

Article

Search for a Relevant Scale to Optimize the Quality Monitoring of Groundwater Bodies in the Occitanie Region (France)

Meryem Jabrane ¹, Abdessamad Touiouine ¹, Vincent Valles ^{2,3}, Abdelhak Bouabdli ¹, Said Chakiri ¹, Ismail Mohsine ⁴, Youssouf El Jarjini ⁵, Moad Morarech ⁵, Yannick Duran ⁶ and Laurent Barbiero ^{7,*}

- ¹ Geosciences Laboratory, Faculty of Sciences, Ibn Tofail University, BP 133, Kénitra 14000, Morocco
² Laboratoire Environnement Méditerranéen et Modélisation des Agro-Hydrosystèmes, Université Avignon, 84000 Avignon, France
³ Faculty of Sciences and Technics (FSTBM), Beni Mellal 23000, Morocco
⁴ Geosciences, Water and Environment Laboratory, Faculty of Sciences Rabat, Mohammed V University, Rabat 10000, Morocco
⁵ Laboratory in Applied and Marine Geosciences, Geotechnics and Georisk (LR3G) Faculty of Science Tetouan (FS), Abdelmalek Essaâdi University (UAE), Tetouan 93002, Morocco
⁶ Agence Régionale de Santé, Services régionaux de Toulouse, 10 Chemin du Raisin, 31050 Toulouse CEDEX 9, France
⁷ Géoscience Environnement Toulouse, IRD, CNRS, UPS, OMP, Mixed Research Unit UMR5563, 14 Av. E. Belin, 31400 Toulouse, France
* Correspondence: laurent.barbiero@get.omp.eu

Abstract: In France, and more generally in Europe, the high number of groundwater bodies (GWB) per administrative region is an obstacle for the management and monitoring of water for human consumption by regional health agencies. Moreover, GWBs show a high spatial, temporal, physico-chemical, and bacteriological variability. The objective is to establish homogeneous groupings of GWB from the point of view of water quality and the processes responsible for this quality. In the Occitanie region in southwestern France, the cross-referencing of two databases, namely the French reference system for groundwater bodies and SISE-EAUX, provided a dataset of 8110 observations and 15 parameters distributed over 106 GWB. The 8-step approach, including data conditioning, dimensional reduction by Principal Component Analysis, and hierarchical clustering, resulted in 20 homogeneous groups of GWB over the whole region. The loss of information caused by this grouping is quantified by the evolution of the explained variance. Splitting the region into two large basins (Adour-Garonne and Rhône Méditerranée) according to the recommendations of the European community does not result in a significant additional loss of information contained in the data. A quick study of a few groups allows to highlight the specificities of each one, thus enabling targeted guidelines or recommendations for water quality management and monitoring. In the future, the method will have to be tested on the scale of large European watersheds, as well as in the context of an increase in the number of parameters.

Keywords: groundwater resource; groundwater management; drinking water; large database; mapping; Occitanie; France



Citation: Jabrane, M.; Touiouine, A.; Valles, V.; Bouabdli, A.; Chakiri, S.; Mohsine, I.; El Jarjini, Y.; Morarech, M.; Duran, Y.; Barbiero, L. Search for a Relevant Scale to Optimize the Quality Monitoring of Groundwater Bodies in the Occitanie Region (France). *Hydrology* **2023**, *10*, 89. <https://doi.org/10.3390/hydrology10040089>

Academic Editors: David Brauer, Nathan Howell and Ryan Bailey

Received: 17 March 2023

Revised: 6 April 2023

Accepted: 8 April 2023

Published: 10 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In 2000, the European Union decided to inventory groundwater in order to optimize the monitoring of the quality of the resource [1–5]. The identification and delimitation of groundwater bodies (GWBs) in the different countries of the European Union [6,7] has led to the development of studies aimed at characterizing the bacteriological and physico-chemical quality of groundwater and the mechanisms responsible for this quality at the scale of GWBs [8–17]. In France, the water agencies have been in charge of this inventory and of the mapping of GWB, which are now listed and regularly updated in the French reference system for groundwater bodies [18]. However, due to the number of GWBs, the

development of specific standards or guidelines for the use or protection of each GWB [19] cannot be managed by the regional health agencies that are responsible for quality control and compliance for human consumption. Therefore, the issue of aggregating these GWBs into larger, homogeneous spatial units is critical in terms of management. Before reaching this goal, significant obstacles may arise due to the increase in unit size, such as the increase in lithological, structural, altitudinal heterogeneity, or related to the spatial distribution of human activity [20]. Working on larger areas automatically increases the number of natural environments and, thus, the number of processes involved in water quality. This can lead to a dilution of information in the mass of the regional data when studying these processes, making their identification difficult. The fact that water quality includes very heterogeneous parameters, such as bacteriology, major ions, pH, trace elements, or forms of nitrogen, makes this task complex. Finally, the aggregation of GWBs into a homogeneous set implies a loss of part of the information contained in the data that needs to be quantified.

A first grouping of GWBs was carried out at the scale of the Provence-Alpes-Côte d'Azur (PACA) region, a French Mediterranean region [20] with significant geological and altitudinal diversity. This study showed that the extreme values for some parameters, mainly those of bacteriological quality, could mask part of the information provided in the dataset, which was moderated by conditioning the data by log transformation [21]. Any regrouping is accompanied by a loss of part of the information conveyed in the dataset, and this loss of information has not been quantified to date. The objective of this work is to test the methodology over a larger region while quantifying the loss of information that accompanies the clustering, aiming to define a relevant scale for the management of monitoring and protection of the groundwater resources. The administrative region chosen is Occitanie, a region two and a half times larger than the PACA region and located on two major climatic zones, Mediterranean and Atlantic, as well as on two major basins, namely the Adour-Garonne and Rhône-Méditerranée basins. With regard to water intended for human consumption, the vast majority of cases of non-compliance with quality limits are related to fecal contamination (*Escherichia Coli* and *Enterococci* [22–24]). Particular attention will therefore be paid to these parameters, especially as they can pose a problem in very varied, even heterogeneous, hydrogeological contexts, and defining the spatialization of the different cases of contamination is an important scientific and health issue.

2. Materials and Methods

2.1. Study Area: Occitanie Administrative Region

The Occitanie region has a surface area of 72,724 km² and a population of 5.8 million inhabitants, with a heterogeneous distribution and a strong seasonal increase during summer, more specifically along the Mediterranean coast. The altitudes vary from 0 to 3298 m at the level of the Pyrenean ridges, and the lithology is very variable, with ancient crystalline formations (Massif Central and Pyrenees), more or less folded detrital sedimentary covers, and recent coastal plains. It has a slope facing the Mediterranean coast, an Atlantic slope corresponding to the upper and middle basin of the Garonne, and bears on the Hercynian basement of the Massif Central to the north and the line of the younger mountains of the Pyrenees to the south. To this lithological and altitudinal variability is added a climatic variability, namely the Atlantic side, with an oceanic influence (Köppen Cfb, Cwb, Cfc), and the Eastern part, under Mediterranean influence (Köppen Csa, Csb). For more details on the presentation of the study area, the reader can refer to a previous work [21].

2.2. Databases

The work is based on cross-referencing the SISE-EAUX database (<https://data.eaufrance.fr/concept/sise-eaux>, accessed on 20 January 2019) and the French reference system for groundwater bodies (<https://services.sandre.eaufrance.fr/geo/sandre>, accessed on 7 February 2022).

The SISE-EAUX database has been generated by the health agencies for about thirty years and is regularly updated as part of the monitoring of water resources. It contains data on various aspects such as physico-chemistry, composition in major ions, metals,

and microbiological parameters of fecal or non-fecal origin, etc. On a national scale, this database includes more than 32,000 catchment stations, which consist of 96% groundwater and 4% surface water. All analyses are performed by laboratories that have received all the international approvals and certifications of quality and reliability.

The French reference system for groundwater bodies is based on the European Water Framework Directive (WFD) published in 2000 [4]. The French Water Agencies, with the support of the French Geological Survey (BRGM), inventoried underground water reservoirs on a national scale, which were then subdivided into groundwater bodies and units of the Water Information System for Europe (WISE). On a European scale, it was decided that the GWBs would be referenced by large European river basins such as the Po for Italy or, for France, the Seine, the Rhône-Méditerranée basin, the Adour-Garonne basin, etc. Each GWB is described in a geological survey, and its geographic contours, are marked on a GIS. At the national level, GWB are referred to by a unique code ranging from FRXG000 to FRXG999, where FR refers to France, X denotes the major watershed (for example D or F for Rhone Mediterranean or Adour Garonne Watersheds, respectively) and G refers to groundwater resource.

2.3. Data Processing

The selected methodology includes 8 steps, of which only 7 are detailed in this article.

