DOI: 10.1007/s11004-005-5955-1

# Two-Way Regionalized Classification of Multivariate Datasets and its Application to the Assessment of Hydrodynamic Dispersion<sup>1</sup>

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Zones of mixing between shallow groundwaters of different composition were unravelled by "twoway regionalized classification," a technique based on correspondence analysis (CA), cluster analysis (ClA) and discriminant analysis (DA), aided by gridding, map-overlay and contouring tools. The shallow groundwaters are from a granitoid plutonite in the Fundão region (central Portugal). Correspondence analysis detected three natural clusters in the working dataset: 1, weathering; 2, domestic effluents; 3, fertilizers. Cluster analysis set an alternative distribution of the samples by the three clusters. Group memberships obtained by correspondence analysis and by cluster analysis were optimized by discriminant analysis, gridded over the entire Fundão region, and converted into "two-way regionalized classification" memberships as follows: codes 1, 2 or 3 were used when classification by correspondence analysis and cluster analysis produced the same results; code 0 when the grid node was first assigned to cluster 1 and then to cluster 2 or vice versa (mixing between weathering and effluents); code 4 in the other cases (mixing between agriculture and the other influences). Code-3 areas were systematically surrounded by code-4 areas, an observation attributed to hydrodynamic dispersion. Accordingly, the extent of code-4 areas in two orthogonal directions was assumed proportional to the longitudinal and transverse dispersivities of local soils. The results (0.7–16.8 and 0.4-4.3 m, respectively) are acceptable at the macroscopic scale. The ratios between longitudinal and transverse dispersivities (1.2-11.1) are also in agreement with results obtained by other studies.

**KEY WORDS:** correspondence analysis, cluster analysis, discriminant analysis, surface mapping tools, regionalized classification, hydrodynamic dispersion.

### **NOTATION**

Below is the alphabetical list of mathematical symbols used throughout this paper.

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## **Latin Symbols**

d	geometric mean diameter of a granular material (e.g. soil sample)
$D(D_{\rm L}, D_{\rm T})$	Coefficient of hydrodynamic dispersion (longitudinal and transverse)
$E_i$	classification score of group $i$
	score of vector $\mathbf{x}$ in the frequency curve ( $f$ ) of group $i$
$f_i(\mathbf{x})$ $F$	- · · · · · · · · · · · · · · · · · · ·
-	factor
grad(h)	hydraulic gradient
h	number of rows along the height of a grid
k	number of groups present in a multivariate site-related dataset
K	hydraulic conductivity
l	number of columns along the width of a grid
$m_{\rm t}$	total porosity
$m_{\mathrm{e}}$	effective porosity
n	number of samples (or sites) in the working database
p	number of variables describing the samples (or sites) in the working
•	database
$prob_i$	prior probability of group's i membership
$Prob_i$	posterior probability of group's <i>i</i> membership
$\mathbf{S}$	matrix of within-group variances and covariances
t	time
ν	velocity of a solute dissolved in water along the mean direction of
	flow
$\boldsymbol{x}_p$	vector containing the values of the $p$ original (or $X$ ) variables
$\mathbf{x}'$	transpose of x
$\bar{\mathbf{x}}$	mean of <b>x</b>
$\mathbf{ar{x}}'$	transpose of $\bar{\mathbf{x}}$
X	set of original variables in the working dataset
$w_{ij}$	loading of variable $j$ in factor $i$
w%-	hydrochemical parameter discriminating between waters with
pollution	weathering-dominated chemistries and waters with chemistries
г элинг	The state of the s

controlled by anthropogenic inputs

hydrochemical parameter discriminating between waters with fertilizer-dominated chemistries and effluents-dominated

chemistries

agriculture

w%-

## **Greek Symbols**

$\alpha (\alpha_{\rm L}, \alpha_{\rm T})$	mechanical dispersivity (longitudinal and transverse)
δ	log standard deviation of a grain size distribution
γ	identification code of a hybrid region
$\sigma$	standard deviation of a membership probability distribution
$\psi$	specific retention of a porous material

#### INTRODUCTION

Regionalized classification (RC) is defined as the probabilistic assignment of sites to groups by using discriminant analysis (DA). Following Olea (1999) and his predecessors Harff and Davis (1990), we see nothing conceptually new in RC but agree that some novelty is introduced by this joint application of a number of well-known mathematical, statistical and geostatistical techniques.

The start of RC requires a training set that usually is provided by cluster analysis (ClA). However, with conventional clustering algorithms the number of groups (k) is defined subjectively, either on the basis of external information or iteratively until a certain function is optimized. A second difficulty in applying RC is the assignment of sites to groups when probabilities are similar among clusters. Again, the problem is solved by assigning to group zero (i.e. by setting to hybrid) all sites for which the difference between the two highest probabilities are less than a pre-established (subjective) threshold.

The primary objective of this study is to clean RC from the reported draw-backs. To define *k* objectively we propose that it is selected by natural clustering. To identify the hybrid sites precisely, we propose that a RC based on the natural groupings (first-way RC) is combined with another RC based on the ClA groupings (second-way RC). By looking simultaneously at two different perspectives of a same reality, we expect that the typical sites maintain their group memberships no matter which clustering method is used, whereas the atypical ones alternate among groups when the clustering technique is changed. Consequently, the atypical sites are recast as hybrid sites and demarcated on a map as hybrid regions.

The spatial relation between true and hybrid regions of groundwater datasets may, in some cases, unravel the mixing between waters of different compositions. The distribution of membership probabilities within regions of fertilizer-dominated water chemistries resembles the distribution of solutes inside pulse-like contaminant plumes. Using the appropriate contaminant transport models, it is possible to quantify processes such as hydrodynamic dispersion from solute distributions inside plumes. As a secondary objective we wished to assess hydrodynamic dispersion across the soils of our study area (Fundão region, central Portugal) using the membership distributions as analogs for solute distributions.

### THE TWO-WAY RC APPROACH

The flowchart in Figure 1 summarizes the method of two-way RC. The sites of a multivariate database are initially assigned to *k* groups by natural clustering, and then the groups are interpreted in terms of controlling sources and/or processes. When working with groundwater databases, the selected method of natural clustering can be the RST algorithm used by Pacheco and Van der Weijden (1996), Pacheco (1998a) or Pacheco and others (1999), or can be the technique based on

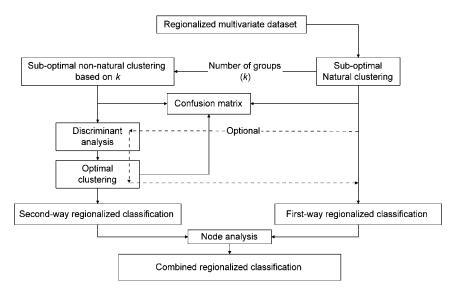


Figure 1. Flowchart illustrating two-way regionalized classification of multivariate datasets.

correspondence analysis (CA) that Pacheco (1998b) developed. The first-way RC can pass through an optimization process using discriminant analysis or terminates. To start the second-way RC we run a conventional clustering algorithm like Ward's method (1963) to obtain a sub-optimal non-natural distribution of the sites by the *k* groups that subsequently is optimized using DA. Node analysis (NA) is a last step in two-way RC whereby the natural and non-natural group memberships are interpolated over grids of regularly spaced nodes. Nodes are then compared among grids, maintaining their original assignments or being reclassified as hybrid in a combined grid. Finally, constant membership contours are drawn across the study area that work as boundaries between different groups as well as between groups and hybrid regions.

The next sections outline the mathematical, statistical and geostatistical procedures involved in two-way RC. Detailed and more mechanically oriented descriptions of these methods are beyond the scope of this paper and can be found elsewhere (Kaufman and Rousseeuw, 1990; Jackson, 1991; Jobson, 1992; among many other neat textbooks). It also should be mentioned that we used Pacheco's (1998b) approach to CA to define the natural clusters and Ward's method to represent the technique of non-natural clustering.

### **Correspondence Analysis**

In this study, CA is used as a natural clustering technique. The set of p original or X variables are first transformed onto a set of p factors or F variables

in a manner that a major portion of the data variation is concentrated on just a few of the latter, the so-called k common factors. The relation between the F and X variables is then set on the basis of a linear equation:

$$F_i = w_{i1}X_1 + w_{i2}X_2 + \dots + w_{ip}X_p. \tag{1}$$

If the signs of factor loadings ( $w_i$  coefficients) are equal, the corresponding X variables are correlated positively in  $F_i$ , otherwise they are correlated negatively. From the observation of these "sympathies" and "antipathies" among signs of factor loadings, Equation (1) may be rewritten in forms that encompass some physical or chemical meaning. That was the approach used by Pacheco (1998b). Working with a shallow groundwater database from a granitoid plutonite (Fundão, central Portugal), he separated waters with weathering-dominated chemistries from waters with compositions controlled by anthropogenic inputs, using the following hydrochemical parameter:

$$w\% - \text{pollution} = \frac{\text{pollution}}{\text{weathering + pollution}} \times 100, \tag{2}$$

where

pollution = 
$$w_{1,Cl}[Cl^-] + w_{1,SO_4}[SO_4^{2-}] + w_{1,NO_3}[NO_3^-]$$
  
weathering =  $w_{1,HCO_3}[HCO_3^-] + w_{1,SiO_2}[SiO_2]$ .

