



## Source Apportionment of Groundwater Pollutants in Apulian Agricultural Sites Using Multivariate Statistical Analyses

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### Abstract

Multivariate statistical techniques, such as Principal Component Analysis, Absolute Principal Component Scores and Cluster Analysis were applied to data set (pH, electrical conductivity, total dissolved solids (TDS), chemical oxygen demand (COD), dissolved oxygen (O<sub>2</sub>), Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, vital organism to 22°C, vital organism to 36°C) on ground waters collected in 219 sites of Foggia province (North of Apulia region) during the “Expansion of regional agro-meteorological network” project, funded by Apulia Region (2003-2007). Multivariate statistical techniques allowed to identify sites with different characteristics as respect to similar characteristics ones. Moreover Absolute Principal Component Scores allowed to identify three pollutant sources: agricultural pollution 1, agricultural pollution 2 and soil run off and municipal waste.

### Introduction

The application of receptor models to the environmental samples allows the identification and quantitative apportionment of pollutants to their sources. Different models including principal component analysis (PCA), absolute principal component scores (APCS), Unmix, chemical mass balance (CMB) are currently used [1-3].

In this paper PCA and APCS methods were applied to the physical-chemical parameters dataset (starting from data correlation matrix) of ground waters collected in 219 sites of Foggia province in order to identify the pollutant sources and estimate their contributions.

### Materials & Methods

Groundwater samplings were performed under dynamic conditions, after flushing a large amounts of water for about 30 minutes. Samples were collected in polyethylene tanks with cap and undercap, filled to the brim in order to prevent the transfer of the analytes in the headspace and their loss at the opening of the tanks. After collection, samples were stored in cooled bags and transported to the laboratory as soon as possible.

All parameters were determined according to “The official methods of analysis of water for agriculture and livestock” (DM, 23/03/2000). In particular, the physical-chemical parameters (pH, electrical conductivity, dissolved O<sub>2</sub>) were determined directly on the sample by means of Hanna Instruments probes. The chemical parameters were determined after filtration of the sample under vacuum on cellulose acetate filters with porosity of 0,45 microns. Cations determination was performed by flame atomic absorption spectroscopy (Perkin-Elmer); anions were determined by ion chromatography (Dionex corporation). Each parameter was analyzed in three replicates.

## Results

The PCA was applied on dataset of 219 samples and 15 parameters. Three Principal Components (PCs) explained 70% of data variance. In table 1 loadings explaining the factor are highlighted.

The first component explaining 44% of the variance showed high loadings in TDS, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, COD, K<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>; NO<sub>3</sub><sup>-</sup>, vital organism to 22 and 36°C were correlated with second component (PC2) explaining 15% of the variance, while the third component showed high values in O<sub>2</sub>, Na<sup>+</sup>, Ca<sup>2+</sup>, COD, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>.

The APCS receptor model has been applied in order to identify the profile sources and their contributions. Observing figure 1 NO<sub>3</sub><sup>-</sup> org 22, org 36 are completely apportioned to a source named Agricultural pollution 1 due to fertilizer applications; Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> are apportioned to source named Agricultural pollution 2 due to salinity, nutrients etc. HCO<sub>3</sub><sup>-</sup>, COD, O<sub>2</sub>, TDS, Cl<sup>-</sup> are mostly apportioned to a source that can be identified as soil run off and municipal waste [2,3].

Cluster analysis has allowed to identify the sites, among the 219 investigated, with different characteristics.

## Conclusions

The application of APCS to data set allowed to identify three pollutant sources: agricultural pollution 1, agricultural pollution 2 and soil run off and municipal waste.

Multivariate statistical methods can be used to understand complex nature of ground waters quality issues, determine priorities in the use of ground waters as irrigation water and suggest interactions between land use and irrigation water quality.

## References

- 1) M. Caselli, G. de Gennaro, P. Ielpo, A comparison between two receptor models to determine the source apportionment of atmospheric pollutants, *Environmet.*, 17(5), (2006), 507–516.
- 2) H. Boyacioglu, H. Boyacioglu, Water pollution sources assessment by multivariate statistical methods in the Tahtali Basin, Turkey, *Environ. Geol.*, 54, (2008), 275-282.
- 3) K. P. Singh, A. Malik, S. Sinha, Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques-a case study, *Anal Chim Acta*, 538, (2005), 355-374.

Table1: Loadings matrix, eigenvalues and percentage of variance explained

Parameters	PC1	PC2	PC3
pH	-0.094	0.092	-0.325
Cond.	0.396	-0.022	0.013
TDS	<b>0.396</b>	-0.022	0.013
O <sub>2</sub>	-0.013	0.032	<b>0.290</b>
Na <sup>+</sup>	<b>0.409</b>	0.000	<b>-0.155</b>
Ca <sup>2+</sup>	<b>0.206</b>	-0.039	<b>0.322</b>
Mg <sup>2+</sup>	<b>0.348</b>	0.028	<b>0.127</b>
K <sup>+</sup>	<b>0.259</b>	0.055	0.072
COD	<b>0.231</b>	0.039	<b>-0.150</b>
Cl <sup>-</sup>	<b>0.402</b>	-0.018	-0.021
NO <sub>3</sub> <sup>-</sup>	-0.115	<b>0.138</b>	<b>0.608</b>
SO <sub>4</sub> <sup>2-</sup>	<b>0.218</b>	-0.034	<b>0.160</b>
HCO <sub>3</sub> <sup>-</sup>	0.049	0.048	<b>-0.491</b>
Org 22	0.018	<b>0.691</b>	-0.016
Org 36	0.024	<b>0.695</b>	-0.017
Eigenvalues	6.37	1.95	1.56
% variance	44.4	15	10.4

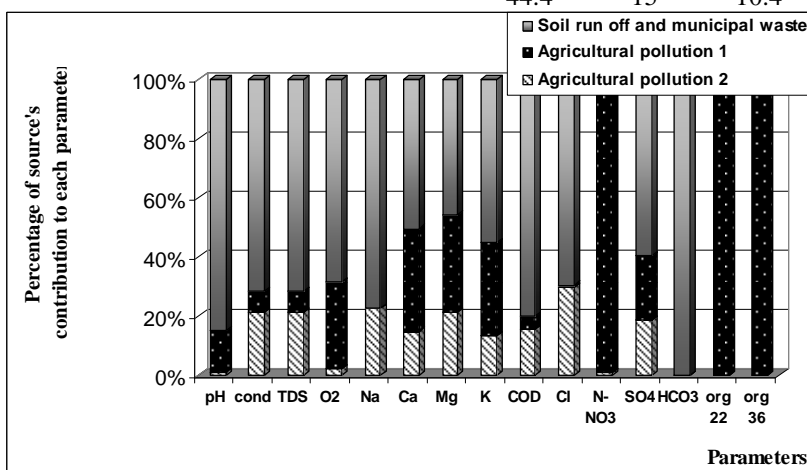


Figure 1: Source's contributions to each parameter