1. The first step was an extraction of data from SISE-EAUX, keeping only raw groundwater, i.e., not having undergone any disinfection or other treatment;
2. These data were then processed by basic univariate statistics, in order to detect possible data entry errors or other anomalies. Extraction of data acquired between 1 January 2007 and 1 December 2018 thus yielded a full matrix of 8110 observations with 15 parameters, namely Enterococcus, Escherichia Coli, electrical conductivity (EC), Na, K, Ca, Mg, Cl, SO₄, HCO₃, NO₃, Fe, Mn, As, and H⁺;
3. In agreement with previous work [21], the data were then conditioned in logarithmic form, which makes their distribution closer to normality and decreases the weight of extreme values;
4. Each water sample was then assigned to a GWB based on its geographic coordinates and depth;
5. A principal component analysis (PCA) was then performed on the log-transformed data to reduce the dimensionality of the data space and to identify and rank the sources of variability in the database. The PCA was based on the correlation matrix and thus considered the reduced centered variables, which allowed to integrate parameters of very diverse natures and units. Furthermore, it was carried out by diagonalization of the correlation matrix in order to identify, quantify, and classify the different sources of variability within the data set. Under these conditions, the factorial axes were perpendicular to each other, and were therefore associated with independent processes responsible for the variability of water quality. The last factorial axes, explaining a small percentage of the variance, and generally considered as statistical noise [25], were eliminated;
6. For each of the selected factorial axes, the average value for the GWB on the factorial axis was calculated. At this stage, each GWB was thus characterized by an X-dimensional vector if X factorial axes were selected. In the Adour-Garonne basin, 10 GWB with few water analyses (less than 10) were not taken into account because they were not sufficiently detailed. They were excluded from the calculation. An ascending unsupervised hierarchical clustering (AHC) was carried out on all remaining GWB by assigning an identical weight to each factorial axis. The objective of this clustering was to partition all the GWB into groups or subgroups and to gather them according to a similarity criteria, all parameters considered. The choice of the number of groups was guided by the variation of the ratio between the inter-group and intra-group variability in order to maximize the intra-group homogeneity and the inter-group heterogeneity. The results are iteratively collated to produce a dendrogram;

7. The result of the classification was then mapped in a GIS;
8. Finally, the last step consisted of the detailed study of each homogeneous group of GWB, a step that was not presented in detail in this article because it is too voluminous.

This approach was conducted in two ways. The first consisted of processing all the data from the Occitanie region, as proposed by Tiouiouine et al. [26], but on a larger and more heterogeneous region. The second modality consisted of processing, separately, the data from each large watershed covering the region, namely the Rhône-Méditerranée (RM) and Adour-Garonne (AdG) basins, in accordance with the European management that structures the mapping of GWBs by large watersheds.

2.4. Clustering and Quantification of the Information Lost

For each parameter, the loss of information induced by aggregating from the sampling points into GWBs and then into GWB groups was estimated from the explained variance (R^2) using an ANOVA analysis of variance [27]. The database includes many sampling points generally sampled on several dates during the 11 years of collection. The total variance is therefore a combination of spatial and temporal variance, if we neglect a small proportion of the variance related to analytical precision. Switching from all analyses to mean values per sampling point leads to a loss of information corresponding to the temporal variability, whereas the spatial variance, for each parameter, corresponds to the variance explained by the “sampling point” criterion. The percentage of variance explained by the GWB and GWB group criteria corresponds to the spatial variance at these respective aggregation scales. For relevant mapping, maximum spatial information (largest possible R^2) should be preserved at a given level of aggregation. In other words, we aim to minimize the number of GWB clusters while maintaining the highest possible R^2 . All statistical calculations were performed with the XLStat software (Addinsoft).

2.5. Spatial and Temporal Study for 3 Groups of GWB

Three groups of GWB were selected, and a PCA was performed on each by separating spatial and temporal variability to better understand the mechanisms associated with water diversity within each group.

3. Results

3.1. Database and Observation Density

The number of collection points, samples collected, and GWBs involved over the entire study area and the two sub-basins (Rhône-Méditerranée and Adour-Garonne) is shown in Table 1. A difference in the density of collection points can be noted (Figure 1). This difference can be explained by a difference in environment, population density, and, consequently, in the monitoring of water quality by the health agencies. In karstic areas, such as the Causses du Quercy or the Grands Causses [21], in the northwest and northeast of the region, respectively, the number of boreholes is limited due to deep aquifers and difficult access. On the other hand, the western part of the Pyrenean sector should normally have a higher density of sampling points, which is not the case because part of the resource is of superficial origin, or concerns a limited population for which the quality monitoring often includes few parameters. For all these reasons, the analyses were excluded during the extraction from the database, which decreases the sampling density as it appears on Figure 1. Finally, in some sectors, proven pollution has resulted in the closure of one or more catchments and, therefore, the absence of data supply to the SISE-EAUX database. Some GWBs with few water analyses (less than 10) were not taken into account because they did not provide enough information. They were excluded from the calculation. At the regional level, these 8110 analyses correspond to 1972 sampling points spread over 106 GWB.

Table 1. Characteristics of the dataset for Occitanie and the two sub-basins, Adour Garonne (AdG) and Rhône Méditerranée (RM).

Title 1	Number of Samples	Number of Sampling Points	Number of GWB Involved
Occitanie region	8110	1972	106
AdG basin	4115	620	46
RM basin	3995	1352	60

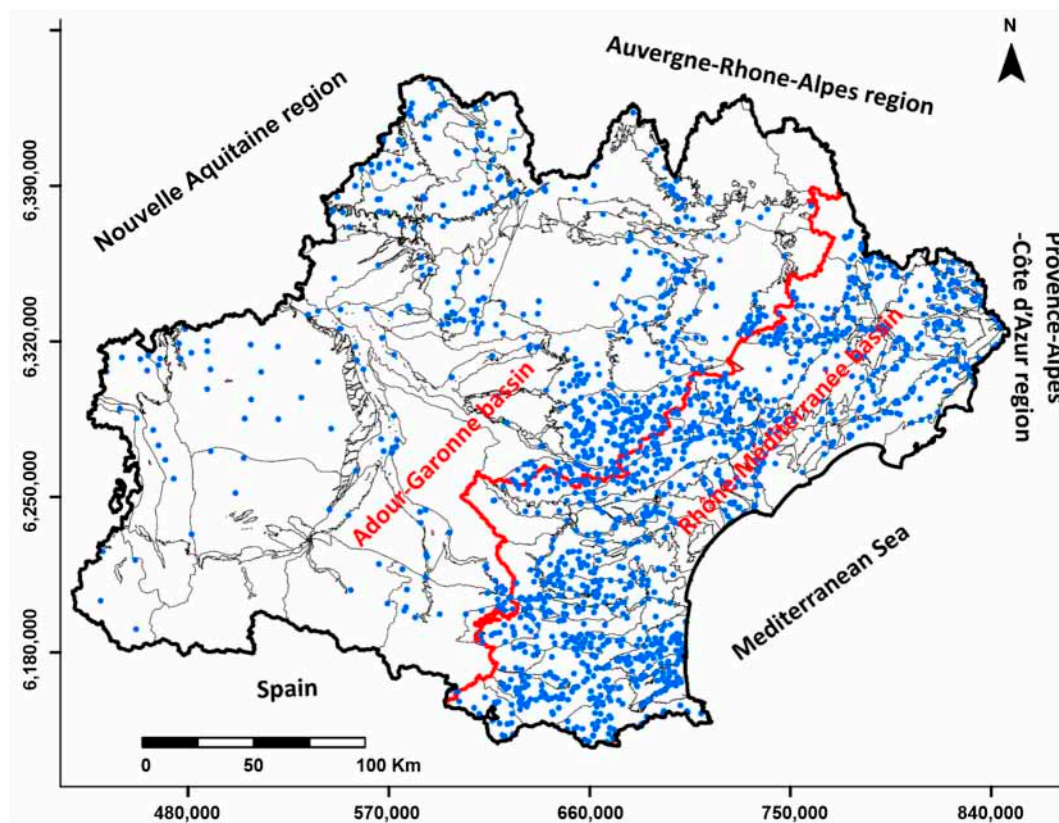


Figure 1. Distribution map of groundwater bodies (GWB) and groundwater sampling in Occitanie (blue spots) and in the two sub-basins, Rhône-Méditerranée (RM) and Adour-Garonne (AdG). The black lines are the limits of the GWB, the red line is the limit between AdG and RM basins, coordinates are UTM in m.

3.2. Principal Component Analysis

The first 10 factorial axes (Principal Components), representing 93% of the total variance of the log-transformed dataset, were retained for the hierarchical classification of GWBs. The contribution of the different parameters on these factorial axes is presented in Tables 2 and 3 for the two sub-regions, Adour-Garonne and Rhône-Méditerranée, respectively. The first axis, strongly correlated to major ions and electrical conductivity, was clearly an axis of water mineral load in both areas. However, it should be noted that the bacteriological parameters showed positive coordinates in the Adour Garonne basin, but negative in the RM basin. This reflected, for the RM basin, a bacterial contamination associated with diluted waters. The second axis was an axis of bacterial contamination in both areas. This contamination was clearly associated with the presence of Fe and Mn, positively scored, while the NO_3 parameter has negative coordinates. It was, therefore, a factorial axis marked by redox processes, with the waters contaminated by bacteria being the reducing waters. However, the chemical profile differed, with, on AdG, a contamination that concerned weakly mineralized waters, and, in particular, characterized by low contents of Ca and HCO_3 . In the AdG basin, the third axis opposed the Na and Cl parameters to the HCO_3 and Ca parameters. This was an opposition of chemical profile with, on the one hand,

rather diluted waters with a sodium chloride chemical profile and oxidizing as shown by the NO₃ coordinate, and on the other hand, more concentrated carbonate–calcium waters, probably deep because they are not very vulnerable to nitrate contamination. In the RM basin, the third factorial axis reflected the bacterial contamination of oxidizing waters positively scored with NO₃ and negatively with metals. Axis 4 reflected moderate bacterial contamination on oxidizing waters, but independently of the chemical profile on AdG, whereas it reflected the opposition of the chemical profile on RM. The fifth axis indicated higher values of As associated with NO₃ on AdG, and reduced acidic waters, positively scored with metals and also with bacteriological parameters. On RM, the fifth axis reflected acidic waters with the presence of metals and fairly vulnerable to bacterial contamination, conditions that can be observed on the crystalline massifs of altitude. In conclusion, on the two basins, the first factorial axis was quite similar, but notable differences appeared on the second factorial axis and on the following ones.

Table 2. Contribution of variables to the main factorial axes (PCs) in the AdG basin.