Square brackets denote molar concentrations of chloride, sulphate, nitrate, bicarbonate and silica in a spring. Springs with w%-pollution less than 50% have weathering-dominated water chemistries and springs with w%-pollution greater than 50% have pollution-dominated water chemistries. The extent to which each component contributes to w%-pollution is determined by the  $w_1$  values. Contaminated spring waters were further linked to sources such as farmland fertilizers or domestic effluents by the following hydrochemical parameter:

$$w\% - \text{agriculture} = \frac{\text{agriculture}}{\text{dom. effluents/atm. input + agriculture}} \times 100, \quad (3)$$

where

agriculture = 
$$w_{2,SO_4}[SO_4^{2-}] + w_{2,NO_3}[NO_3^-]$$
  
dom. effluents/atm. input =  $w_{2,CI}[CI^-]$ .

Springs with w%-agriculture greater than 50% were assigned to agricultural activities and springs with w%-agriculture less than 50% were attributed to urban pollution plus atmospheric inputs.

In total, the hydrochemical parameters defined above accounted for about 80% of the system variance. The bi-univocal association (extent and significance) between hydrochemical parameters and factors was checked by multiple linear regression (MLR) with satisfactory results. Because the Fundão's spring water chemistries have been explained by three different sources (weathering, agriculture and domestic effluents), Pacheco (1998b) classified his dataset as a system of triple influence. In this study, these sources or influences provide a value for k, the number of natural clusters feeding Ward's method of ClA.

### Cluster Analysis (Ward's Method)

ClA in this study is used as an alternative clustering technique. The adopted Ward's method (1963) belongs to the category of agglomerative hierarchical methods. The aggregate is gradually built on a similarity coefficient between samples or sites. First the algorithm gathers all most-similar pairs and then aggregates the other samples/sites or already-formed groups according to their similarities until k groups are formed. Distinct from other hierarchical methods, Ward's method is a minimum variance agglomerative technique because the two clusters to be joined in each round of clustering are those generating the smallest increase in the within-cluster variation.

#### **Discriminant Analysis**

For the present case study, DA is used as a classification tool, namely for optimizing the location of sites pre-assigned by CA or ClA. A general approach to the problem of (re)classifying an observation  $\mathbf{x}$  may be stated as follows:

$$E_i = \mathbf{x}' \times \mathbf{S}^{-1} \times \bar{\mathbf{x}}_i - \frac{1}{2} \bar{\mathbf{x}}_i' \times S^{-1} \times \bar{\mathbf{x}}_i + \ln(\text{prob}_i), \quad i = 1, 2, \dots, k \quad (4)$$

where  $E_i$  is the classification score of group i;  $\mathbf{x}'$  the transpose of  $\mathbf{x}$ ;  $\bar{\mathbf{x}}_i$  and  $\bar{\mathbf{x}}_i'$  are the mean of group i observations and the transpose of that vector, respectively;  $\mathbf{S}^{-1}$  the inverse of the within-group variance—covariance matrix; prob<sub>i</sub> the prior probability of group membership manifest in the observed  $n_i/n$  proportion, where  $n_i$  is the number of observations in group i and n the number of observations in the dataset. According to this criterion, an observation  $\mathbf{x}$  will be (re)classified into the group for which the E value is highest. The new (posterior) probability of group

membership  $(Prob_i)$  is given by:

$$Prob_{i} = \frac{prob_{i} \times f_{i}(\mathbf{x})}{\sum_{i=1}^{k} prob_{i} \times f_{i}(\mathbf{x})}$$
(5)

where  $f_i(\mathbf{x})$  is the score of  $\mathbf{x}$  in the frequency curve of group i. The relation between prior and post assignments is frequently reported in a confusion matrix that shows the number of correctly classified cases in the main diagonal and the number of misclassified cases in the off-diagonals. Confusion matrices are also useful to compare classification results obtained by different approaches [Eqs. (2) and (3), and Ward's method].

### **Node Analysis**

The scope of NA, as employed in this study, is threefold. First we looked at this procedure as a gridding tool. Using methods such as kriging, gridding produces a regularly spaced array of z values from randomly spaced (x, y, z)observation points. When the (x, y, z) observations are spaced randomly over the study area, there are usually many holes in their distribution. Gridding fills in the holes by extrapolating or interpolating z values in those locations where no data exists. We interpolated the CA/DA group memberships to be used in NA over a grid with  $l \times h$  nodes, where l is the number of columns along the width and h the number of rows along the height of the study area, and did the same with the ClA/DA results. After gridding we compared nodes between the CA/ClA or one-way RC grids and constructed a combined or two-way RC grid. If the membership of a node was equal in the first grids, then the node stayed in its group in the combined grid. Otherwise the node was reclassified as group- $\gamma$  node (hybrid), where  $\gamma$  is an arbitrary identification code. In the last stage of NA we drew constant membership contours across the grids that became boundaries between different groups and between groups and hybrid regions.

### THE TWO-WAY RC MODEL FOR THE FUNDÃO AREA

In this study we used the set of 160 spring water samples that were collected in the Fundão area (central Portugal) by Van der Weijden and others (1983). The sampling was carried out in June–July. The samples' locations are plotted in Figure 2 and the chemical analyses are given in the Appendix.

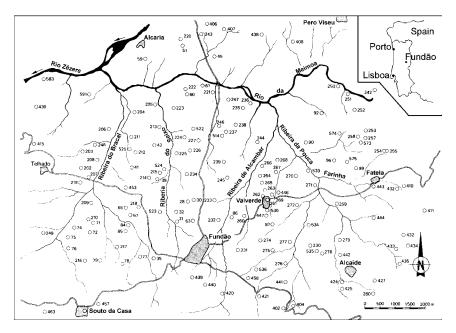


Figure 2. Location of the Fundão area and water sampling sites. Adapted from Pacheco (1998b).

Original drawings in Van der Weijden and others (1983).

#### Results of CA/DA

CA was applied by Pacheco (1998b) to the Fundão dataset using the major anions and dissolved silica as variables (concentrations in  $\mu$ mol/L). The results are shown in Table 1.

From the observation of sympathies and antipathies between factor loadings, the first two factors were represented by:

- the *w*%-pollution (factor 1), with pollution =  $443.0[\text{Cl}^-] + 370.8[\text{SO}_4{}^{2-}] + 748.9[\text{NO}_3{}^-]$  weathering =  $313.4[\text{HCO}_3{}^-] + 421.0[\text{SiO}_2]$
- the *w*%-agriculture (factor 2), with agriculture = 63.4[SO<sub>4</sub><sup>2-</sup>] + 591.6[NO<sub>3</sub><sup>-</sup>] dom. effluents/atm. input = 377.0[Cl<sup>-</sup>].

The water samples were assembled into three groups: 1, weathering (w%-pollution < 50%); 2, domestic effluents (w%-pollution > 50% and w%-agriculture < 50%); 3, farmland fertilizers (w%-pollution > 50% and w%-agriculture > 50%).

	$F_1$	$F_2$	$F_3$	$F_4$							
Distribution of variance											
Eigenvalue (×1000)	190.5	74.8	44.9	34.6							
$\%F_i$	55.3	21.7	13.0	10.0							
Cum-%F	55.3	77.0	90.0	100.0							
Correspondence factor loadings (×1000)											
HCO <sub>3</sub> -	313.4	92.0	-202.6	164.6							
Cl <sup>-</sup>	-443.0	377.0	178.3	14.6							
$SO_4^{2-}$	-370.8	-63.4	-346.5	-394.1							
$NO_3$	-748.9	-591.6	35.7	235.5							
SiO <sub>2</sub>	421.0	-160.3	210.3	-114.7							
MLR model relating hydroc	hemical param	eters with fac	etors								
	$B_1$	$B_2$	$B_3$	$R^2$ (%)							
w%-Pollution	51.4	1.4	0.6	99.1							
w%-Agriculture	22.1	68.5	12.0	77.9							

Table 1. Results of the CA Procedure

Source. Adapted from Pacheco (1998b). Symbols:  $\%F_i$ , percentage of data variation explained by  $F_i$ ; Cum-%F, cumulative  $\%F_i$ ;  $B_i$ , standardized regression coefficient of factor  $F_i$ ;  $R^2$ , adjusted coefficient of multiple determination; w%-pollution and w%-agriculture, hydrochemical parameters calculated by Equations (2) and (3).

