reservoir are consumed by the surrounding communities; both can pose risks to human health.

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Therefore, further studies are required to determine the presence of pesticides in water and in other trophic levels of the VGD, so as to determine the route and the environmental fate of the compounds used in agricultural activities. Toxicological risk studies are necessary to identify the effects of pesticides on human health due to the consumption of aquaculture products and water from reservoirs.

Annexes

Annex A. Mean values (µg/kg) ± monthly standard deviation of pesticides found in sediment by sampling site.

Site	AME	AMZ	ETN	MAL	MFS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN
December													
S1	3.43 ± 1.46	4.26 ± 0.40	<LOD	2.56 ± 0.45	2.63 ± 1.04	2.93 ± 0.61	3.7 ± 0.45	0.76 ± 0.68	2.46 ± 0.75	<LOD	<LOD	1.7 ± 0.43	<LOD
S2	1.5 ± 0.70	2.25 ± 0.21	2.5 ± 0.28	3.5 ± 0.14	1.85 ± 0.21	1.15 ± 0.07	1.85 ± 0.35	2.5 ± 0.28	1.55 ± 0.35	<LOD	<LOD	1.25 ± 0.35	<LOD
S3	2.16 ± 0.47	1.13 ± 0.15	1.73 ± 0.40	1.76 ± 0.32	1.4 ± 0.3	1.33 ± 0.35	2.1 ± 0.45	2.23 ± 0.73	<LOD	2.8 ± 0.2	3.36 ± 0.35	1.5 ± 0.4	1.96 ± 0.35
S4	2.96 ± 0.80	1.6 ± 0.26	2.16 ± 0.60	2.16 ± 0.40	1.26 ± 0.25	2.06 ± 0.77	1.33 ± 0.30	2.2 ± 0.55	2.73 ± 0.30	<LOD	<LOD	2.2 ± 0.5	2.4 ± 0.65
S5	2.13 ± 0.49	3.3 ± 0.60	1.76 ± 0.25	2.3 ± 0.70	<LOD	1.36 ± 0.37	2.76 ± 0.32	1.76 ± 0.45	3 ± 0.1	<LOD	<LOD	1.66 ± 0.90	<LOD
January													
S1	1.36 ± 0.37	2.63 ± 0.55	1.76 ± 0.35	2.46 ± 0.45	1.46 ± 0.32	2.46 ± 0.35	1.5 ± 0.36	1.53 ± 0.25	2 ± 0.3	<LOD	<LOD	2.66 ± 0.45	1.23 ± 0.25
S2	1.13 ± 0.15	1.5 ± 0.3	1.33 ± 0.35	2.33 ± 0.25	1.16 ± 0.15	3.16 ± 0.15	2.2 ± 0.26	2.23 ± 0.32	1.2 ± 0.26	<LOD	<LOD	1.4 ± 0.20	<LOD
S3	<LOD	1.63 ± 0.47	2.93 ± 0.20	3.03 ± 0.20	2.36 ± 0.30	1.46 ± 0.41	2.03 ± 0.20	2.13 ± 0.41	<LOD	1.33 ± 0.30	2.2 ± 0.45	1.43 ± 0.30	2.06 ± 0.25
S4	3 ± 0.1	2.2 ± 0.39	3.06 ± 0.41	2.6 ± 0.52	1.4 ± 0.3	2.43 ± 0.40	1.6 ± 0.26	1.43 ± 0.40	2.4 ± 0.36	<LOD	<LOD	1.2 ± 0.26	2.5 ± 0.45
S5	<LOD	1.2 ± 0.1	1.73 ± 0.15	<LOD	<LOD	<LOD	1.8 ± 0.43	<LOD	1.26 ± 0.15	<LOD	<LOD	<LOD	1.43 ± 0.45
February													
S1	1.23 ± 0.25	2.23 ± 0.41	1.36 ± 0.30	1.36 ± 0.32	1.36 ± 0.30	1.27 ± 1.01	1.4 ± 0.4	1.26 ± 0.37	2.23 ± 0.32	<LOD	<LOD	2.13 ± 0.15	1.3 ± 0.36
S2	1.46 ± 0.40	2.63 ± 0.30	1.86 ± 0.25	5.46 ± 0.47	1.46 ± 0.40	1.96 ± 0.30	1.3 ± 0.3	1.66 ± 0.32	1.26 ± 0.30	<LOD	2.73 ± 0.35	6.1 ± 0.85	<LOD
S3	<LOD	2.6 ± 0.28	1.8 ± 0.28	3.85 ± 0.49	1.7 ± 0.14	1.3 ± 0.14	1.4 ± 0.42	0.37 ± 0.21	<LOD	3.85 ± 0.21	5.4 ± 0.42	6.35 ± 0.35	2.5 ± 0.42
S4	1.36 ± 0.40	2.43 ± 0.50	1.6 ± 0.29	3.46 ± 0.32	1.4 ± 0.20	1.46 ± 0.40	2.23 ± 0.32	3.3 ± 0.3	1.33 ± 0.35	<LOD	<LOD	4.86 ± 0.66	1.8 ± 0.26
S5	<LOD	1.1 ± 0.17	<LOD	2.06 ± 0.75	<LOD	<LOD	1.83 ± 0.20	<LOD	<LOD	<LOD	<LOD	<LOD	1.16 ± 0.20