Adour-Garonne	PC1	PC2	PC3	PC4	PC5	PC6
Enterococcus	0.3597	0.6786	−0.1726	0.3704	−0.0764	−0.2819
E. coli	0.3968	0.7394	−0.1526	0.2952	−0.1184	−0.2071
EC	0.8325	−0.4114	−0.1636	0.1124	0.0986	−0.0236
K	0.7269	0.0936	0.3645	−0.0211	−0.1114	0.1886
Na	0.5668	−0.0038	0.4626	−0.3770	−0.0304	−0.3254
Ca	0.7950	−0.3896	−0.2814	0.1169	0.1000	0.0060
Mg	0.7142	−0.3540	−0.1002	0.0523	0.1392	0.1936
Cl	0.6951	−0.0715	0.4663	−0.0858	−0.2910	−0.0647
SO ₄	0.8170	−0.0911	0.0530	−0.1040	−0.3168	0.0195
HCO ₃	0.7659	−0.3031	−0.3327	0.0439	0.0071	0.0857
NO ₃	0.3160	−0.1793	0.5437	0.5722	0.4036	−0.1119
Fe	0.2399	0.8071	0.0491	−0.0436	0.0448	0.2022
Mn	0.3567	0.6217	0.1680	0.0027	0.1163	0.5006
As	0.4117	0.3801	−0.0573	−0.5069	0.5455	−0.1824
H ⁺	−0.6530	−0.2187	0.4681	0.1481	0.0567	0.0700

Table 3. Contribution of variables to the main factorial axes (PCs) in the RM basin.

Rhône-Méditerranée	PC1	PC2	PC3	PC4	PC5	PC6
Enterococcus	−0.2881	0.6905	−0.4392	0.2580	0.2405	0.0776
E. coli	−0.3149	0.6670	−0.4600	0.2577	0.2389	0.0373
EC	0.9405	0.0618	−0.1633	−0.1629	0.0511	0.0662
K	0.3522	0.1933	0.4710	0.5462	−0.1248	−0.2555
Na	0.7342	−0.0293	0.2402	0.3308	0.1182	−0.0739
Ca	0.8768	0.0636	−0.2462	−0.2349	0.0686	0.1124
Mg	0.7502	0.2078	−0.0677	−0.2018	−0.2252	0.0778
Cl	0.8062	−0.0050	0.0734	0.2561	0.1686	−0.0882
SO ₄	0.7773	0.1077	0.0705	0.1384	0.0019	−0.0103
HCO ₃	0.7747	0.1542	−0.2525	−0.3032	−0.0862	0.1147
NO ₃	0.3935	−0.3637	−0.2675	0.5010	0.1810	0.0889
Fe	0.0004	0.4098	0.5498	−0.2210	0.3460	−0.0087
Mn	0.0692	0.4586	0.5104	−0.3111	0.3051	−0.0471
As	−0.0799	0.3431	0.3744	0.2629	−0.4959	0.6248
H ⁺	−0.0668	−0.4813	0.1819	0.0429	0.6034	0.4832

3.3. Clustering

The tree structure resulting from the unsupervised clustering (dendrogram) for the AdG and RM basins is presented in Figures 2 and 3, respectively. In total, 10 clusters were retained on each sub-basin. All parameters considered, the clustering structure showed, for both AdG and RM, large differences between GWB groups but also strong similarities

of characteristics within GWB groups, with the dissimilarity between GWBs of the same group being often very small compared to the difference between groups. In order to be able to compare the loss of information related to clustering, 20 GWB groups were retained over the whole Occitanie region (cluster tree not shown).

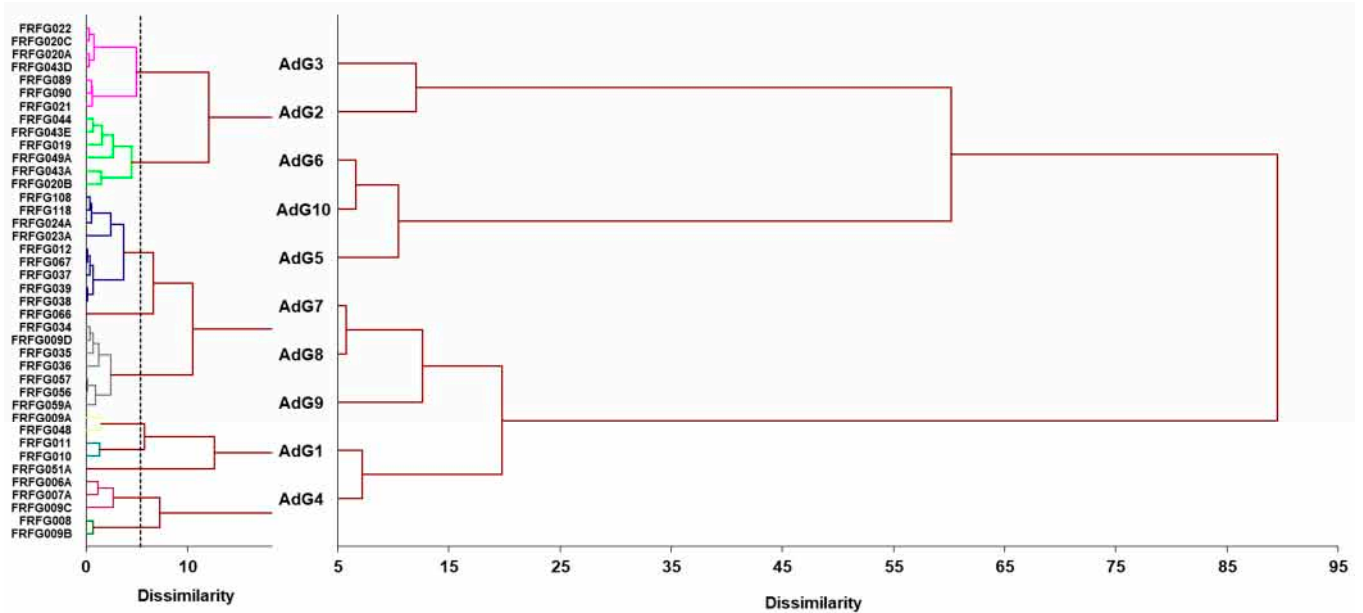


Figure 2. Clustering and grouping of GWB in 10 classes on the Adour-Garonne basin (AdG1 to AdG10).

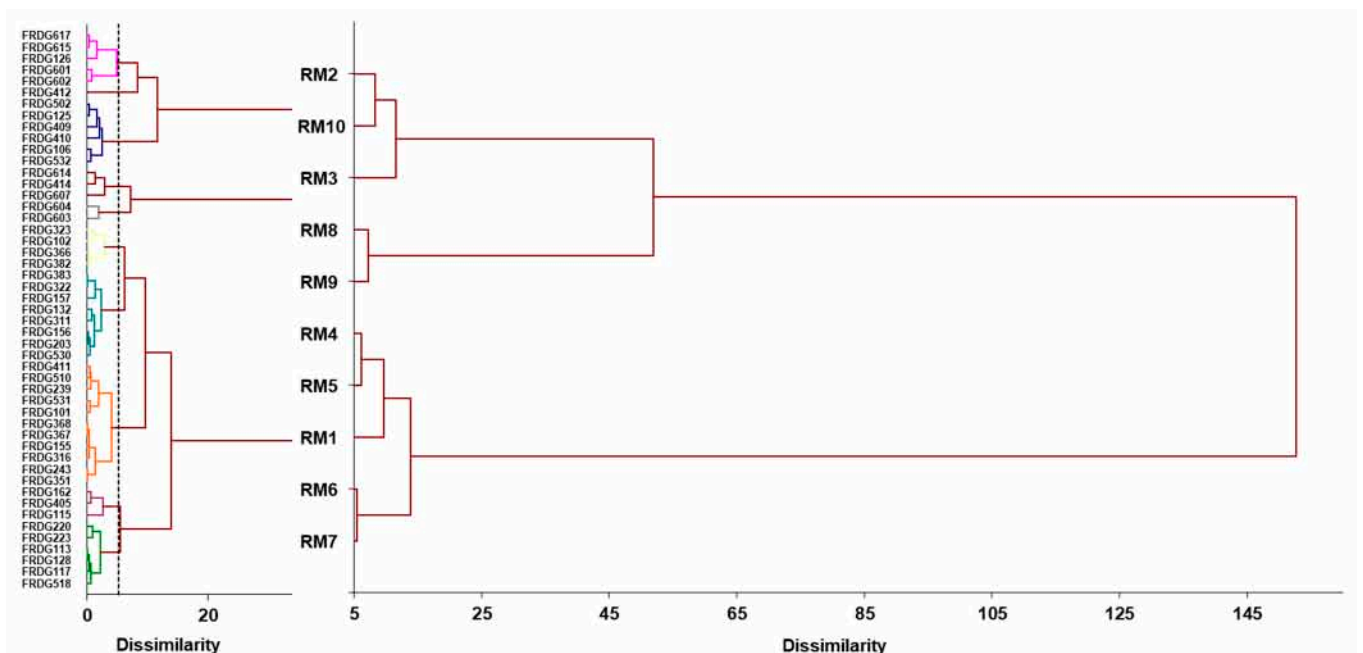


Figure 3. Clustering and grouping of GWB in 10 classes on the Rhône Méditerranée basin (RM1 to RM10).

3.4. Characteristics and Distribution of GWB Groups

The distribution map of GWB groups for the AdG and RM basins is shown in Figure 4a,b. The coherence of the classification appears in the grouping of neighboring GWBs, or belonging to the same geological complex.