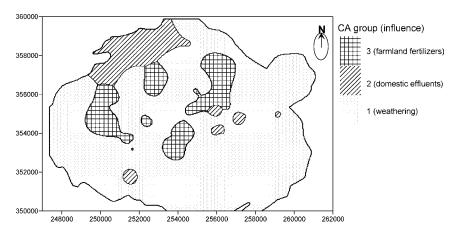
The results of this classification are listed in the Appendix under the heading CA/DA-prior.

The relation between hydrochemical parameters and factors was set on the basis of MLR and the results are summarized in the last two rows of Table 1. The MLR model for w%-pollution holds a  $R^2 = 99.1\%$  indicating a tight regression between this parameter and  $F_1$ , but no similar link exists between the w%-agriculture parameter and  $F_2$  (in the latter case  $R^2 = 77.9\%$ ). In view of such uncertainty, we used DA to optimize the location of the samples with respect to the three pre-defined groups. The results are in column CA/DA-post of the Appendix and reveal that 15 samples (9.4%) were reclassified into a different group. Using the optimized memberships of the samples and gridding as explained above, we drew Figure 3 that illustrates the areas of influence of each CA group.

#### Results of ClA/DA

The results from Ward's method are described in detail in the Appendix (column ClA/DA-prior). These groupings were used as a training set for DA which provided the post assignments listed in column ClA/DA-post.

The confusion matrix comparing the CA/DA and ClA/DA results is shown in Table 2. There is little doubt that group A is equivalent to group 1 (the weathering



**Figure 3.** Spatial distribution of group memberships determined by the results of CA optimized by DA.

group), but the associations between groups 2/3 and B/C are less evident. The medians of w%-pollution and w%-agriculture suggest that group B and group 3 are influenced by farmland fertilizers, whereas group C, although falling in the field of weathering, has a median w%-agriculture compatible with group 2 (influence by domestic effluents). Based on these associations we drew Figure 4 to show the areas of influence of each ClA/DA group.

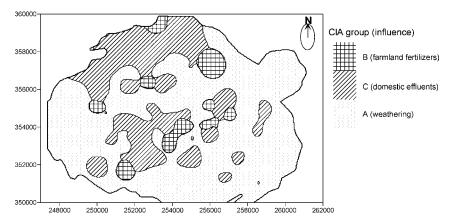
### **Results of Node Analysis**

Employing NA we combined Figures 3 and 4 obtaining Figure 5. The grids used were rectangles with l = 400 columns and h = 300 rows. The recasting of grid nodes was performed as follows: (1) when nodes in the one-way RC grids

<b>Table 2.</b> Confusion Matrix Comparing the Results Obtained by CA/DA (1, 2 and 3) and ClA/DA
(A, B and C) Groupings

	A	В	C	Total	w%-Pollution	w%-Agriculture
1	88	0	36	124	29.0	35.6
2	1	7	5	13	74.2	36.1
3	12	5	6	23	63.3	64.4
Total	101	12	47	160		
w%-Pollution	30.5	78.4	40.8			
w%-Agriculture	37.5	56.7	38.7			

*Note*. Associated medians of the w%-pollution and w%-agriculture parameters as determined by Equations (2) and (3).



**Figure 4.** Spatial distribution of group memberships determined by the results of CIA optimized by DA.

(Figs. 3 and 4) had the same value (1, 2 or 3 depending on whether their group memberships were 1/A, 2/C or 3/B) they preserved this value in the two-way RC (Fig. 5); (2) when group memberships in the original grids differ but one had the a value of 3 (fertilizer's influence) they were recast as 4 (mixing between fertilizer and other influences) in the combined grid; (3) in all other cases the two-way RC nodes were recast as 0 (mixing between weathering and domestic effluents).

The areas with weathering-dominated water chemistries occupy most of the studied region, working out as areas of background hydrochemistry. The dominance of effluents is restricted to the region of Alcaria, where the Meimoa river intersects the Zêzere river and some streamlets intersect the Meimoa river

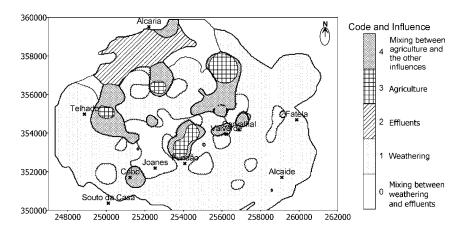


Figure 5. Results of node analysis.

(Fig. 2). However, a substantial surface area upstream from the Meimoa river is occupied by regions where effluents blur the background compositions generated by weathering (white areas). Apparently the direct discharge of domestic effluents into streams and streamlets produces regions of mixing that are converted by some concentration process into a region of effluent-dominated water chemistries south of Alcaria. In all cases the areas with fertilizer-dominated water chemistries are spots surrounded by a zone of fluid mixing.

### TWO-WAY RC AND THE ASSESSMENT OF HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion of a solute in groundwater occurs as a consequence of two different processes: mechanical dispersion and molecular diffusion. Mechanical dispersion is a process of fluid mixing that causes a zone of mixing to develop between a fluid of one composition that is adjacent to or is being displaced by a fluid of another composition. It occurs as a result of variations around some mean velocity of flow. These variations are caused by the porous medium heterogeneities at the microscopic, macroscopic and megascopic scales (e.g. variations in the hydraulic conductivity, grain's sorting, etc.). Molecular diffusion originates because of mixing caused by random molecular motions due to the thermal kinetic energy of the solute, i.e. it is a chemical rather than a physical (advective) process.

The results of two-way RC regarding the areas with fertilizer-dominated water chemistries (cross-hatched areas in Fig. 5) suggest that some dispersion of the fertilizers took place after their application on farmland, because these areas are completely surrounded by a region of mixing (dark grey areas). It seems like the fertilizers applied in Spring (starting in early March) to feed the Summer crops have moved downstream and formed pulse-like contaminant plumes, which in turn have grown large and get diluted in their outer rims due to hydrodynamic dispersion. The sampling made in June–July worked out as a snapshot of the plumes when they were 4 months old. The purpose now is to quantify the hydrodynamic dispersion, but first some mathematical background must be introduced.

### Mathematical Background on Hydrodynamic Dispersion

When a solute is subject to effective leaching, as usually happens in soils and saprolites derived from granites, mechanical dispersion grows several orders of magnitude higher than molecular diffusion, swamping the effects of this latter phenomenon (Pfannkuch, 1962). In such cases hydrodynamic dispersion is represented mathematically by:

$$D = v \times \alpha \tag{6a}$$

with

$$v = \frac{K \times \operatorname{grad}(h)}{m_{e}} \tag{6b}$$

where D is the coefficient of hydrodynamic dispersion, v the solute's velocity in the mean direction of flow and  $\alpha$  a characteristic property of mechanical dispersivity; K,  $\operatorname{grad}(h)$  and  $m_{\rm e}$  are the hydraulic conductivity, hydraulic gradient and effective porosity. Hydrodynamic dispersion may be expressed by longitudinal (in the direction of flow) and transverse (at right angles) spreadings where the D and  $\alpha$  coefficients are represented with L or T subscripts (e.g.  $D_{\rm L}$  or  $\alpha_{\rm T}$ ).

Assessment of the dispersion coefficients is essential for models of contaminant transport to work. Among the models in use, we focus on those dealing with localized and non-continuous sources of contamination, like the periodic application of fertilizers to farmland. According to these pulse-type models, the movement of a contaminant (e.g. sulphate) across the porous medium generates a growing plume due to hydrodynamic dispersion. One important feature of the concentration distribution inside the plume is that after a short period of time it becomes normal. The mean of the distribution describes the position of the plume and the variance ( $\sigma_L^2$  or  $\sigma_T^2$  of the longitudinal and transverse dispersions. The corresponding coefficients of hydrodynamic dispersion are given by (Domenico and Schwartz, 1990):

$$D_{\rm L} = \frac{\sigma_{\rm L}^2}{2t} \qquad D_{\rm T} = \frac{\sigma_{\rm T}^2}{2t} \tag{7}$$

where *t* is the time passed since the contaminant entered the system.

### The Analog Pulse-Type Model Based on Group Memberships

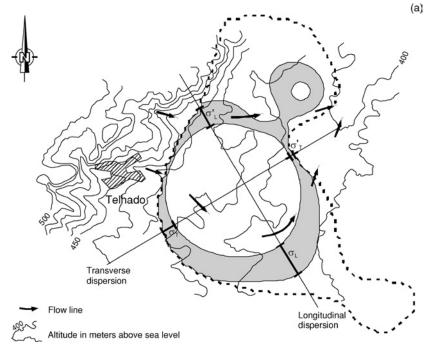
Application of pulse-type models [estimation of  $\sigma$  in Eq. (7)] requires that concentration distributions within contaminant plumes are well defined. This occurs when plumes are composed of a solute introduced artificially in the system (a tracer). In these cases solute concentrations inside and outside the plumes usually contrast. Contrarily, when plumes result from dissolution of fertilizers in ground waters also affected by weathering and domestic effluents (present case), the overlapping of several and sometimes similar sources of solutes masks the boundaries between plumes and the natural environment, making it difficult to quantify the mass transport parameters. In these cases we would need first to define a sharp boundary around the plumes and then use a proxy to describe the concentration distributions inside them. We believe that this is performed adequately by the two-way RC approach: the boundary of a plume is defined by the outer limit of a dark grey area enclosing a cross-hatched area (Fig. 5). The concentrations are represented by the membership probabilities of groups linked

to the agriculture influence (1/2  $\times$  (group 3 + group B)), listed in the Appendix under the heading Prob-3/B.