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Site	AME	AMZ	ETN	MAL	MFS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN
March													
S1	1.46 ± 0.37	2.36 ± 0.30	1.4 ± 0.36	6.6 ± 0.62	1.53 ± 0.30	1.7 ± 0.2	2.3 ± 0.29	7.36 ± 0.30	3.1 ± 0.60	<LOD	<LOD	5.6 ± 0.5	2.53 ± 0.35
S2	1.56 ± 0.35	1.4 ± 0.36	1.7 ± 0.36	7.76 ± 0.58	1.53 ± 0.30	1.4 ± 0.3	3.1 ± 1.11	6.1 ± 1.80	1.53 ± 0.25	<LOD	<LOD	1.7 ± 0.52	1.7 ± 0.45
S3	<LOD	5.9 ± 0.3	3.2 ± 1.1	7.36 ± 1.00	1.33 ± 0.25	1.5 ± 0.52	1.5 ± 0.3	7.16 ± 1.05	<LOD	3.5 ± 0.75	5.4 ± 0.79	5.66 ± 0.41	3.7 ± 1.04
S4	1.66 ± 0.15	1.23 ± 0.15	1.53 ± 0.40	6.13 ± 0.80	3.46 ± 0.37	1.66 ± 0.30	1.46 ± 0.35	8.33 ± 0.51	2.43 ± 1.13	<LOD	<LOD	8.03 ± 0.15	1.43 ± 0.30
S5	<LOD	1.3 ± 0.3	1.46 ± 0.40	<LOD	<LOD	<LOD	1.5 ± 0.36	<LOD	2.13 ± 0.58	<LOD	4.86 ± 0.94	<LOD	2.3 ± 0.52
April													
S1	1.8 ± 0.14	1.4 ± 0.56	1.9 ± 0.28	6.2 ± 1.41	1.15 ± 0.21	2.6 ± 0.70	1.8 ± 0.70	5.7 ± 0.70	2.95 ± 1.34	<LOD	<LOD	4.85 ± 1.48	1.95 ± 0.07
S2	1.3 ± 0.30	3.73 ± 0.47	3.4 ± 0.70	1.6 ± 0.29	1.53 ± 0.25	1.93 ± 0.35	1.53 ± 0.45	1.46 ± 0.30	2.73 ± 0.45	<LOD	2.6 ± 0.49	3.1 ± 0.43	1.36 ± 0.47
S3	<LOD	1.8 ± 0.79	3.73 ± 0.60	6.83 ± 0.60	4.3 ± 1.25	2.6 ± 1.01	2.33 ± 0.41	5.23 ± 0.95	<LOD	2.86 ± 0.86	4.33 ± 1.00	2.7 ± 0.7	2.8 ± 1.01
S4	2.16 ± 0.70	3.43 ± 0.70	1.76 ± 0.41	7.2 ± 1.05	1.26 ± 0.25	1.16 ± 1.00	2.16 ± 0.90	5.9 ± 0.75	2.76 ± 0.45	<LOD	<LOD	5.53 ± 1.35	1.96 ± 0.50
S5	<LOD	2.65 ± 0.77	1.9 ± 0.14	<LOD	<LOD	<LOD	2 ± 1.27	<LOD	2.4 ± 0.70	<LOD	4.85 ± 0.49	<LOD	4.35 ± 2.47
May													
S1	1.53 ± 0.40	2.76 ± 0.45	3.8 ± 0.55	3.66 ± 1.07	2.03 ± 0.41	1.96 ± 0.30	3.36 ± 0.76	3.43 ± 0.68	1.3 ± 0.26	<LOD	<LOD	1.86 ± 0.40	1.6 ± 0.55
S2	1.7 ± 0.43	1.9 ± 0.36	2.23 ± 0.61	2.73 ± 0.45	1.4 ± 0.45	1.9 ± 0.55	2.8 ± 0.91	2.33 ± 0.66	1.63 ± 0.65	<LOD	3.73 ± 1.00	1.56 ± 0.30	2.06 ± 1.17
S3	<LOD	5.23 ± 0.65	1.36 ± 0.30	7.96 ± 0.70	2.3 ± 0.45	3.4 ± 0.89	1.4 ± 0.26	5.63 ± 0.55	<LOD	2.59 ± 1.96	2.5 ± 0.65	3.16 ± 1.35	4.36 ± 1.04
S4	3.33 ± 1.12	2.7 ± 0.65	2.2 ± 0.36	4.16 ± 1.05	2.53 ± 0.83	4.53 ± 0.81	2.43 ± 0.47	3.46 ± 0.60	5.4 ± 0.75	<LOD	<LOD	3.53 ± 0.60	4.6 ± 0.96
S5	<LOD	1.96 ± 0.50	2.33 ± 0.45	<LOD	<LOD	<LOD	1.86 ± 0.76	<LOD	2 ± 0.62	<LOD	<LOD	<LOD	1.93 ± 0.55