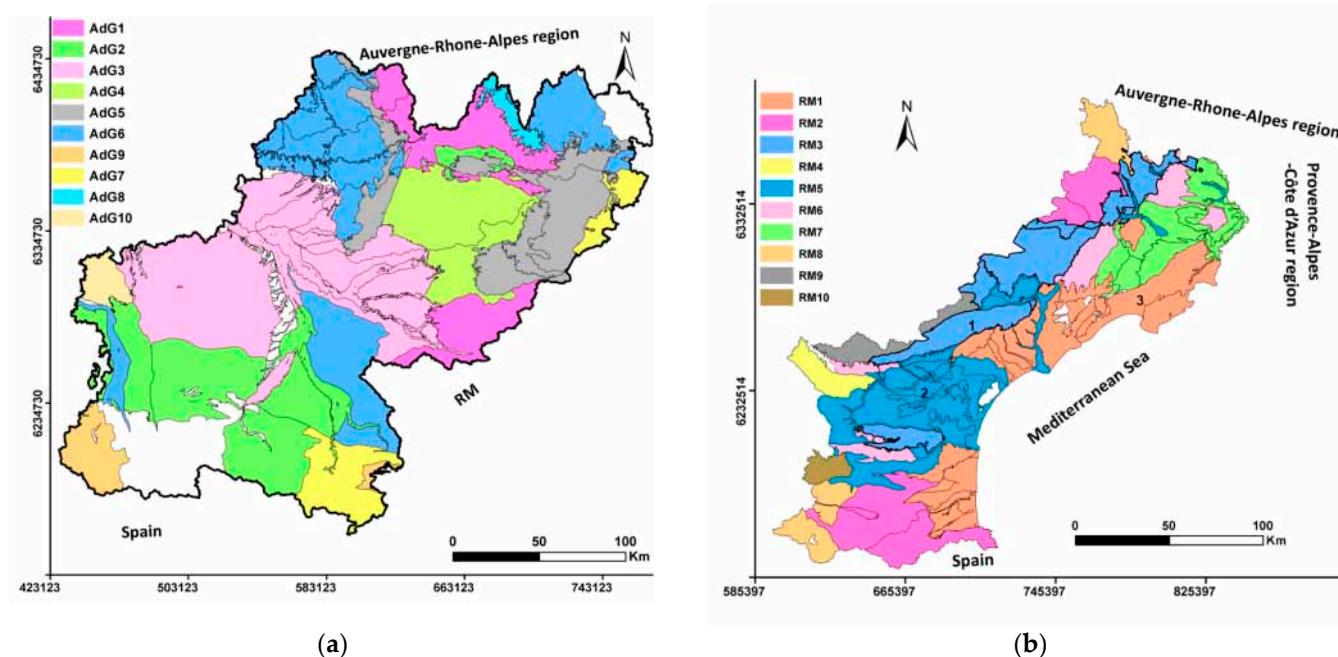


Figure 4. Distribution map of GWB groups on (a) Adour-Garonne and (b) Rhône-Mediterranée basins. GWBs that were excluded from the study appear in white. Notations 1, 2, and 3 are karst areas, porous calcareous plains, and calcareous coastal plains, respectively.

The calculation leading to the determination of the clusters presents differences depending on whether one considers 20 clusters on the whole Occitanie region (Figure 5) or 10 clusters on each major catchment area (Figure 4a,b). For example, the clustering into 20 groups (Figure 5) associated karst-type limestone aquifers, high porosity limestone aquifers, and low plains or coastal plains (1, 2, and 3 on Figure 5, respectively). In contrast, the classification into 10 groups on the RM basin showed a distinction between these aquifers (RM3, RM5, and RM1), which is more consistent from a geological point of view and preferable for water quality protection management. As another example, the differentiation between the middle and the upper Garonne valley was mainly organized in two large clusters in Figure 4a (AdG3 and AdG2), whereas it appeared more fragmented and therefore more confused in Figure 5.

The mean values of the different parameters by GWB groups are reported in Tables 4 and 5 for AdG and RM, respectively. Data are in logarithm decimal, EC in $\mu\text{S cm}^{-1}$, major ions and nitrates in mol L^{-1} , Fe and Mn in mg L^{-1} , and bacteriological parameters in units per 100 mL.

3.5. ANOVA and Explained Variance

The results of the ANOVA and the explained variance (R^2) by parameter and by level of clustering are summarized in Figure 6.

In general, the grouping of the collection point level to the GWB level was accompanied by a significant decrease in the R^2 , while the grouping of the GWB in 20 homogeneous groups caused a limited loss of information. Splitting the region into two entities with 10 GWB groups each, compared to 20 GWB groups across the Occitanie region, did not result in a significant decrease in explained variance, except for a slight decrease for metals.

3.6. Processes Responsible for the Quality of Some GWB Groups

Classification of GWBs into 10 groups each in the RM and AdG basins leads to groups with distinct chemical characteristics. However, a difference in chemical quality does not necessarily reflect a difference in the processes responsible for this quality. By studying the first factorial axes of a few groups, we should be able to verify whether these groups also differ in terms of the processes responsible for the acquisition of chemical

characteristics. As an illustration, we have chosen the AdG1, AdG2, and AdG3 groups, the most strongly affected by fecal contamination, with average values of *E. coli* and *Enterococcus* approximately 3 to 10 times higher than in the other groups. These three groups also have the highest levels of metals (Fe and Mn). AdG1 groups the GWB in the crystalline basement of the southwestern edge of the Massif Central and the Montagne Noire [21]. AdG3 consists of the alluvial valleys of the middle Garonne valley and its tributaries. AdG2 is located just upstream of AdG3 on the Pyrenean foothills, consisting of the sub-catchments of the Ariège, the Garonne, and the upstream of Lannemezan. These last two groups are geographically and geologically close, developed in tertiary molasses with low permeability, and, therefore, with limited exploitable water resources. Secondary limestones also outcrop in the AdG2 sector, and the alluvial valleys are covered by decarbonated and poorly mineralized alluvium. They are also distinguished by higher arsenic levels, especially in AdG3. Agricultural activities on these three GWB groups are marked by the presence of cattle breeding, which is intensive on AdG3, intermediate on AdG2, and more traditional on AdG1. The large agglomerations (Toulouse, Montauban) are located on the AdG3 territory, while the AdG1 and AdG2 territories present small mountain towns.