In total there are four contaminant plumes in Figure 5, which were termed Telhado, South of Alcaria, Fundão and North of Valverde in reference to the closest town. From data in column Prob-3/B of the Appendix, we drew contours of membership probability inside the plumes and shaded the space between those corresponding to the means and means minus standard deviations (Fig. 6a–d). The thicknesses of the shaded areas in the directions of elongation and at right angles are measures of  $\sigma_L$  and  $\sigma_T$ , respectively.

### Hydrology of the Fundão Soils

Apart from the estimation of  $\sigma$ , quantification of dispersivities [Eq. (6a)] requires that some hydrologic information is available on the studied porous media; namely, mean velocities of flow, which in turn are dependent on hydraulic



**Figure 6.** Topography around the contaminant plumes: (a) Telhado, (b) South of Alcaria, (c) Fundão, and (d) North of Valverde. The plumes are represented by dashed thick polygons. The shaded areas describe the regions inside the plumes where group-3/B membership probabilities range from the mean to the mean minus standard deviation. The thickness of the shaded areas is a measure of  $\sigma$  [Eq. (7)]. The samples' group-3/B memberships are listed in the Appendix.

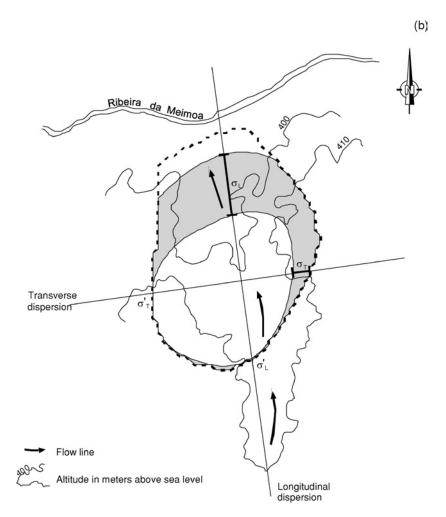


Figure 6. Continued.

gradients, hydraulic conductivities and effective porosities [Eq. (6b)]. Hydraulic gradients may be approached by topographic gradients. The other necessary hydrologic information is compiled in the next paragraph.

Costa and others (1971) collected a set of 37 soil samples from the region of Fundão and analysed them for grain size (Table 3). Hydraulic conductivities were estimated from the grain size distributions using the formula of Krumbein and Monk (1943):

$$K = 760d^2e^{-1.31\delta} (8)$$

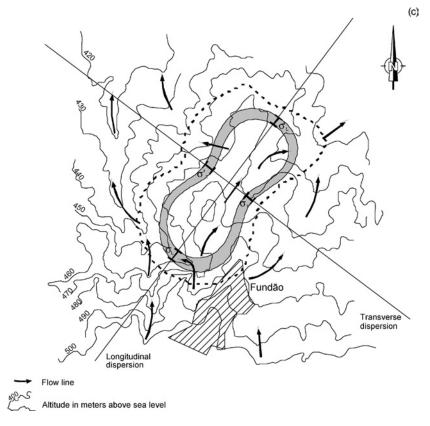


Figure 6. Continued.

where K is the hydraulic conductivity given in darcys (conversion to m/s implies a division by 1,04,000), d the geometric mean diameter (in millimeters) and  $\delta$  the log standard deviation of the grain size distribution. The  $\log(K)$  values are listed in the last column of Table 3 and their spatial distribution is shown in Figure 7. Effective porosities have been estimated by an analytical method cited in Custodio and Llamas (1983):

$$m_e = m_t - \Psi$$
  $\Psi = 0.03 \times \text{sand} + 0.35 \times \text{loam} + 1.65 \times \text{clay}$  (9)

where  $m_t$  and  $m_e$  are the total and effective porosities of the soil and  $\psi$  is its specific retention; *sand*, *loam* and *clay* are the proportions of the sand, loam and clay fractions in the sample (Table 3). For  $m_t$  we assumed a value of 50%, which is common for soils derived from granites. The  $m_e$  values obtained by Equation (9) were interpolated across the Fundão area and some contours were drawn (Fig. 8).

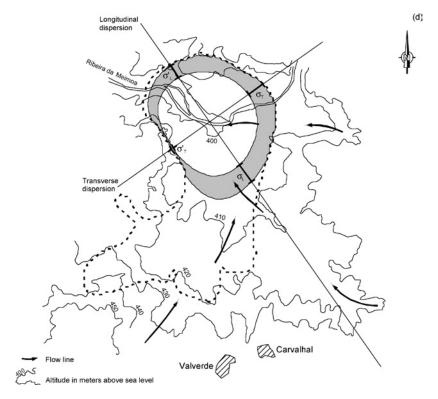


Figure 6. Continued.

### Dispersivities of the Fundão Soils

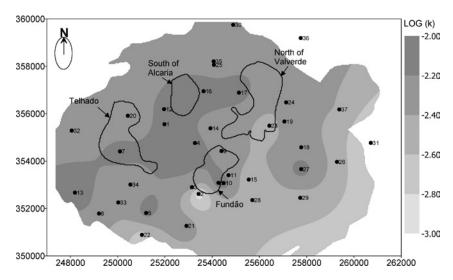
From Figure 6a–d we estimated the plumes'  $\sigma_L^2$  and  $\sigma_T^2$  and then calculated the plumes' hydrodynamic dispersions using Equation (7), assuming that t=4 months (the age of the plumes). From Figures 7 and 8 we averaged the plumes' hydraulic conductivities and effective porosities. Using this information in combination with hydraulic gradients deduced from Figure 6a–d, we determined flow velocities [Eq. (6b)] that when combined with the previously calculated hydrodynamic dispersions gave estimates for the longitudinal and transverse dispersivities [Eq. (6a)]. All results are shown in Table 4.

The values of  $\alpha_L$  range from 0.7 to 16.8 m. They are acceptable because in this study we are dealing with the assessment of dispersivities at the macroscopic scale. As expected, the  $\alpha_T$  values are always smaller than the  $\alpha_L$  values. The ratios  $\alpha_L/\alpha_T$  are within the interval [1.2, 12.6] m, a range that has already been found by other authors. The use of a single t is obviously a source of uncertainty because application of fertilizers is not restricted to a single day. The value of 4 months is

**Table 3.** Grain Size Distributions, Hydraulic Conductivities and Effective Porosities of 37 Soil Samples From the Fundão Region