Ametryn (AME), Amitraz (AMZ), Ethion (ETN), Malathion (MAL), Methamidophos (MPS), Parathion (PAR), Parathion-methyl (P-MET), Pyrimethanil (PML), Pyriproxyfen (PFN), Propargite (PRO), Propiconazole (PZL), Thiabendazole (TZL) and Trifloxystrobin (TBN). S1, S2, S3, S4, S5 described in Table 1.

Annex B. Mean values (µg/kg) ± monthly standard deviation of pesticides found in largemouth bass muscle by sampling site.

Site	AME	AMZ	ETN	MAL	MFS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN
December													
S1	0.19 ± 0.07	0.61 ± 0.35	0.47 ± 0.17	0.4 ± 0.12	0.38 ± 0.09	0.18 ± 0.06	0.71 ± 0.14	0.8 ± 0.11	0.28 ± 0.14	<LOD	<LOD	0.73 ± 0.11	<LOD
S2	0.41 ± 0.57	0.08 ± 0.11	0.15 ± 0.04	0.87 ± 0.05	0.66 ± 0.07	0.57 ± 0.12	0.4 ± 0.15	0.77 ± 0.06	0.18 ± 0.12	<LOD	<LOD	0.05 ± 0.07	<LOD
S3	<LOD	0.32 ± 0.21	0.62 ± 0.24	0.85 ± 0.07	0.38 ± 0.09	0.18 ± 0.06	0.71 ± 0.14	0.25 ± 0.13	<LOD	0.64 ± 0.08	0.23 ± 0.12	0.18 ± 0.07	0.20 ± 0.05
S4	0.37 ± 0.18	0.80 ± 0.04	0.53 ± 0.16	0.56 ± 0.14	0.68 ± 0.14	0.82 ± 0.11	0.71 ± 0.25	0.25 ± 0.08	0.38 ± 0.17	<LOD	<LOD	0.65 ± 0.13	0.80 ± 0.17
S5	0.37 ± 0.20	0.54 ± 0.07	0.65 ± 0.28	0.92 ± 0.03	0.14 ± 0.03	0.77 ± 0.12	0.84 ± 0.11	0.16 ± 0.06	0.62 ± 0.20	<LOD	<LOD	0.59 ± 0.13	0.64 ± 0.23