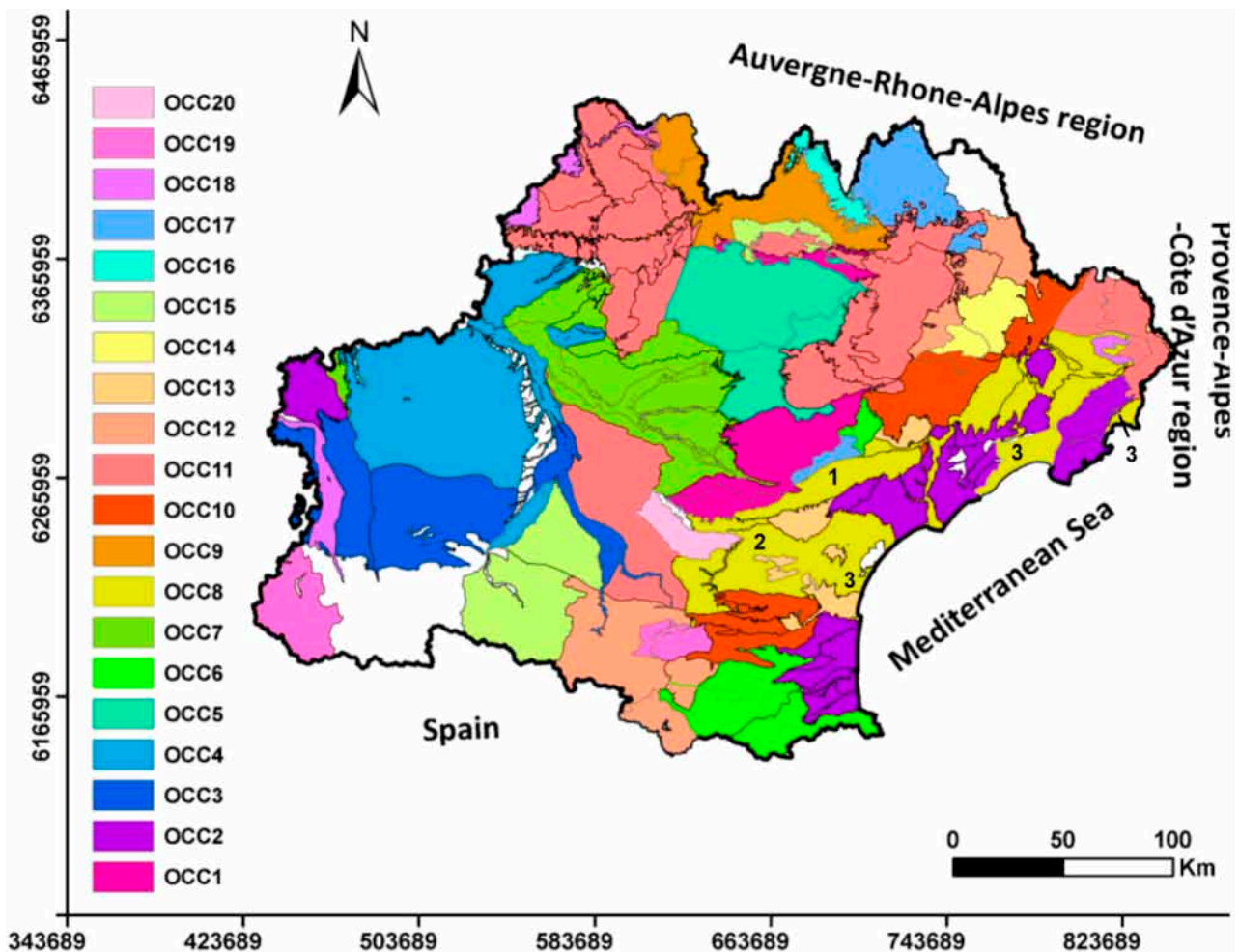


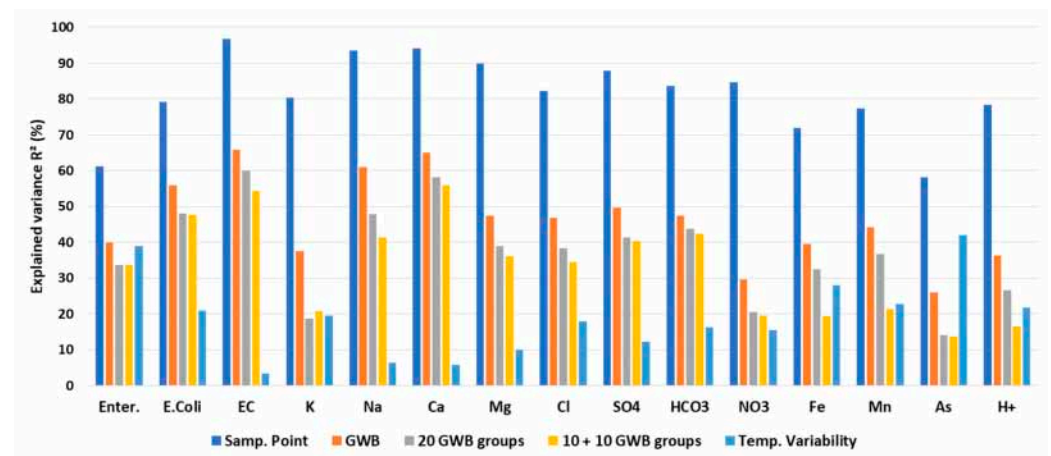
Figure 5. Distribution map of 20 GWB groups on the Occitanie region. Notations 1, 2, and 3 are karst areas, porous calcareous plains, and calcareous coastal plains, respectively.

Table 4. Mean values of the different parameters by GWB group in the Adour-Garonne basin.

AdG	Enter.	E. coli	E.C.	K	Na	Ca	Mg	Cl	SO ₄	HCO ₃	NO ₃	Fe	Mn	As	H ⁺
1	0.95	1.81	1.93	-4.48	-3.72	-4.09	-4.04	-3.77	-4.67	-3.85	-4.03	-6.03	-6.65	-3.47	-7.24
2	1.59	2.24	2.39	-4.53	-3.71	-3.01	-3.85	-3.62	-3.78	-2.72	-4.18	-6.23	-6.41	-3.11	-7.94
3	1.44	2.13	2.49	-4.34	-3.50	-2.96	-3.62	-3.37	-3.72	-2.64	-3.98	-6.19	-6.29	-1.59	-7.97
4	0.73	1.08	2.20	-4.19	-3.59	-3.41	-3.74	-3.43	-4.12	-3.12	-3.79	-6.25	-6.05	-3.73	-7.24
5	0.68	0.98	2.63	-4.56	-3.78	-2.84	-3.20	-3.60	-3.95	-2.44	-3.91	-6.67	-6.84	-4.30	-7.44
6	0.53	0.83	2.72	-4.47	-3.71	-2.61	-3.73	-3.49	-4.09	-2.30	-3.83	-6.84	-6.90	-5.69	-7.19
7	0.52	0.77	1.99	-4.92	-3.76	-3.67	-4.19	-3.95	-4.53	-3.71	-4.13	-6.62	-6.66	-5.57	-7.11
8	0.75	1.20	1.79	-4.82	-3.90	-3.85	-3.96	-4.10	-5.35	-3.27	-4.67	-6.24	-6.73	-4.81	-7.45
9	0.39	0.65	2.43	-5.16	-4.43	-3.00	-3.55	-4.22	-4.37	-2.59	-4.55	-6.84	-6.94	-7.00	-8.14
10	0.00	0.26	2.82	-4.43	-3.30	-2.53	-3.66	-3.02	-3.79	-2.29	-3.37	-6.92	-7.00	-0.66	-7.34

Table 5. Mean values of the different parameters by GWB group in the Rhône-Méditerranée basin.

RM	Enter.	E. coli	E.C.	K	Na	Ca	Mg	Cl	SO ₄	HCO ₃	NO ₃	Fe	Mn	As	H ⁺
1	0.09	0.12	2.68	-4.61	-3.11	-2.80	-3.32	-3.04	-3.38	-2.48	-4.06	-6.85	-6.94	-4.18	-7.33
2	0.32	0.37	2.19	-4.77	-3.65	-3.38	-3.84	-4.15	-4.05	-3.03	-4.78	-6.84	-6.89	-3.77	-7.36
3	0.34	0.45	2.52	-5.34	-3.61	-2.95	-3.24	-3.97	-3.96	-2.55	-4.76	-6.91	-6.95	-4.95	-7.44
4	0.28	0.23	2.70	-4.47	-3.23	-2.65	-3.50	-3.04	-3.24	-2.42	-4.20	-6.69	-6.66	-3.35	-7.43
5	0.09	0.09	2.71	-4.74	-3.38	-2.69	-3.20	-3.30	-3.35	-2.36	-4.46	-6.87	-6.93	-3.60	-7.40
6	0.45	0.59	2.70	-5.38	-3.60	-2.61	-3.54	-3.69	-3.82	-2.31	-4.48	-6.89	-6.82	-5.63	-7.25
7	0.21	0.30	2.73	-5.04	-3.39	-2.59	-3.67	-3.22	-3.67	-2.31	-4.10	-6.87	-6.94	-6.06	-7.21
8	0.24	0.38	1.78	-5.11	-3.93	-3.83	-4.31	-5.17	-4.55	-3.70	-4.77	-6.83	-6.98	-3.50	-7.30
9	0.27	0.28	1.90	-5.38	-3.66	-3.83	-4.69	-4.11	-5.09	-4.24	-4.57	-6.81	-6.93	-3.94	-6.72
10	0.18	0.22	2.51	-5.54	-4.11	-2.83	-3.85	-5.03	-4.17	-2.65	-4.57	-7.00	-6.96	-6.64	-7.40

**Figure 6.** Rate of variance explained as a function of the number of spatial units for some parameters. Comparison between 20 GWB groups for the whole Occitanie and 10 GWB groups each for the Adour-Garonne and Rhône-Méditerranée basins.

The inertia of the factorial axes for the three groups are shown in Figure 7. The variance explained by the two first factorial axes was lower on AdG1 (49%), reflecting greater process complexity. It was slightly higher for AdG3 (52%) and reached 63% for AdG2.

The first two factorial plans PC1-PC2 and PC1-PC3 are shown in Figure 8. For the three groups, the first factorial axis showed strong similarities: opposing mineralized waters, positively scored by nitrates and therefore having an oxidizing character, to diluted waters vulnerable to fecal contamination, with higher Fe and Mn contents, and therefore reducing. The contribution of the bacteriological parameters E. coli and Enterococci to the first factorial axis was slightly higher for AdG3 than for AdG2 and AdG1. For all three groups, the second PC was clearly marked by fecal contamination and solubilization of metals Fe and Mn, but the coordinates of these parameters are higher for AdG2 than for AdG1 and AdG3. Potassium was associated with ferromanganese waters and contamination by E. coli and Enterococci. For AdG1 fecal contamination, metals and nitrates were associated with sodium chloride waters, while, for AdG2 and AdG3, they were only weakly correlated with major ions, i.e., with any chemical profile. The third factorial axis was very different.

For AdG3, it reflected a contrast in chemical profile between calcium carbonate and nitrate waters, and sodium sulfate–chloride waters with the highest arsenic levels (see Table 4). Fecal contamination had no influence on this axis. For AdG2, the third factorial axis was also strongly influenced by arsenic levels, which were, on average, 20 times lower than those for AdG3 (Table 4). This axis contrasted sodium chloride waters, also nitrated, with magnesium sulfate waters, and were marked by fecal contamination. Finally, on AdG1, axis 3 reflected a contrast in chemical profile between calcic carbonate waters, reducing and marked by fecal contamination, and the more acidic, sodium chloride oxidizing waters.

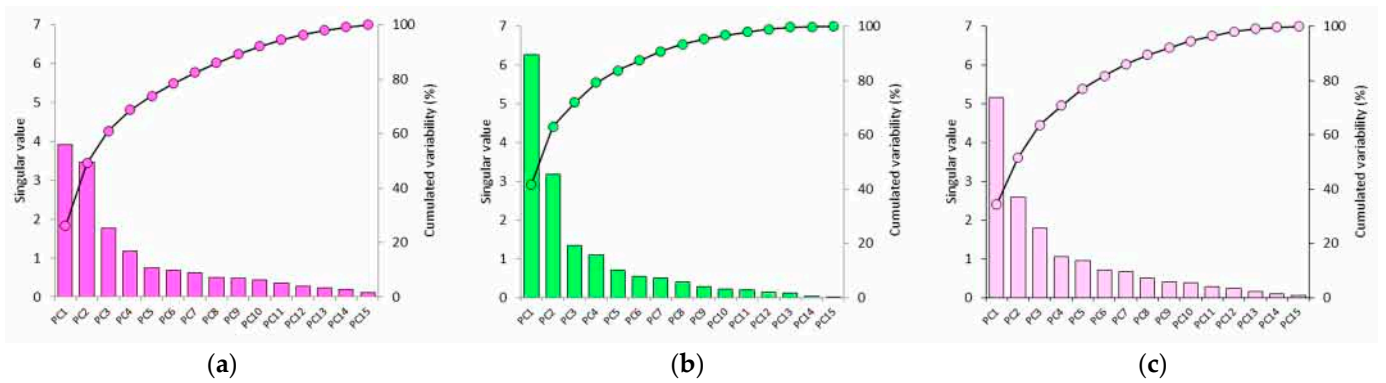


Figure 7. Inertia of the factorial axes for (a) AdG1, (b) AdG2, and (c) AdG3.