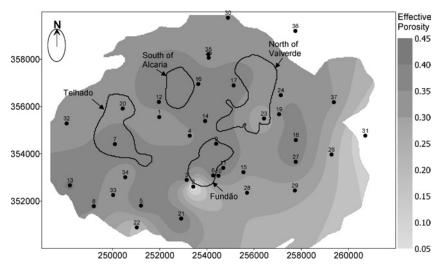
	Grain size distribution (ranges in mm, values in wt%)											
	Identificat	tion	5	Sand	Lo	oam	Clay	Phys param				
nr	M(m)	P (m)	>2	2-0.05	0.05-0.02	0.02-0.002	< 0.002	$\log(K)$	$m_e$			
1	2,51,980	3,55,554	24.6	51.0	6.2	10.4	5.7	-2.08	0.32			
2	2,53,424	3,52,614	5.9	36.9	14.5	24.1	18.4	-2.52	0.05			
3	2,53,144	3,52,897	11.4	63.9	6.3	9.6	3.4	-2.17	0.36			
4	2,53,271	3,54,764	25.1	52.9	4.7	12.1	5.0	-2.06	0.33			
5	2,51,206	3,51,810	18.5	67.1	5.7	6.4	1.5	-2.06	0.41			
6	2,54,266	3,53,084	28.4	51.4	6.2	10.0	2.2	-2.03	0.38			
7	2,50,099	3,54,408	18.2	65.3	3.8	8.0	3.2	-2.07	0.38			
8	2,49,208	3,51,786	10.0	71.7	5.3	7.8	4.3	-2.14	0.36			
9	2,54,393	3,54,426	9.2	72.1	4.9	11.4	1.5	-2.15	0.39			
10	2,54,490	3,53,072	29.1	49.5	5.0	10.3	4.2	-2.04	0.35			
11	2,54,691	3,53,406	8.9	71.7	5.0	11.2	1.3	-2.15	0.40			
12	2,51,966	3,56,192	18.1	65.7	4.3	7.6	3.4	-2.07	0.38			
13	2,48,191	3,52,669	12.5	77.8	1.8	5.2	2.5	-2.07	0.41			
14	2,53,926	3,55,384	2.2	80.6	6.0	8.3	1.7	-2.19	0.40			
15	2,55,549	3,53,221	3.0	65.2	10.0	15.0	4.8	-2.30	0.31			
16	2,53,636	3,56,950	18.8	69.6	3.8	4.2	2.8	-2.04	0.40			
17	2,55,132	3,56,889	18.5	66.8	3.5	7.4	3.2	-2.06	0.38			
18	2,57,768	3,54,582	1.6	80.3	5.0	10.5	2.2	-2.20	0.38			
19	2,57,059	3,55,671	2.3	81.0	1.3	9.8	5.3	-2.19	0.35			
20	2,50,432	3,55,914	7.2	67.8	11.5	4.8	4.6	-2.21	0.34			
21	2,52,911	3,51,265	3.2	82.2	4.7	7.8	1.1	-2.16	0.41			
22	2,51,028	3,50,888	5.2	50.9	10.4	20.3	11.7	-2.39	0.18			
23	2,56,420	3,55,492	3.0	65.9	7.1	12.1	10.2	-2.29	0.24			
24	2,57,132	3,56,479	1.3	76.8	5.9	10.9	4.5	-2.23	0.34			
25	2,54,075	3,58,061	5.2	74.8	2.4	10.3	6.8	-2.19	0.32			
26	2,59,283	3,53,968	2.1	68.7	4.3	12.7	11.5	-2.28	0.23			
27	2,57,763	3,53,661	21.4	63.4	3.0	6.8	4.4	-2.05	0.37			
28	2,55,701	3,52,352	1.6	66.3	7.0	16.4	8.0	-2.31	0.26			
29	2,57,728	3,52,449	3.5	65.1	7.4	13.2	7.6	-2.29	0.27			
30	2,54,891	3,59,752	17.0	53.1	9.8	14.3	4.8	-2.17	0.31			
31	2,60,713	3,54,768	10.8	30.2	9.8	29.9	14.9	-2.48	0.08			
32	2,48,056	3,55,286	13.2	61.0	5.8	12.0	7.0	-2.17	0.30			
33	2,50,026	3,52,255	3.9	73.7	3.8	11.5	6.1	-2.21	0.32			
34	2,50,539	3,53,009	7.8	69.7	5.4	10.9	5.6	-2.18	0.33			
35	2,54,066	3,58,209	6.0	71.7	6.6	10.6	4.4	-2.20	0.34			
36	2,57,749	3,59,193	24.6	51.0	6.2	10.4	5.7	-2.08	0.32			
37	2,59,381	3,56,181	4.9	68.0	7.1	12.6	6.4	-2.24	0.30			

Source. Original data (grain sizes) compiled from Costa and others (1971). Hydraulic conductivities estimated by the method of Krumbein and Monk (1943), and effective porosities by a method cited in Custodio and Llamas (1983) assuming an average total porosity of 50%. Symbols: nr, number of the soil sample; M and P, Hayford–Gauss coordinates of the soil samples (locations in Figs. 7 and 8); K, hydraulic conductivity;  $m_e$ , effective porosity.



**Figure 7.** Spatial distribution of the Fundão soils' hydraulic conductivities. The numbers near the dots are sample numbers as listed in Table 3. The labelled polygons are the four contaminant plumes.

the largest gap between the actions of fertilizing and water sampling. A value for the smallest gap would be 2 months or so, for crops seeded in late April. Adoption of t=2 months would raise the  $\alpha_{\rm L}$  and  $\alpha_{\rm T}$  dispersivities by a factor of 2, but their ranges would be kept under acceptable values.



**Figure 8.** Spatial distribution of the Fundão soils' effective porosities. The numbers near the dots are sample numbers as listed in Table 3. The labelled polygons are the four contaminant plumes.

**Table 4.** Results of the Procedures Used to Estimate the Longitudinal and Transverse Dispersivities of the Fundão Soils

		Contaminant Plume									
Direction	Parameter	A (Telhado)	B (South of Alcaria)	C (Fundão)	D (North of Valverde)						
	Mean group-3/B probability	0.4	0.4	0.6	0.5						
	Associated standard deviation	0.1	0.2	0.1	0.1						
	$m_e$	0.35	0.38	0.35	0.33						
	$\log(K)$	-2.13	-2.08	-2.15	-2.18						
	grad(h)	0.041	0.0068	0.0382	0.0094						
	$v \times 10^{-4} \text{ (m/s)}$	8.5	1.5	7.7	1.9						
Longitudinal	$\sigma_L$ (m)	328.75	445.47	117.85	276.54						
	$\sigma'_{L}$ (m)	200.18	13.21	92.8	202.47						
	$D_L$ (cm <sup>2</sup> /s)	33.7	25.4	5.3	27.7						
	$\alpha_L$ (m)	3.9	16.8	0.7	14.8						
Transverse	$\sigma_T$ (m)	129.16	124.3	98.76	237.58						
	$\sigma_T'$ (m)	29.46	5	94.84	20.74						
	$D_T$ (cm <sup>2</sup> /s)	3.0	2.0	4.5	8.0						
	$\alpha_T$ (m)	0.4	1.3	0.6	4.3						
Cross	$D_L/D_T$	11.1	12.6	1.2	3.4						

*Note.*  $m_{\rm e}$ , effective porosity; K, hydraulic conductivity;  ${\rm grad}(h)$ , hydraulic gradient; v, mean velocity of flow;  $\sigma_{\rm L}$ ,  $\sigma_{\rm L}'$ ,  $\sigma_{\rm T}$ ,  $\sigma_{\rm T}'$ , standard deviations of group-3/B membership probabilities (spatial representation);  $D_{\rm L}$  and  $D_{\rm T}$ , coefficients of hydrodynamic dispersion;  $\alpha_{\rm L}$  and  $\alpha_{\rm T}$ , mechanical dispersivities.

#### CONCLUSIONS

Hydrodynamic dispersion at the macroscopic and larger scales is an interesting and still unsolved research topic. In the previous sections of this paper we showed how the shapes and concentration distributions of contaminant plumes can be assessed by the application of our two-way RC and, notwithstanding limitations in accounting for the age of the plumes, demonstrated that quantification of mechanical dispersivities by this method leads to reliable results not only at the level of absolute values of the longitudinal and transverse components but also at the level of the ratios between them.

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#### **APPENDIX**

Location of the sampling sites (Hayford–Gauss M and P coordinates). Concentrations of major anions and silica in the 160 spring water samples collected by Van der Weijden and others (1983); the values were scaled to  $\mu$ mol/L. For some reason, some of the values in this appendix were transferred incorrectly from the original dataset to Pacheco and Van der Weijden (1996) and Pacheco (1998b). Some values regarding the cations (not shown in this appendix) are also incorrect in those papers, and the correct values are ( $\mu$ mol/L): K(215) = 34, Mg(226) = 65, Mg(269) = 861, Ca(42) = 107, Ca(85) = 171, Ca(226) = 131, Ca(267) = 327, Ca(271) = 128, and Ca(439) = 157, where values within brackets represent sample numbers. The chart shows prior and post assignments of samples to the CA and ClA groups. Prob-3/B is the sample's average posterior probability of group 3 (CA) and group B (ClA) memberships (agriculture influence).