Site	AME	AMZ	ETN	MAL	MFS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN
January													
S1	0.29 ± 0.14	0.48 ± 0.15	0.36 ± 0.22	0.27 ± 0.10	0.16 ± 0.05	0.54 ± 0.18	0.52 ± 0.21	0.54 ± 0.25	0.13 ± 0.03	<LOD	<LOD	0.45 ± 0.12	0.14 ± 0.03
S2	0.27 ± 0.17	0.24 ± 0.08	0.19 ± 0.05	0.60 ± 0.02	0.36 ± 0.08	0.27 ± 0.13	0.25 ± 0.11	0.35 ± 0.07	0.19 ± 0.06	<LOD	<LOD	0.18 ± 0.07	<LOD
S3	<LOD	0.48 ± 0.15	0.69 ± 0.22	0.52 ± 0.25	0.30 ± 0.18	0.17 ± 0.04	0.34 ± 0.07	0.37 ± 0.09	<LOD	0.51 ± 0.10	0.5 ± 0.15	0.49 ± 0.10	0.49 ± 0.33
S4	0.74 ± 0.28	0.86 ± 0.14	0.82 ± 0.12	0.79 ± 0.13	0.87 ± 0.05	0.66 ± 0.20	0.7 ± 0.20	0.50 ± 0.20	0.90 ± 0.08	<LOD	<LOD	0.84 ± 0.07	0.66 ± 0.17
S5	<LOD	0.13 ± 0.04	0.17 ± 0.05	<LOD	<LOD	<LOD	0.13 ± 0.03	0.14 ± 0.03	<LOD	<LOD	<LOD	<LOD	0.26 ± 0.04
February													
S1	0.20 ± 0.10	0.51 ± 0.07	0.20 ± 0.05	0.17 ± 0.07	0.19 ± 0.07	0.14 ± 0.05	0.42 ± 0.04	0.25 ± 0.04	0.15 ± 0.02	<LOD	<LOD	0.19 ± 0.09	0.12 ± 0.01
S2	0.28 ± 0.21	0.25 ± 0.07	0.25 ± 0.03	0.74 ± 0.06	0.58 ± 0.19	0.35 ± 0.20	0.40 ± 0.10	0.48 ± 0.16	0.29 ± 0.08	<LOD	<LOD	0.38 ± 0.15	<LOD
S3	<LOD	0.93 ± 0.00	0.88 ± 0.04	0.45 ± 0.02	0.58 ± 0.12	0.42 ± 0.12	0.43 ± 0.05	0.37 ± 0.21	<LOD	0.64 ± 0.03	0.70 ± 0.07	0.67 ± 0.20	0.47 ± 0.21
S4	0.70 ± 0.19	0.80 ± 0.04	0.71 ± 0.07	0.78 ± 0.20	0.68 ± 0.16	0.86 ± 0.04	0.74 ± 0.06	0.73 ± 0.12	0.63 ± 0.12	<LOD	<LOD	0.66 ± 0.20	0.65 ± 0.08
S5	<LOD	0.15 ± 0.02	0.15 ± 0.03	<LOD	<LOD	<LOD	0.12 ± 0.03	<LOD	0.18 ± 0.03	<LOD	<LOD	<LOD	0.17 ± 0.03
March													
S1	0.17 ± 0.03	0.38 ± 0.08	0.13 ± 0.03	0.12 ± 0.03	0.16 ± 0.04	0.40 ± 0.25	0.29 ± 0.02	0.25 ± 0.06	0.17 ± 0.04	<LOD	<LOD	0.16 ± 0.06	0.16 ± 0.05
S2	0.2 ± 0.12	0.26 ± 0.04	0.15 ± 0.04	0.61 ± 0.10	0.41 ± 0.17	0.22 ± 0.04	0.33 ± 0.06	0.53 ± 0.04	0.13 ± 0.02	<LOD	<LOD	0.38 ± 0.09	<LOD