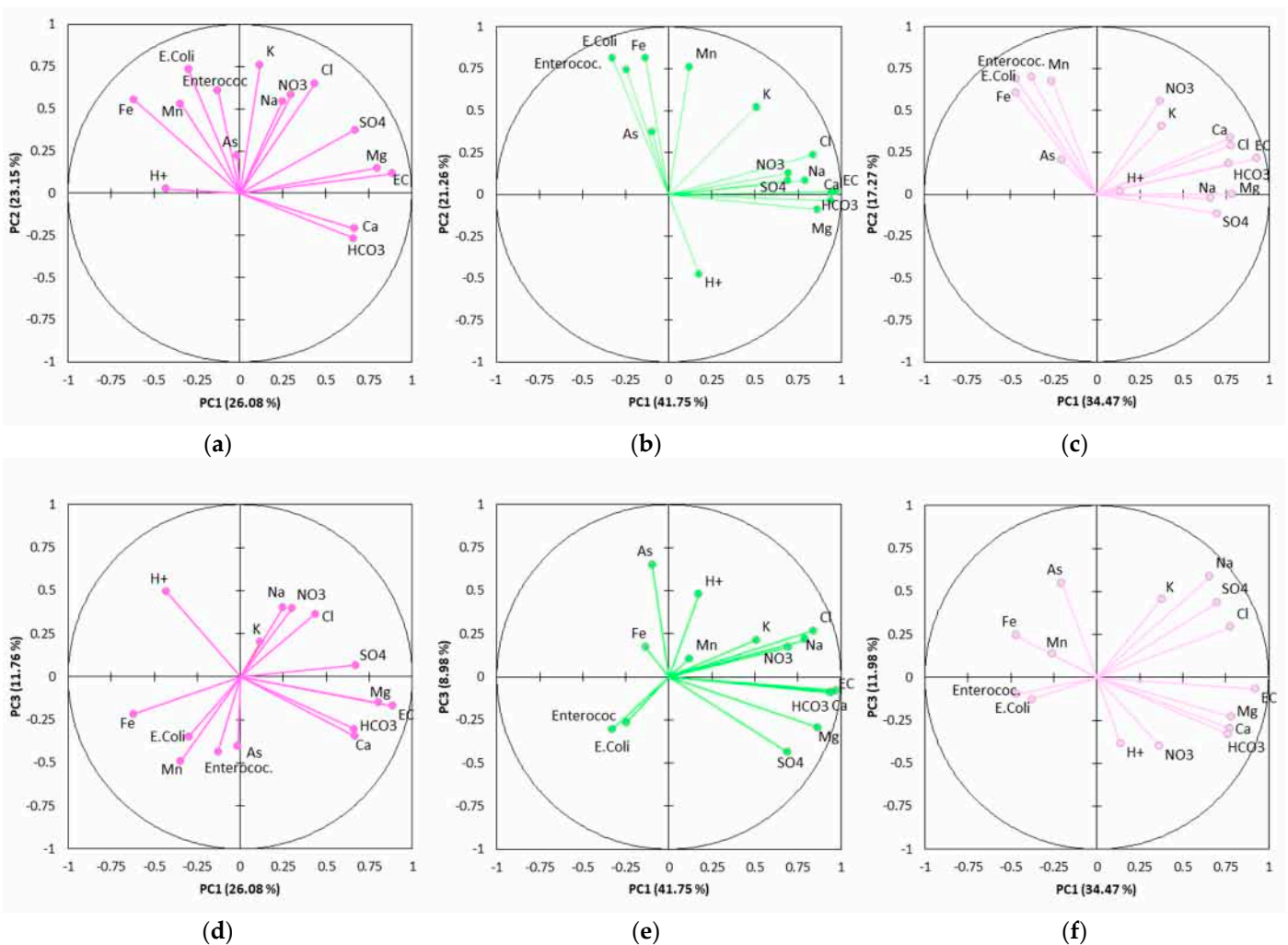


Figure 8. PC1-PC2 and PC1-PC3 factorial plans for AdG1 (a,d), AdG2 (b,e), and AdG3 (c,f).

For these three groups, the results of the PCA carried out by distinguishing spatial variability, i.e., between sampling points, and temporal variability, i.e., variations around the mean between the different samples collected at the same sampling point, are presented in Figure 9.

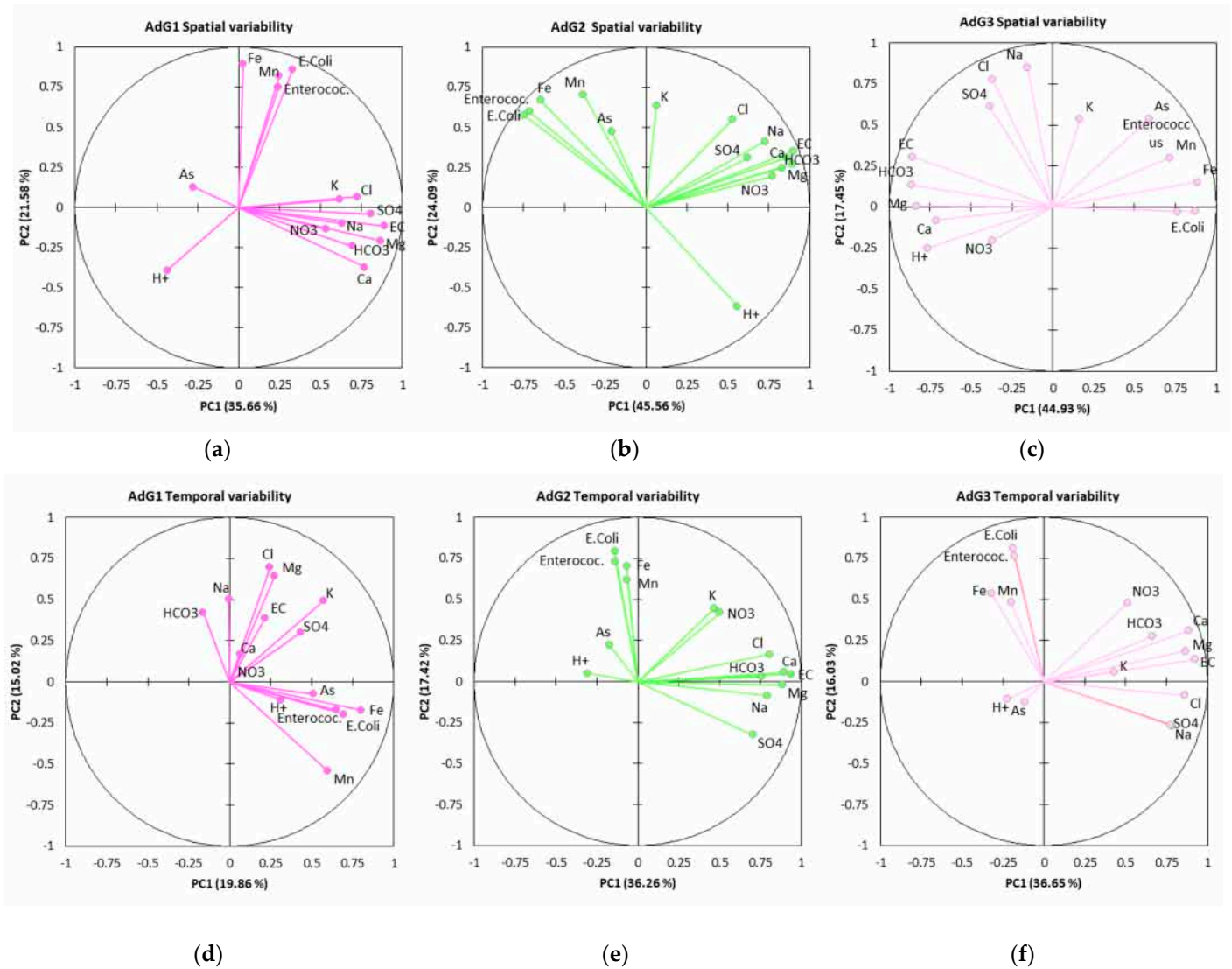


Figure 9. First factorial plans for groups AdG1, AdG2, and AdG3, considering spatial (a–c), and temporal variability (d–f).

In terms of spatial variability, for AdG1, PC1 contrasted diluted waters with mineralized waters regardless of fecal contamination, whereas, for AdG2 and AdG3, the first factorial axis reflected a contrast between mineralized waters and diluted waters contaminated with *E. coli* and *Enterococcus*. An altitudinal gradient can be observed regarding axis 2. For AdG1, higher in altitude, PC2 exclusively carries the bacterial contamination associated with Fe and Mn metals. This contribution was less important for AdG2 and practically null for AdG3. In terms of temporal variability, fecal contamination associated with Mn and Fe shifted to axis 1 for the high altitude GWBs of AdG1 and increased on axis 2 for the Pyrenean foothills, AdG2, and the alluvial plains, AdG3. Note the contrast with nitrates associated with fecal contamination and metals for AdG2 and AdG3 but not for AdG1.

4. Discussion

In the context of groundwater resource quality, the question of creating a map goes beyond the framework of a purely geostatistical approach, because belonging to functional

units such as GWBs constitutes essential information, i.e., a knowledge constraint that must obviously be taken into consideration. The classical methods of mapping, by kriging or other methods independent of the knowledge of groundwater bodies, are relevant for smaller areas of about 1000 to 3000 km², in which the heterogeneity of the structural geology is less [7,11,17,28,29]. It is, therefore, necessary to find a method adapted to large areas (here, more than 70,000 km²) that combines the study of spatial variability of water quality with the hydrogeological structure mapped by entities that are the GWB. The crossing of the French reference system for groundwater bodies and SISE-EAUX database meets this expectation.