nr         M (m)         P (m)         [HCO <sub>3</sub> <sup>-</sup> ] [Cl <sup>-</sup> ] [SO <sub>4</sub> <sup>2</sup> ] [NO <sub>3</sub> <sup>-</sup> ] [SiO <sub>2</sub> ]         Prior Post         Prior Post         Prob-3/Prior Post           28         2,53,614         3,53,895         780         440         356         371         656         3         1         C         C         0.21           30         2,53,789         3,53,965         844         485         458         460         639         3         3         C         C         0.33           31         2,53,263         3,53,298         490         423         185         387         506         3         3         A         A         0.27           32         2,53,228         3,53,579         390         282         129         371         558         3         1         A         A         0.24           35         2,52,491         3,52,105         729         347         341         221         614         1         1         C         C         0.13           39         2,52,631         3,54,666         619         231         129         216         260         3         3         A         A         0.23           41
30  2,53,789  3,53,965  844  485  458  460  639  3  3  C  C  0.33  31  2,53,263  3,53,298  490  423  185  387  506  3  3  A  A  0.27  32  2,53,228  3,53,579  390  282  129  371  558  3  1  A   A  0.24  35  2,52,491  3,52,105  729  347  341  221  614  1  1  C   C  0.13  39  2,52,631  3,54,666  619  231  129  216  260  3  3  A   A  0.23  41  2,51,789  3,55,052  261  189  198  55  463  1  1  A   A  0.12  42  2,52,526  3,55,754  370  130  127  139  421  1  1  A   A  0.16  45  2,54,526  3,58,596  1280  668  464  121  571  1  2  C   C  0.03  51  2,53,474  3,58,982  780  499  458  189  100  2  2  C   C  0.06  59  2,52,281  3,58,526  2260  2115  635  150  674  2  2  B   C  0.02  60  2,53,614  3,57,603  560  248  158  63  524  1  1  A   A  0.05  61  2,54,105  3,57,684  580  231  83  18  560  1  1  A   A  0.02  63  2,53,754  3,53,298  229  790  735  998  399  3  3  B  B  1.00  66  2,51,579  3,53,719  480  296  325  366  474  3  3  A   A  0.37  67  2,51,754  3,53,298  229  790  735  998  399  3  3  B  B  1.00  66  2,51,579  3,53,719  480  296  325  366  474  3  3  A   A  0.37  67  2,51,754  3,53,263  639  183  433  0  626  1  1  C   C  0.00  71  2,50,526  3,53,263  639  183  433  0  626  1  1  C   C  0.00  72  2,50,421  3,52,947  239  164  56  1  478  1  1  A   A  0.05  74  2,49,930  3,53,123  660  149  44  32  609  1  1  A   A  0.05  74  2,49,930  3,53,123  660  149  44  32  609  1  1  A   A  0.05  76  2,49,754  3,52,421  810  155  92  0  503  1  1  C   C  0.00
31 2,53,263 3,53,298 490 423 185 387 506 3 3 3 A A 0.27 32 2,53,228 3,53,579 390 282 129 371 558 3 1 A A 0.24 35 2,52,491 3,52,105 729 347 341 221 614 1 1 C C 0.13 39 2,52,631 3,54,666 619 231 129 216 260 3 3 A A 0.23 41 2,51,789 3,55,052 261 189 198 55 463 1 1 A A 0.12 42 2,52,526 3,55,754 370 130 127 139 421 1 1 A A 0.16 45 2,54,526 3,58,596 1280 668 464 121 571 1 2 C C 0.03 51 2,53,474 3,58,982 780 499 458 189 100 2 2 C C 0.06 59 2,52,281 3,58,526 2260 2115 635 150 674 2 2 B C 0.02 60 2,53,614 3,57,403 560 248 158 63 524 1 1 A A 0.05 61 2,54,105 3,57,684 580 231 83 18 560 1 1 A A 0.05 61 2,54,105 3,57,684 580 231 83 18 560 1 1 A A 0.02 63 2,53,754 3,53,298 229 790 735 998 399 3 3 B B 1.00 66 2,51,579 3,53,719 480 296 325 366 474 3 3 A A 0.37 67 2,51,754 3,53,509 1052 243 4 0 684 1 1 C C 0.00 71 2,50,526 3,53,263 639 183 433 0 626 1 1 C C 0.07 72 2,50,421 3,52,947 239 164 56 1 478 1 1 A A 0.05 74 2,49,930 3,53,123 660 149 44 32 609 1 1 A A 0.05 75 2,49,719 3,52,772 480 138 62 0 399 1 1 A A 0.05 76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
32         2,53,228         3,53,579         390         282         129         371         558         3         1         A         A         0.24           35         2,52,491         3,52,105         729         347         341         221         614         1         1         C         C         0.13           39         2,52,631         3,54,666         619         231         129         216         260         3         3         A         A         0.23           41         2,51,789         3,55,052         261         189         198         55         463         1         1         A         A         0.12           42         2,52,526         3,55,754         370         130         127         139         421         1         1         A         A         0.16           45         2,54,526         3,58,596         1280         668         464         121         571         1         2         C         C         0.03           51         2,53,474         3,58,982         780         499         458         189         100         2         2         C         C         0.06 </td
35 2,52,491 3,52,105 729 347 341 221 614 1 1 C C 0.13 39 2,52,631 3,54,666 619 231 129 216 260 3 3 A A 0.23 41 2,51,789 3,55,052 261 189 198 55 463 1 1 A A 0.12 42 2,52,526 3,55,754 370 130 127 139 421 1 1 A A 0.16 45 2,54,526 3,58,596 1280 668 464 121 571 1 2 C C 0.03 51 2,53,474 3,58,982 780 499 458 189 100 2 2 C C 0.06 59 2,52,281 3,58,526 2260 2115 635 150 674 2 2 B C 0.02 60 2,53,614 3,57,403 560 248 158 63 524 1 1 A A 0.05 61 2,54,105 3,57,684 580 231 83 18 560 1 1 A A 0.02 63 2,53,754 3,53,298 229 790 735 998 399 3 3 B B 1.00 66 2,51,579 3,53,719 480 296 325 366 474 3 3 A A 0.37 67 2,51,754 3,53,263 639 183 433 0 626 1 1 C C 0.00 71 2,50,526 3,53,263 639 183 433 0 626 1 1 C C 0.00 72 2,50,421 3,52,947 239 164 56 1 478 1 1 A A 0.05 74 2,49,930 3,53,123 660 149 44 32 609 1 1 A A 0.05 75 2,49,719 3,52,772 480 138 62 0 399 1 1 A A 0.05 76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
39  2,52,631  3,54,666  619  231  129  216  260  3  3  3  A  A  0.23  41  2,51,789  3,55,052  261  189  198  55  463  1  1  A   A  0.12  42  2,52,526  3,55,754  370  130  127  139  421  1  1  A   A  0.16  45  2,54,526  3,58,596  1280  668  464  121  571  1  2   C  C  0.03  51  2,53,474  3,58,982  780  499  458  189  100  2  2  C  C  0.06  59  2,52,281  3,58,526  2260  2115  635  150  674  2  2  B  C  0.02  60  2,53,614  3,57,403  560  248  158  63  524  1  1  A   A  0.05  61  2,54,105  3,57,684  580  231  83  18  560  1  1  A   A  0.05  63  2,53,754  3,53,298  229  790  735  998  399  3  3  B  B  1.00  66  2,51,579  3,53,719  480  296  325  366  474  3  3  A   A  0.37  67  2,51,754  3,53,509  1052  243  4  0  684  1  1  C  C  0.00  71  2,50,526  3,53,263  639  183  433  0  626  1  1  C  C  0.07  72  2,50,421  3,52,947  239  164  56  1  478  1  1  A   A  0.05  74  2,49,930  3,53,123  660  149  44  32  609  1  1  A   A  0.05  74  2,49,930  3,53,123  660  149  44  32  609  1  1  A   A  0.05  76  2,49,754  3,52,421  810  155  92  0  503  1  1  C  C  0.00
41       2,51,789       3,55,052       261       189       198       55       463       1       1       A       A       0.12         42       2,52,526       3,55,754       370       130       127       139       421       1       1       A       A       0.16         45       2,54,526       3,58,596       1280       668       464       121       571       1       2       C       C       0.03         51       2,53,474       3,58,982       780       499       458       189       100       2       2       C       C       0.06         59       2,52,281       3,58,526       2260       2115       635       150       674       2       2       B       C       0.02         60       2,53,614       3,57,403       560       248       158       63       524       1       1       A       A       0.05         61       2,54,105       3,57,684       580       231       83       18       560       1       1       A       A       0.02         63       2,53,754       3,53,298       229       790       735       998 <t< td=""></t<>
42       2,52,526       3,55,754       370       130       127       139       421       1       1       A       A       0.16         45       2,54,526       3,58,596       1280       668       464       121       571       1       2       C       C       0.03         51       2,53,474       3,58,982       780       499       458       189       100       2       2       C       C       0.06         59       2,52,281       3,58,526       2260       2115       635       150       674       2       2       B       C       0.02         60       2,53,614       3,57,403       560       248       158       63       524       1       1       A       A       0.05         61       2,54,105       3,57,684       580       231       83       18       560       1       1       A       A       0.02         63       2,53,754       3,53,298       229       790       735       998       399       3       3       B       B       1.00         66       2,51,579       3,53,719       480       296       325       366       <
45
51         2,53,474         3,58,982         780         499         458         189         100         2         2         C         C         0.06           59         2,52,281         3,58,526         2260         2115         635         150         674         2         2         B         C         0.02           60         2,53,614         3,57,403         560         248         158         63         524         1         1         A         A         0.05           61         2,54,105         3,57,684         580         231         83         18         560         1         1         A         A         0.02           63         2,53,754         3,53,298         229         790         735         998         399         3         3         B         B         1.00           66         2,51,579         3,53,719         480         296         325         366         474         3         3         A         A         0.37           67         2,51,754         3,53,509         1052         243         4         0         684         1         1         C         C         0.00
59         2,52,281         3,58,526         2260         2115         635         150         674         2         2         B         C         0.02           60         2,53,614         3,57,403         560         248         158         63         524         1         1         A         A         0.05           61         2,54,105         3,57,684         580         231         83         18         560         1         1         A         A         0.02           63         2,53,754         3,53,298         229         790         735         998         399         3         3         B         B         1.00           66         2,51,579         3,53,719         480         296         325         366         474         3         3         A         A         0.37           67         2,51,754         3,53,509         1052         243         4         0         684         1         1         C         C         0.00           71         2,50,526         3,53,263         639         183         433         0         626         1         1         C         C         0.07
60 2,53,614 3,57,403 560 248 158 63 524 1 1 A A 0.05 61 2,54,105 3,57,684 580 231 83 18 560 1 1 A A 0.02 63 2,53,754 3,53,298 229 790 735 998 399 3 3 B B 1.00 66 2,51,579 3,53,719 480 296 325 366 474 3 3 A A 0.37 67 2,51,754 3,53,509 1052 243 4 0 684 1 1 C C 0.00 71 2,50,526 3,53,263 639 183 433 0 626 1 1 C C 0.07 72 2,50,421 3,52,947 239 164 56 1 478 1 1 A A 0.05 74 2,49,930 3,53,123 660 149 44 32 609 1 1 A A 0.02 75 2,49,719 3,52,772 480 138 62 0 399 1 1 A A 0.05 76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
61 2,54,105 3,57,684 580 231 83 18 560 1 1 A A 0.02 63 2,53,754 3,53,298 229 790 735 998 399 3 3 B B 1.00 66 2,51,579 3,53,719 480 296 325 366 474 3 3 A A 0.37 67 2,51,754 3,53,509 1052 243 4 0 684 1 1 C C 0.00 71 2,50,526 3,53,263 639 183 433 0 626 1 1 C C 0.07 72 2,50,421 3,52,947 239 164 56 1 478 1 1 A A 0.05 74 2,49,930 3,53,123 660 149 44 32 609 1 1 A A 0.02 75 2,49,719 3,52,772 480 138 62 0 399 1 1 A A 0.05 76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
63       2,53,754       3,53,298       229       790       735       998       399       3       3       B       B       1.00         66       2,51,579       3,53,719       480       296       325       366       474       3       3       A       A       0.37         67       2,51,754       3,53,509       1052       243       4       0       684       1       1       C       C       0.00         71       2,50,526       3,53,263       639       183       433       0       626       1       1       C       C       0.07         72       2,50,421       3,52,947       239       164       56       1       478       1       1       A       A       0.05         74       2,49,930       3,53,123       660       149       44       32       609       1       1       A       A       0.05         75       2,49,719       3,52,772       480       138       62       0       399       1       1       A       A       0.05         76       2,49,754       3,52,421       810       155       92       0       503
66       2,51,579       3,53,719       480       296       325       366       474       3       3       A       A       0.37         67       2,51,754       3,53,509       1052       243       4       0       684       1       1       C       C       0.00         71       2,50,526       3,53,263       639       183       433       0       626       1       1       C       C       0.07         72       2,50,421       3,52,947       239       164       56       1       478       1       1       A       A       0.05         74       2,49,930       3,53,123       660       149       44       32       609       1       1       A       A       0.05         75       2,49,719       3,52,772       480       138       62       0       399       1       1       A       A       0.05         76       2,49,754       3,52,421       810       155       92       0       503       1       1       C       C       0.02
67       2,51,754       3,53,509       1052       243       4       0       684       1       1       C       C       0.00         71       2,50,526       3,53,263       639       183       433       0       626       1       1       C       C       0.07         72       2,50,421       3,52,947       239       164       56       1       478       1       1       A       A       0.05         74       2,49,930       3,53,123       660       149       44       32       609       1       1       A       A       0.02         75       2,49,719       3,52,772       480       138       62       0       399       1       1       A       A       0.05         76       2,49,754       3,52,421       810       155       92       0       503       1       1       C       C       0.02
71     2,50,526     3,53,263     639     183     433     0     626     1     1     C     C     0.07       72     2,50,421     3,52,947     239     164     56     1     478     1     1     A     A     0.05       74     2,49,930     3,53,123     660     149     44     32     609     1     1     A     A     0.02       75     2,49,719     3,52,772     480     138     62     0     399     1     1     A     A     0.05       76     2,49,754     3,52,421     810     155     92     0     503     1     1     C     C     0.02
72     2,50,421     3,52,947     239     164     56     1     478     1     1     A     A     0.05       74     2,49,930     3,53,123     660     149     44     32     609     1     1     A     A     0.02       75     2,49,719     3,52,772     480     138     62     0     399     1     1     A     A     0.05       76     2,49,754     3,52,421     810     155     92     0     503     1     1     C     C     0.02
74     2,49,930     3,53,123     660     149     44     32     609     1     1     A     A     0.02       75     2,49,719     3,52,772     480     138     62     0     399     1     1     A     A     0.05       76     2,49,754     3,52,421     810     155     92     0     503     1     1     C     C     0.02
75 2,49,719 3,52,772 480 138 62 0 399 1 1 A A 0.05 76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
76 2,49,754 3,52,421 810 155 92 0 503 1 1 C C 0.02
// 2,32,033 3,32,140 031 330 23/ 230 477 2 1 C C 0.11
78 2,51,474 3,51,930 918 1664 473 874 438 2 2 B B 0.61
79 2,50,737 3,52,035 410 181 125 121 634 1 1 A A 0.05
84 2,51,649 3,53,158 451 307 323 211 426 3 3 A A 0.27
85 2,51,579 3,52,982 590 169 94 82 606 1 1 A A 0.03
86 2,55,017 3,53,403 870 279 35 60 663 1 1 C C 0.01
87 2.56.316 3.53.158 451 243 177 1 613 1 1 A A 0.03
90 2,57,438 3,55,474 760 248 125 47 506 1 1 C A 0.03
92 2,58,000 3,56,737 580 186 117 0 552 1 1 A A 0.03
96 2,58,386 3,55,228 480 336 58 32 652 1 1 A A 0.01
99 2,59,123 3,54,982 600 567 366 37 353 2 2 C C 0.06
202 2,50,175 3,55,017 239 1297 1307 839 573 3 3 B B 0.91
203 2,50,210 3,55,579 610 372 417 185 440 2 3 C C 0.23
204 2,51,895 3,56,807 352 254 172 158 657 1 1 A A 0.07
205 2,52,561 3,57,052 716 536 404 379 485 3 3 C C 0.30
206 2,51,052 3,56,281 472 677 289 37 441 2 1 C A 0.05
207 2,50,421 3,54,737 244 621 580 500 489 3 3 B C 0.50
208 2,50,666 3,55,298 328 181 171 92 474 1 1 A A 0.12
209 2,50,456 3,53,895 367 231 323 240 532 3 3 A A 0.28
210 2,50,386 3,53,368 388 183 76 82 626 1 1 A A 0.03
211 2,51,789 3,56,035 1080 395 383 71 587 1 1 C C 0.04
212 2,51,930 3,55,544 357 85 173 144 603 1 1 A A 0.10
213 2,52,702 3,56,351 429 691 431 855 405 3 3 B B 0.92
214 2,52,351 3,54,702 215 220 437 203 437 3 3 A A 0.38
215 2,52,702 3,54,877 690 121 173 18 564 1 1 C C 0.03
216 2,50,245 3,52,035 1113 189 227 53 660 1 1 C C 0.02