S3	<LOD	0.85 ± 0.06	0.66 ± 0.11	0.72 ± 0.11	0.73 ± 0.07	0.9 ± 0.06	0.40 ± 0.18	0.84 ± 0.06	<LOD	0.56 ± 0.35	0.82 ± 0.09	0.82 ± 0.12	2.24 ± 2.39
S4	0.85 ± 0.06	0.94 ± 0.02	0.87 ± 0.05	0.74 ± 0.09	0.89 ± 0.09	0.6 ± 0.06	0.85 ± 0.07	0.53 ± 0.18	0.58 ± 0.23	<LOD	<LOD	0.63 ± 0.08	0.8 ± 0.05
S5	<LOD	0.10 ± 0.10	0.24 ± 0.06	<LOD	<LOD	<LOD	0.16 ± 0.02	<LOD	0.23 ± 0.04	<LOD	<LOD	<LOD	0.23 ± 0.09
April													
S1	0.15 ± 0.04	0.34 ± 0.10	0.20 ± 0.04	0.14 ± 0.01	0.3 ± 0.14	0.25 ± 0.20	0.14 ± 0.02	0.21 ± 0.02	0.29 ± 0.16	<LOD	<LOD	0.18 ± 0.02	0.20 ± 0.13
S2	0.56 ± 0.09	0.60 ± 0.08	0.18 ± 0.09	0.71 ± 0.11	0.73 ± 0.12	0.13 ± 0.05	0.66 ± 0.04	0.32 ± 0.06	0.29 ± 0.10	<LOD	<LOD	0.77 ± 0.08	N.D.
S3	<LOD	0.95 ± 0.04	0.63 ± 0.14	0.61 ± 0.08	0.63 ± 0.11	0.76 ± 0.06	0.57 ± 0.05	0.74 ± 0.08	<LOD	0.16 ± 0.11	0.32 ± 0.04	0.81 ± 0.08	0.72 ± 0.25
S4	0.72 ± 0.09	0.71 ± 0.13	0.67 ± 0.06	0.61 ± 0.11	0.76 ± 0.17	0.68 ± 0.15	0.51 ± 0.22	0.88 ± 0.04	0.64 ± 0.09	<LOD	<LOD	0.84 ± 0.06	0.42 ± 0.10
S5	<LOD	0.17 ± 0.00	0.13 ± 0.03	<LOD	<LOD	<LOD	0.2 ± 0.01	<LOD	0.15 ± 0.01	<LOD	<LOD	<LOD	0.15 ± 0.07
May													
S1	0.13 ± 0.02	0.63 ± 0.20	0.69 ± 0.14	0.48 ± 0.17	0.65 ± 0.11	0.79 ± 0.06	0.47 ± 0.16	0.77 ± 0.08	0.7 ± 0.18	<LOD	<LOD	0.73 ± 0.04	0.71 ± 0.04
S2	0.69 ± 0.11	0.70 ± 0.09	0.27 ± 0.04	0.46 ± 0.15	0.80 ± 0.09	0.47 ± 0.05	0.94 ± 0.03	0.70 ± 0.07	2.88 ± 3.74	<LOD	<LOD	0.66 ± 0.11	N.D.
S3	<LOD	0.68 ± 0.15	0.78 ± 0.05	0.67 ± 0.09	0.6 ± 0.22	0.78 ± 0.22	0.82 ± 0.09	0.73 ± 0.10	<LOD	0.59 ± 0.10	0.62 ± 0.10	0.64 ± 0.10	2.34 ± 3.25
S4	0.93 ± 0.03	0.76 ± 0.07	0.87 ± 0.12	0.75 ± 0.07	0.73 ± 0.04	0.82 ± 0.10	0.84 ± 0.11	0.86 ± 0.07	0.88 ± 0.08	<LOD	<LOD	0.94 ± 0.04	0.75 ± 0.02
S5	<LOD	0.24 ± 0.06	0.14 ± 0.04	<LOD	<LOD	<LOD	0.30 ± 0.01	<LOD	0.29 ± 0.09	<LOD	<LOD	<LOD	0.12 ± 0.02