4.1. Physico-Chemical and Bacteriological Variability of Groundwater in Occitanie

Differences in the processes responsible for water quality variability between the two basins can be expected due to differences in climatic regime, agricultural activity, or seasonal tourist pressure near the Mediterranean coast. Whatever the area considered, i.e., Occitanie, Adour-Garonne, or Rhône-Méditerranée, the first factor of variability is the water minerality. This observation is classic in hydrochemical studies and has been reported by many authors at different scales [21,26,30–32]. The range of water mineral load is high, as shown on the first factorial axis and in Tables 2 and 3. However, this result is less pronounced in the wetter AdG basin than in the RM basin characterized by higher evaporation. The effects of the climate difference between the RM and AdG basins can also be observed in the bacteriological parameters, which are more strongly associated with diluted water in the RM basin (Table 3), probably reflecting particle-attached bacteria contamination by runoff with low chemical load but high turbidity during late summer storms, a process classically observed in the Mediterranean climate. In our results, the differences between the two basins are important, especially the relationship between bacteriology and other parameters. Tables 4 and 5 show that the level of fecal contamination is, however, much lower for the RM basin than for the AdG basin. Only the RM6 group has a high average, without reaching the maximums observed in AdG. Human activity, and, more particularly, agricultural activities, are also very different, with livestock farming being practically non-existent in the RM basin, where most districts are mainly oriented towards viticulture, whereas field crops (cereals and sunflower), permanent fruit crops, and livestock farming (cattle, sheep, and goats) make up the bulk of the agricultural landscapes in the AdG basin [33]. It is likely that the importance of livestock farming and the fragility of the aquifers are responsible for these high values of fecal contamination of groundwater in AdG.

Although bacterial contamination is essentially driven by the second PC, the mechanisms that lead to this contamination are diverse, as they are also driven by factorial axes 1 and 4 on AdG (Table 2) and axis 3 on RM (Table 3). The factorial axes are orthogonal, and they reflect distinct and independent contamination processes. Thus, bacteriological contamination cannot be summed up in the context of “rain > runoff > solid load > transport of bacteria”, but seems to result from more diverse and complex paths [26].

In both basins, high arsenic levels are associated with viticulture practices, with, on the one hand, some high levels in the vineyards of Roussillon near the Mediterranean coast, but, on the other hand, significant pollution in the Armagnac terroir in the west of the AdG basin (group AdG10). These pollutants must be attributed to vine treatments with arsenic-containing pesticide mixtures, a practice used from the beginning of the 20th century [34,35] against grapevine wood diseases such as Esca or Black Dead Arm [36], and banned since 2003 due to the proven carcinogenic properties of arsenic derivatives.

Thus, although the monitoring of water quality for human consumption is managed at the scale of the Occitanie region, applying the recommendations of the European commission, i.e., working by large watersheds, is fully justified in view of the differences, mainly climatic and human activity, between the two basins, AdG and RM. In our study, splitting the Occitanie region into the two large basins does not lead to a significant degradation of the information contained in the database (Figure 4). The variances explained by grouping

the GWBs into 10 groups on each basin or by 20 groups of GWBs on the whole Occitanie region are very close. Moreover, as detailed above, the grouping seems more coherent by separating the two basins. Working by large basins therefore seems preferable, which justifies, a posteriori, the choice made by the European Commission.

4.2. The GWB Grouping, a Relevant Management Scale

The area covered by a homogeneous zone of the same value in the map replaces a diversity of values measured on each sampling point, values that may be close but different. By replacing all the measurements made on a sample point at different dates by their average value on that sample point, there is a loss of variability that corresponds to the temporal variance. It should be kept in mind, however, that the temporal variance depends, in part, on the average number of analyses per sampling point. The differences observed between the two basins, AdG and RM, are therefore also partly explained by the difference in the ratios between the number of samples collected and the number of sampling points. The values of the temporal variance differ, of course, according to the parameters considered, some, such as metals, arsenic, or bacteriological parameters, having a high temporal variability (Figure 6). Similarly, by replacing the values acquired at the different sampling points by the average over the corresponding GWB, an additional part of the variance is lost, corresponding to the internal variability of the GWB. This loss of information is high for nitrate and potassium, which present a very local spatial variability, reflected by a strong decrease in R^2 . The other major ions and electrical conductivity show spatial variability on a much larger scale, depending mainly on the geological structure, and, for these parameters, the decrease in R^2 from the GWB to the GWB group scale is limited. The loss of information when clustering GWBs is small despite the large reduction in units from 106 to 20.

4.3. More homogeneous GWB Groups

The GWB groups resulting from the ascendant hierarchical clustering are homogeneous, grouping together GWBs whose processes responsible for water diversity and quality are similar, which facilitates their interpretation and, in the long run, the monitoring and management of the water resource. This can be illustrated by the analysis of the AdG2 and AdG3 groups. According to the descriptions associated with the groundwater bodies in the French reference system, there is a contrast between the recent alluvial deposits of the lower plain, whose water table interacts with the river, and the older, slightly higher terraces, whose water is poorly mineralized, acidic, and more reducing. Thus, the soils of the alluvial valleys on ancient sediments are marked by a strong hydromorphy with mobilization of iron and manganese, locally called “grepp”, in the deep horizon of the “boulbènes” soils (Gleyic Luvisols [37] or Luvi-redoxisols [38]). This process is absent in recent alluvium and appears as the second factor of variability for the AdG2 and AdG3 groups (Figures 8 and 9). Thus, the analytical data from the SISE-EAUX database are in agreement with the description made independently by geologists and soil scientists in the French reference system for groundwater bodies. Crossing these two sources of information makes sense. Moreover, for these two groups of GWB, the PCA conducted on the whole data set, thus including a portion of temporal variability, even if small, and spatial variability, indicates that fecal contamination is mainly related to diluted water. Two interpretations are possible. The first is temporal, linking contamination to rainfall events, with runoff water carrying bacterial pollution from manure spreading to collection points. This so-called “recent” water is opposed to “old” water (present before rainfall events), which is generally more mineralized. The second interpretation is spatial, with the waters of the reducing and poorly mineralized aquifers within the ancient terraces in the first place. These waters do not flocculate colloids well, which facilitates the transport of suspended matter and the associated bacterial load. These waters contrast with those collected in the accompanying water table of the rivers, which are generally more mineralized, more impacted by various crops on the low terraces than by livestock, and coming more

from upstream than from local precipitation. Here, the distinction of spatial and temporal components of variability (Figure 9) highlights the coexistence of these two interpretations, and, in general, it allows to better highlight the behavior of quality parameters within and between GWB groups.

4.4. Future Directions

Thus, the mapping of GWB groups proposed by Touiouine et al. [20,26] is a very relevant mapping strategy, provided that one works on log-transformed data [21], even for large areas such as the Occitanie region. This methodology leads to the mapping of coherent units. The number of 20 large units per large administrative region is much more manageable than the more than 100 units based on GWBs. The detailed study of each group, which is not elaborated here, should lead to targeted recommendations and a specific roadmap, specific to each group of GWBs, for monitoring and protecting the water resource. Although this work constitutes a step forward for a relevant multi-parameter zonation of GWBs at the scale of an administrative region of about 70,000 km², there is no guarantee that this result can be generalized to other administrative regions, nor that it will work if extended to other parameters not taken into account in our study (pesticides, land use types, etc.). In addition, the approaches adopted by the European Union favor even larger scales than that of the administrative region: those of the large European watersheds. At this scale, the space is divided into large geological units that will require either adapting or upgrading the approach. A research work in this sense, of a general nature, has already begun and should be the subject of future publications.

Author Contributions: Conceptualization, V.V. and A.B.; methodology, A.T. and V.V.; software, M.J., Y.E.J. and I.M.; validation, A.T., V.V., Y.D., M.M. and S.C.; formal analysis, M.J., A.T. and A.B.; investigation, M.J.; resources, V.V., Y.D. and M.M.; data curation, A.T., V.V., Y.E.J., I.M. and L.B.; writing—original draft preparation, M.J.; writing—review and editing, V.V., L.B. and I.M.; supervision, A.B., V.V. and L.B.; project administration, A.B. and S.C.; funding acquisition, not applicable. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data here analyzed were extracted from the public SISE-EAUX database (<https://data.eaufrance.fr/concept/sise-eaux>, accessed on 20 January 2019) and the French reference system for groundwater bodies (<https://services.sandre.eaufrance.fr/geo/sandre>, accessed on 7 February 2022).

Acknowledgments: The authors are very grateful to the Occitanie Regional Health Agency for helping in data extraction from the SISE-EAUX Database.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. European Commission. *Guidance on Groundwater Status and Trend Assessment, Guidance Document #18*; European Communities: Luxembourg, 2009; ISBN 978-92-79-11374-1.
2. European Commission. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Off. J. Eur. Union* **2006**, *372*, 19–31.
3. Martínez Navarrete, C.; Grima Olmedo, J.; Durán Valsero, J.J.; Gómez Gómez, J.D.; Luque Espinar, J.A.; de la Orden Gómez, J.A. Groundwater protection in Mediterranean countries after the European water framework directive. *Environ. Geol.* **2008**, *54*, 537–549. [[CrossRef](#)]
4. European Commission. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Off. J. Eur. Communities* **2000**, *22*, 2000.
5. European Commission. Directive 2014/80/EU of 20 June 2014 amending Annex II to Directive 2006/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration. *Off. J. Eur. Union* **2014**, *580*, 182/52.
6. De Stefano, L.; Fornés, J.M.; López-Geta, J.A.; Villarroya, F. Groundwater use in Spain: An overview in light of the EU Water Framework Directive. *Int. J. Water Resour. Dev.* **2015**, *31*, 640–656. [[CrossRef](#)]