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	Identif	fication			Raw data	ļ		CA/	DΑ	ClA	/DA	
nr	<i>M</i> (m)	P (m)	[HCO <sub>3</sub>	-] [Cl-]	[SO <sub>4</sub> <sup>2-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SiO <sub>2</sub> ]	Prior	Post	Prior	Post	Prob-3/B
217		3,52,456	787	243	90	3	654	1	1	C	C	0.01
218	2,52,000	3,53,754	2994	485	228	181	635	1	1	C	C	0.00
219		3,54,561	167	762	139	871	465	3	3	В	Α	0.55
220	2,53,403	3,59,158		2482	1047	1081	264	2	2	В	В	0.50
221	2,54,456	3,57,438	477	209	137	3	522	1	1	Α	Α	0.04
222	2,53,544	3,57,544	642	259	194	216	634	1	1	Α	Α	0.08
223	2,53,158	3,56,947	326	254	371	435	485	3	3	Α	Α	0.44
224	2,53,509	3,56,035		130	138	77	411	1	1	C	C	0.04
225	2,53,263	3,55,474	372	133	227	58	472	1	1	Α	Α	0.13
226	2,53,684	3,55,579	436	113	158	85	545	1	1	Α	Α	0.08
227	2,53,965	3,55,895	367	124	154	226	581	1	1	A	A	0.15
228	2,52,526	3,52,245	836	268	342	177	750	1	1	C	C	0.05
229	2,55,684	3,51,684	557	536	162	205	666	1	1	Α	Α	0.04
230	2,57,544	3,52,456	664	203	318	21	546	1	1	C	C	0.07
231	2,55,193	3,52,351	626	178	448	124	508	1	1	C	C	0.22
232	2,54,561	3,53,333	334	175	81	435	745	3	1	A	A	0.17
233	2,54,456	3,53,965	690	790	514	2903	687	3	3	В	В	1.00
234	2,53,579	3,54,807	433	158	278	132	670	1	1	A	A	0.09
235	2,55,403	3,56,947	523	155	70	65	668	1	1	A	A	0.02
236	2,55,649	3,57,088	601	1354	1144	1387	586	3	3	В	В	0.99
237	2,54,877	3,56,175	400	118	96	248	207	3	3	A	A	0.35
238	2,55,158	3,56,386	438	141	135	68	535	1	1	A	A	0.06
239	2,54,772	3,55,193	600	324	274	500	558	3	3	A	A	0.38
241	2,60,210	3,57,193	231	79	24	61	514	1	1	A	A	0.06
242	2,59,754	3,57,509	136	65	10	71	445	1	1	A	A	0.09
243	2,54,105	3,59,333	1529	874	515	435	776	2	1	C	C	0.07
244	2,55,859	3,55,824	323	265	336	250	476	3	3	A	Α	0.33
245	2,54,912	3,54,702	692	310	173	131	608	1	1	A	C	0.04
246	2,54,631	3,56,351	564	127	151	131	519	1	1	A	Α	0.09
247	2,54,947	3,57,193	454	282	372	166	532	3	1	A	C	0.21
248	2,50,596	3,55,789	526	195	384	500	415	3	3	A	C	0.47
249	2,48,877	3,52,947	408	107	170	52	560	1	1	A	A	0.06
250	2,58,561	3,57,614	187	268	279	324	579	3	3	A	A	0.32
251	2,58,842	3,57,368	203	93	15	35	467	1	1	A	A	0.06
252	2,59,088	3,56,842	128	104	7	66	414	1	1	A	A	0.10
253	2,59,438	3,56,175	249	90	66	61	619	1	1	A	A	0.04
254	2,60,000	3,55,509	295	116	75	29	600	1	1	A	A	0.03
255	2,60,105	3,55,509	293	124	72	66	672	1	1	A	A	0.03
256	2,59,614	3,56,140	236	130	75	35	520	1	1	A	A	0.06
257	2,59,438	3,55,930	243	144	99	140	613	1	1	A	A	0.07
258	2,59,193	3,56,000	59	96	9	66	237	1	1	A	Α	0.21
259	2,58,456	3,53,824	723	262	173	190	740	1	1	Α	C	0.03
260	2,55,403	3,53,438	647	141	62	44	760	1	1	Α	Α	0.01
261	2,56,140	3,53,965	675	931	365	452	620	2	1	C	C	0.21
262	2,56,035	3,54,070	1047	3328	749	1516	617	2	2	В	В	0.51
263		3,54,281	1721	3159	1450	1242	740	2	2	В	В	0.50
264	2,55,930	3,54,737	451	333	204	250	550	3	1	A	A	0.16