Ametryn (AME), Amitraz (AMZ), Ethion (ETN), Malathion (MAL), Methamidophos (MPS), Parathion (PAR), Parathion-methyl (P-MET), Pyrimethanil (PML), Pyriproxyfen (PFN), Propargite (PRO), Propiconazole (PZL), Thiabendazole (TZL) and Trifloxystrobin (TBN). S1, S2, S3, S4, S5 described in Table 1.

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Annex C. Matrices of statistical significance (f/p) to determine the spatial and temporal variations of pesticides in sediment and fish.

Spatial

Sediment

F

*p**		S1	S2	S3	S4	S5
	S1		10.833	31.963	10.147	4.558
	S2	0.000		36.591	11.049	16.525
	S3	0.000	0.000		40.884	36.354
	S4	0.000	0.000	0.000		20.485
	S5	0.000	0.000	0.000	0.000	

Fish

F

*p**		S1	S2	S3	S4	S5
	S1		10.833	31.963	10.147	4.558
	S2	0.000		36.591	11.049	16.525
	S3	0.000	0.000		40.884	36.354
	S4	0.000	0.000	0.000		20.485
	S5	0.000	0.000	0.000	0.000	

Seasonal

F

*p**		DEC	JAN	FEB	MAR	APR	MAY
	DEC		4.023	6.346	12.109	7.847	6.308
	JAN	0.000		3.767	12.304	6.082	3.220
	FEB	0.000	0.000		12.482	7.868	7.560
	MAR	0.000	0.000	0.000		1.966	6.448
	APR	0.000	0.000	0.000	0.037		2.044
	MAY	0.000	0.000	0.000	0.000	0.029	

F

*p**		DEC	JAN	FEB	MAR	APR	MAY
	DEC		2.267	2.172	2.767	3.251	2.279
	JAN	0.015		0.260	0.448	0.858	1.990
	FEB	0.020	0.995		0.217	0.724	1.881
	MAR	0.003	0.945	0.998		0.755	1.753
	APR	0.001	0.599	0.733	0.703		2.390
	MAY	0.015	0.035	0.048	0.069	0.010	

*$p < 0.05$

S1, S2, S3, S4, S5 as described in Table 1.

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Annex D. Clusters by pollution degree and centroids generated by the K-means analysis for the monthly sediment samples.