7. Pantaleone, D.V.; Vincenzo, A.; Fulvio, C.; Silvia, F.; Cesaria, M.; Giuseppina, M.; Ilaria, M.; Vincenzo, P.; Rosa, S.A.; Gianpietro, S.; et al. Hydrogeology of continental southern Italy. *J. Maps* **2018**, *14*, 230–241. [[CrossRef](#)]
8. Danielopol, D.L.; Griebler, C.; Gunatilaka, A.; Notenboom, J. Present state and future prospects for groundwater ecosystems. *Environ. Conserv.* **2003**, *30*, 104–130. [[CrossRef](#)]
9. Edmunds, W.M.; Shand, P.; Hart, P.; Ward, R.S. The natural (baseline) quality of groundwater: A UK pilot study. *Sci. Total Environ.* **2003**, *310*, 25–35. [[CrossRef](#)]
10. Hinsby, K.; Condeso de Melo, M.T.; Dahl, M. European case studies supporting the derivation of natural background levels and groundwater threshold values for the protection of dependent ecosystems and human health. *Sci. Total Environ.* **2008**, *401*, 1–20. [[CrossRef](#)]
11. Masciale, R.; Amalfitano, S.; Frollini, E.; Ghergo, S.; Melita, M.; Parrone, D.; Preziosi, E.; Vurro, M.; Zoppini, A.; Passarella, G. Assessing Natural Background Levels in the Groundwater Bodies of the Apulia Region (Southern Italy). *Water* **2021**, *13*, 958. [[CrossRef](#)]
12. Nakić, Z.; Kovač, Z.; Parlov, J.; Perković, D. Ambient Background Values of Selected Chemical Substances in Four Groundwater Bodies in the Pannonian Region of Croatia. *Water* **2020**, *12*, 2671. [[CrossRef](#)]
13. Quevauviller, P.; Balabanis, P.; Fragakis, C.; Weydert, M.; Oliver, M.; Kaschl, A.; Arnold, G.; Kroll, A.; Galbiati, L.; Zaldivar, J.M.; et al. Science-policy integration needs in support of the implementation of the EU Water Framework Directive. *Environ. Sci. Policy* **2005**, *8*, 203–211. [[CrossRef](#)]
14. Smith, J.W.N.; Bonell, M.; Gibert, J.; McDowell, W.H.; Sudicky, E.A.; Turner, J.V.; Harris, R.C. Groundwater–surface water interactions, nutrient fluxes and ecological response in river corridors: Translating science into effective environmental management. *Hydrol. Process.* **2008**, *22*, 151–157. [[CrossRef](#)]
15. Urresti-Estala, B.; Carrasco-Cantos, F.; Vadillo-Pérez, I.; Jiménez-Gavilán, P. Determination of background levels on water quality of groundwater bodies: A methodological proposal applied to a Mediterranean River basin (Guadalhorce River, Málaga, southern Spain). *J. Environ. Manag.* **2013**, *117*, 121–130. [[CrossRef](#)]
16. Wendland, F.; Hannappel, S.; Kunkel, R.; Schenk, R.; Voigt, H.J.; Wolter, R. A procedure to define natural groundwater conditions of groundwater bodies in Germany. *Water Sci. Technol.* **2005**, *51*, 249–257. [[CrossRef](#)]
17. Frollini, E.; Preziosi, E.; Calace, N.; Guerra, M.; Guyennon, N.; Marcaccio, M.; Menichetti, S.; Romano, E.; Ghergo, S. Groundwater quality trend and trend reversal assessment in the European Water Framework Directive context: An example with nitrates in Italy. *Environ. Sci. Pollut. Res.* **2021**, *28*, 22092–22104. [[CrossRef](#)]
18. Maréchal, J.-C.; Rouillard, J. Groundwater in France: Resources, Use and Management Issues. In *Sustainable Groundwater Management: A Comparative Analysis of French and Australian Policies and Implications to Other Countries*; Rinaudo, J.-D., Holley, C., Barnett, S., Montginoul, M., Eds.; Springer International Publishing: Cham, Switzerland, 2020; pp. 17–45. ISBN 978-3-030-32766-8.
19. Martínez-Navarrete, C.; Jiménez-Madrid, A.; Sánchez-Navarro, I.; Carrasco-Cantos, F.; Moreno-Merino, L. Conceptual Framework for Protecting Groundwater Quality. *Int. J. Water Resour. Dev.* **2011**, *27*, 227–243. [[CrossRef](#)]
20. Tiouiouine, A.; Jabrane, M.; Kacimi, I.; Morarech, M.; Bouramtane, T.; Bahaj, T.; Yameogo, S.; Rezende-Filho, A.T.; Dassonville, F.; Moulin, M.; et al. Determining the relevant scale to analyze the quality of regional groundwater resources while combining groundwater bodies, physicochemical and biological databases in southeastern France. *Water* **2020**, *12*, 3476. [[CrossRef](#)]
21. Jabrane, M.; Touiouine, A.; Bouabdli, A.; Chakiri, S.; Mohsine, I.; Valles, V.; Barbiero, L. Data Conditioning Modes for the Study of Groundwater Resource Quality Using a Large Physico-Chemical and Bacteriological Database, Occitanie Region, France. *Water* **2023**, *15*, 84. [[CrossRef](#)]
22. Pachepsky, Y.A.; Shelton, D.R. Escherichia Coli and Fecal Coliforms in Freshwater and Estuarine Sediments. *Crit. Rev. Environ. Sci. Technol.* **2011**, *41*, 1067–1110. [[CrossRef](#)]
23. John, D.E.; Rose, J.B. Review of Factors Affecting Microbial Survival in Groundwater. *Environ. Sci. Technol.* **2005**, *39*, 7345–7356. [[CrossRef](#)] [[PubMed](#)]
24. Pandey, P.K.; Kass, P.H.; Soupir, M.L.; Biswas, S.; Singh, V.P. Contamination of water resources by pathogenic bacteria. *AMB Express* **2014**, *4*, 51. [[CrossRef](#)]
25. Rezende Filho, A.; Furian, S.; Victoria, R.; Mascré, C.; Valles, V.; Barbiero, L. Hydrochemical variability at the upper paraguay basin and pantanal wetland. *Hydrol. Earth Syst. Sci.* **2012**, *16*, 2723–2737. [[CrossRef](#)]
26. Tiouiouine, A.; Yameogo, S.; Valles, V.; Barbiero, L.; Dassonville, F.; Moulin, M.; Bouramtane, T.; Bahaj, T.; Morarech, M.; Kacimi, I. Dimension reduction and analysis of a 10-year physicochemical and biological water database applied to water resources intended for human consumption in the provence-alpes-cote d’azur region, France. *Water* **2020**, *12*, 525. [[CrossRef](#)]
27. Miles, J. R Squared, Adjusted R Squared. In *Wiley StatsRef: Statistics Reference Online*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2014; ISBN 9781118445112.
28. El Osta, M.; Masoud, M.; Alqarawy, A.; Elsayed, S.; Gad, M. Groundwater Suitability for Drinking and Irrigation Using Water Quality Indices and Multivariate Modeling in Makkah Al-Mukarramah Province, Saudi Arabia. *Water* **2022**, *14*, 483. [[CrossRef](#)]
29. Masoud, M.; El Osta, M.; Alqarawy, A.; Elsayed, S.; Gad, M. Evaluation of groundwater quality for agricultural under different conditions using water quality indices, partial least squares regression models, and GIS approaches. *Appl. Water Sci.* **2022**, *12*, 244. [[CrossRef](#)]
30. Rezende Filho, A.; Valles, V.; Furian, S.; Oliveira, C.M.S.C.; Ouardi, J.; Barbiero, L. Impacts of lithological and anthropogenic factors affecting water chemistry in the Upper Paraguay River Basin. *J. Environ. Qual.* **2015**, *44*, 1832–1842. [[CrossRef](#)]

31. Barbel-Périneau, A.; Barbiero, L.; Danquigny, C.; Emblanch, C.; Mazzilli, N.; Babic, M.; Simler, R.; Valles, V. Karst flow processes explored through analysis of long-term unsaturated-zone discharge hydrochemistry: A 10-year study in Rustrel, France. *Hydrogeol. J.* **2019**, *27*, 1711–1723. [[CrossRef](#)]
32. Mackay, A.W.; Davidson, T.; Wolski, P.; Mazebedi, R.; Masamba, W.R.L.; Huntsman-Mapila, P.; Todd, M. Spatial and Seasonal Variability in Surface Water Chemistry in the Okavango Delta, Botswana: A Multivariate Approach. *Wetlands* **2011**, *31*, 815. [[CrossRef](#)]
33. DRAAF-Occitanie Cartothèque (Regularly Updated). Available online: <https://draaf.occitanie.agriculture.gouv.fr/cartotheque-r101.html> (accessed on 7 January 2023).
34. Greven, M.; Green, S.; Robinson, B.; Clothier, B.; Vogeler, I.; Agnew, R.; Neal, S.; Sivakumaran, S. The impact of CCA-treated posts in vineyards on soil and ground water. *Water Sci. Technol.* **2007**, *56*, 161–168. [[CrossRef](#)]
35. Ko, B.-G.; Vogeler, I.; Bolan, N.S.; Clothier, B.; Green, S.; Kennedy, J. Mobility of copper, chromium and arsenic from treated timber into grapevines. *Sci. Total Environ.* **2007**, *388*, 35–42. [[CrossRef](#)]
36. Bruez, E.; Larignon, P.; Bertsch, C.; Robert-Siegwald, G.; Lebrun, M.-H.; Rey, P.; Fontaine, F. Impacts of Sodium Arsenite on Wood Microbiota of Esca-Diseased Grapevines. *J. Fungi* **2021**, *7*, 498. [[CrossRef](#)]
37. Favrot, J.C.; Bouzigues, R.; Tessier, D.; Valles, V. Contrasting structures in the subsoil of the boubènes of the Garonne basin, France. *Geoderma* **1992**, *53*, 125–137. [[CrossRef](#)]
38. Gavalda, D. Devenir des Eléments Traces Métalliques dans les Boulbenes (Luvi-Redoxisol) Après Epanchage de Boues Granulées. Ph.D. Thesis, National Polytechnic Institute of Toulouse, Toulouse, France, 2001.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.