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	Identif	ication			Raw data	ļ		CA/	DΑ	ClA	/DA	
nr	<i>M</i> (m)	P (m)	[HCO <sub>3</sub>	[Cl <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SiO <sub>2</sub> ]	Prior	Post	Prior	Post	Prob-3/B
265		3,54,526	567	152	43	9	697	1	1	A	A	0.01
266		3,55,052	533	1297	1784	532	486	2	2	В	В	0.54
267	2,56,456	3,54,877	1278	564	113	182	739	1	1	C	C	0.01
268		3,55,263	526	527	439	282	581	2	3	C	C	0.25
269		3,54,105	877	6770	1117	1048	567	2	2	В	В	0.50
270		3,54,702		1326	675	726	452	2	2	В	В	0.58
271	2,57,754	3,54,386	449	214	50	139	842	1	1	Α	Α	0.01
272		3,53,789	367	259	12	187	573	1	1	Α	Α	0.06
273		3,51,684	652	164	24	4	723	1	1	Α	Α	0.01
274	2,55,930		470	305	105	150	530	1	1	Α	A	0.07
275		3,52,316	516	282	25	105	662	1	1	Α	Α	0.02
276		3,51,895	531	480	71	176	615	1	1	Α	Α	0.03
277		3,52,596	606	361	119	113	736	1	1	A	A	0.02
278		3,52,210	375	203	37	113	760	1	1	A	A	0.02
279		3,52,631	688	592	134	118	692	1	1	C	Α	0.01
280		3,50,912	434	152	23	13	583	1	1	Α	Α	0.02
402		3,50,421	150	115	14	22	211	1	1	A	A	0.16
404		3,50,526	308	188	19	32	399	1	1	A	A	0.06
406		3,59,684	853	623	151	60	692	1	1	C	C	0.01
407		3,59,474		745	399	106	757	1	1	C	C	0.00
408		3,59,052	551	268	140	113	711	1	1	Α	A	0.02
410		3,54,386	272	107	25	74	530	1	1	A	A	0.05
411		3,53,579	214	199	93	30	209	1	1	Α	A	0.18
415		3,55,824	470	244	34	8	612	1	1	Α	A	0.01
420		3,50,947	390	209	46	14	340	1	1	Α	A	0.07
421		3,50,842	353	188	45	23	339	1	1	Α	A	0.08
423		3,54,245	262	88	32	29	352	1	1	Α	A	0.10
424		3,51,298	365	232	79	81	445	1	1	A	A	0.08
425		3,51,088	819	91	21	11	812	1	1	C	C	0.00
427		3,51,333	433	162	10	30	534	1	1	A	A	0.03
430		3,57,017	725	241	324	34	464	1	1	C	C	0.09
432		3,52,807	338	161	19	25	689	1	1	A	A	0.01
433	2,60,386		280	107	82	24	524	1	1	A	A	0.05
434		3,52,456	292	79	16	13	524	1	1	A	A	0.03
435		3,51,859	421	64	10	5	581	1	1	A	A	0.02
438		3,59,298	430	152	60	30	487	1	1	A	A	0.04
439		3,51,474	714	128	25	0	709	1	1	A	A	0.01
440		3,51,228	636	127	58	7	729	1	1	A	A	0.01
441		3,51,298	956	166	67	8	875	1	1	С	C	0.00
442		3,52,175	607 540	832	50	75 22	838 569	1	1	C	A	0.00
443		3,54,386	549	378	65 27	33		1	1	A	A	0.02
444		3,53,333	351	157	27	36	442	1	1	A	A	0.05
446		3,54,175	651	255	28	33	887 548	1	1	A	A	0.00
447		3,53,438	974	533	189	107	548	1	1 1	C C	C C	0.02
452	2,52,631		838	338	351	105	774 752	1 1	1	C	C	0.03
453		3,54,386		276	92	17	752					0.00
457	2,50,666	3,50,631	566	93	3	1	568	1	1	A	Α	0.02

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	Identif	ication		Raw data					DΑ	ClA	/DA	
nr	<i>M</i> (m)	P (m)	[HCO <sub>3</sub> -	] [Cl <sup>-</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]	[SiO <sub>2</sub> ]	Prior	Post	Prior	Post	Prob-3/B
458	255509	351438	526	195	18	22	670	1	1	A	A	0.01
463	248947	350386	231	241	67	31	366	1	1	A	A	0.09
514	254737	356035	558	161	133	27	497	1	1	A	Α	0.05
522	253824	356281	1149	181	95	32	600	1	1	C	C	0.01
523	252702	353579	650	302	299	34	860	1	1	C	C	0.01
524	2,52,842	3,54,982	918	248	228	21	679	1	1	C	C	0.01
525	2,51,754	3,55,649	503	126	138	48	554	1	1	A	A	0.05
530	2,56,140	3,53,614	643	454	356	62	742	1	1	C	C	0.03
534	2,57,509	3,53,123	310	277	162	100	604	1	1	A	Α	0.06
535	2,57,754	3,52,281	625	725	286	105	568	2	1	C	C	0.04
536	2,55,824	3,51,719	529	236	111	42	431	1	1	A	A	0.06
539	2,57,509	3,54,912	600	685	226	150	375	2	1	C	A	0.08
540	2,56,491	3,54,105	520	224	46	63	806	1	1	A	Α	0.01
573	2,59,298	3,55,789	96	195	20	19	280	1	1	A	Α	0.13
574	2,58,561	3,56,105	652	914	189	29	515	2	1	C	A	0.01
575	2,58,842	3,55,193	875	426	261	30	514	1	1	C	C	0.03
583	2,48,947	3,57,895	305	2350	269	284	415	2	2	В	A	0.19
589	2,56,316	3,52,316	501	205	39	24	679	1	1	A	A	0.01
591	2,50,421	3,57,403	572	412	418	20	228	2	2	C	C	0.08