Groups	AME	AMZ	ETN	MAL	MPS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN	PD
December														
C1	2.750	1.917	2.167	2.042	1.000	2.083	1.583	2.208	2.583	0.083	0.208	2.125	2.250	IV
C2	3.080	3.760	0.520	2.600	2.160	2.560	3.320	0.920	2.160	0.200	0.440	1.960	0.080	V
C3	2.071	3.179	2.000	2.286	0.036	1.429	2.750	1.857	2.643	0.036	0.214	1.929	0.429	II
C4	2.076	2.182	1.894	2.364	1.409	1.530	2.121	2.061	1.682	0.621	0.924	1.803	0.879	III
C5	2.074	1.630	1.815	1.963	1.296	1.481	2.074	2.148	0.630	2.222	2.593	1.778	1.704	I
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
January														
C1	1.045	1.886	1.864	2.250	1.386	2.386	2.000	1.932	1.091	0.000	0.432	1.386	0.886	II
C2	3.000	3.000	3.000	2.500	1.000	2.000	2.000	2.000	2.000	0.000	0.000	1.000	2.000	VII
C3	0.370	1.957	2.500	2.478	1.891	1.652	2.000	1.913	0.717	1.022	1.304	1.217	1.826	V
C4	1.444	2.778	1.889	2.222	1.444	2.333	2.000	1.778	2.000	0.000	0.000	2.667	1.111	IV
C5	2.071	2.000	2.714	2.250	1.036	2.000	1.964	1.250	1.857	0.000	0.071	1.000	2.214	III
C6	1.000	3.000	2.000	2.750	1.500	2.000	1.000	2.000	2.000	0.000	0.000	2.750	1.000	VI
C7	0.324	1.235	2.000	1.059	0.618	0.735	1.971	0.765	1.029	0.059	0.294	0.412	1.765	I
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
February														
C1	0.790	2.048	1.331	3.556	1.065	1.089	2.000	1.508	0.726	0.968	1.815	4.266	1.661	II
C2	0.000	1.536	0.286	2.786	0.143	0.000	2.000	0.464	0.000	0.250	0.607	1.393	1.000	I
C3	0.146	2.293	1.951	3.878	1.659	1.000	1.098	0.707	0.293	2.829	4.244	5.512	2.098	IV
C4	1.057	2.271	1.729	3.557	1.186	1.400	1.000	1.257	1.300	0.657	1.986	4.386	0.914	III
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	

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Groups	AME	AMZ	ETN	MAL	MPS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN	PD
March														
C1	0.304	2.638	2.000	3.696	1.043	1.000	2.000	4.130	1.638	1.029	3.768	3.449	2.406	II
C2	0.000	1.565	1.870	1.000	0.261	0.000	1.870	1.217	2.000	0.130	4.435	0.913	2.087	I
C3	0.011	5.319	3.044	7.077	1.143	1.451	1.736	6.912	0.374	3.044	4.725	5.385	3.440	VI
C4	1.065	1.968	2.000	6.430	2.022	1.000	2.226	6.376	1.645	0.548	1.355	4.151	2.000	III
C5	0.967	3.370	2.109	6.326	1.859	1.304	2.000	6.446	1.174	1.413	2.870	4.848	2.696	IV
C6	1.532	1.894	1.638	6.553	2.319	1.957	2.064	7.319	2.617	0.064	0.255	5.872	2.170	V
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
April														
C1	3.000	3.000	1.000	7.000	1.000	1.000	2.000	6.000	3.000	0.000	0.000	2.000	5.500	VII
C2	1.536	1.536	2.000	6.071	1.321	2.214	1.893	5.393	2.964	0.143	0.607	2.000	4.714	IV
C3	1.024	3.571	3.190	2.048	1.643	2.000	1.714	1.810	2.786	0.000	2.595	1.429	3.071	II
C4	1.958	3.167	2.000	6.250	1.167	1.083	2.083	5.042	2.542	0.000	0.625	2.000	4.708	VI
C5	1.035	2.947	2.070	4.702	1.509	1.263	2.000	3.772	2.000	0.526	2.246	2.509	3.333	III
C6	0.250	2.682	2.000	2.114	0.795	0.705	1.977	1.705	2.045	0.455	4.045	3.455	1.250	I
C7	0.779	2.221	2.974	5.000	2.039	2.091	2.000	3.896	1.571	1.182	2.792	2.377	2.922	V
C8	0.024	1.610	3.195	6.537	3.293	2.780	2.000	4.854	0.415	2.561	3.780	2.220	2.756	VIII
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
May														
C1	2.163	2.918	3.612	2.000	2.122	3.367	2.041	2.959	3.735	0.122	0.612	2.673	3.980	IV
C2	1.766	2.362	3.383	2.532	1.766	2.021	2.830	2.851	1.447	0.064	2.447	1.851	2.128	II
C3	0.571	2.571	1.889	2.048	0.810	1.270	2.000	1.429	2.270	0.206	0.413	1.048	2.746	I
C4	0.045	4.909	7.466	1.602	2.102	3.114	1.432	5.364	0.148	2.057	2.341	2.898	4.330	V
C5	0.903	3.544	4.680	2.068	1.893	2.670	2.078	3.505	1.612	1.126	1.573	2.126	3.282	III
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	

PD = Pollution Degree

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Annex E. Clusters by degree of contamination and centroids generated by the K-means analysis for monthly samples of bass tissue.

Groups	AME	AMZ	ETN	MAL	MPS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN	PD
December														
C1	0.000	0.750	0.417	0.417	0.000	1.000	0.000	1.000	0.000	0.000	–	1.000	0.333	II
C2	0.154	0.038	0.269	1.000	0.577	0.731	0.500	0.462	0.000	0.077	–	0.000	0.000	I
C3	0.188	0.875	0.813	0.938	0.313	0.938	0.969	0.000	0.156	0.031	–	0.594	0.844	III
p=	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.005	0.192	–	0.001	0.001	
January														
C1	–	0.300	0.200	0.000	0.000	0.200	0.800	0.000	–	–	–	0.000	0.000	I
C2	–	0.200	0.840	0.680	0.040	0.000	0.000	0.000	–	–	–	0.080	0.360	II
C3	–	1.000	1.000	1.000	1.000	0.875	0.375	1.000	–	–	–	1.000	0.750	IV
C4	–	1.000	0.824	0.647	0.588	0.059	0.000	0.118	–	–	–	0.765	0.118	III
p=	–	0.001	0.001	0.001	0.001	0.001	0.001	0.001	–	–	–	0.001	0.001	
February														
C1	0.038	0.423	0.192	0.769	0.385	0.038	0.115	0.192	0.000	0.000	0.000	0.077	0.000	I
C2	0.174	1.000	0.870	1.000	0.783	0.870	0.913	0.565	0.087	0.000	0.000	0.261	0.217	III
C3	0.000	1.000	1.000	0.083	0.667	0.000	0.083	0.167	0.000	0.583	0.417	0.917	0.167	II
p=	0.016	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.115	0.001	0.001	0.001	0.002	
March														
C1	0.000	0.667	0.500	0.125	0.250	0.083	0.458	0.083	0.000	0.000	0.000	0.083	0.833	I
C2	0.533	1.000	1.000	1.000	1.000	1.000	0.667	0.467	0.133	0.067	0.067	0.867	1.000	III
C3	0.000	0.795	0.436	0.872	0.795	0.026	0.590	0.949	0.000	0.077	0.231	0.692	1.282	II
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.008	0.089	0.001	0.001	0.001	

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Groups	AME	AMZ	ETN	MAL	MPS	P-MET	PAR	PML	PFN	PRO	PZL	TZL	TBN	PD
April														
C1	0.154	0.923	0.000	0.538	0.731	0.423	0.000	0.423	0.000	–	–	0.846	0.000	I
C2	0.214	1.000	0.679	0.500	0.964	0.464	0.857	1.000	0.107	–	–	1.000	0.321	II
p=	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.027	–	–	0.001	0.001	
May														
C1	1.000	1.000	0.000	0.000	1.000	1.000	0.182	1.000	3.455	–	–	1.000	0.000	II
C2	0.057	0.971	1.000	0.743	0.800	0.886	1.000	1.000	0.486	–	–	1.000	1.571	III
C3	1.000	1.000	0.231	1.000	1.000	1.000	0.769	1.000	1.692	–	–	1.000	0.308	IV
C4	0.000	0.611	0.500	0.000	0.000	0.833	0.222	0.222	0.556	–	–	0.111	0.778	I
p=	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	–	–	0.001	0.001	

PD = Pollution degree

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