EVALUATION OF MACRO- AND MICROELEMENTS IN WASTEWATERS AND SURFACE WATER BODIES OF THE EASTERN PO RIVER BASIN

VALUATION DES MACRO ET DES MICROELEMENTS DANS LES EAUX REJETEES ET DANS LES COURS D'EAUX DU BASSIN PADANO ORIENTAL

VALUTAZIONE DI MACRO E MICROELEMENTI NELLE ACQUE REFLUE E IN CORPI IDRICI DEL BACINO PADANO ORIENTALE

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Abstract

The growing shortage of water combined with the sharp increase in population and the development of large cities due to rapid urbanization are different aspects of an important problem, and the competition among the various consumers of water increases concerns about the protection of the environment and health. Agriculture represents the greatest burden on the availability of water and most international projects dealing with water reuse are aimed at this sector. The reuse of water for irrigation cannot overlook certain risks for human health and the environment which depend on the quality of the recycled water, its use, soil characteristics and climatic conditions. Urban wastewaters, if separated from those of industrial origin, contain concentrations of organic and inorganic compounds that present only limited problems for human health in the case of reuse for irrigation. On this basis, the present study examines various characteristics of wastewaters coming from different urban wastewater treatment plants and surface water bodies situated in the eastern Po basin and in particular the Provinces of Bologna and Ferrara. The application of multivariate statistical methods can allow us to interpret the large and complex matrices of analytical data obtained during monitoring campaigns. In particular, cluster analysis, which discriminates data on the basis of the degree of similarity among different classes of quality, was able to characterize the quality of the wastewaters of the various plants. Moreover, it was possible to distinguish different types of water in the surface water bodies of the sub-basins in the Provinces of Ferrara and Bologna.
Key words: wastewaters; Cluster analysis; Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

Résumé

Le manque d'eau toujours croissant, associé à la rapide augmentation de la population et au développement des grandes villes, dû à la rapide urbanisation, représente plusieurs aspects d'un important problème. En outre, la compétition

parmi les utilisateurs d'eau est en train d'augmenter les préoccupations à propos de l'environnement et de la santé.

Le secteur agricole consomme la majorité de l'eau disponible et une grande partie de projets qui s'occupent de la réutilisation de l'eau, sont finalisés à ce secteur. La réutilisation de l'eau pour l'irrigation ne peut pas laisser de côté les risques pour la santé et pour l'environnement qui sont déterminés par la quantité d'eau recyclée, par les applications, par les caractéristiques du sol et par les conditions climatiques. Dans le cas de la réutilisation de l'eau, les eaux urbaines, si elles viennent séparées des eaux industrielles, contiennent des concentrations d'éléments organiques et inorganiques telles qu'elles peuvent présenter des problèmes plus limités pour la santé. Sur la base de cette considération, dans ce travail, on examine plusieurs caractéristiques des eaux rejetées qui arrivent des dépurateurs urbains mais aussi des cours d'eaux du bassin Padano Oriental, en particulier des provinces de Bologne et de Ferrara. L'application des approches statistiques "multivariées", permet d'interpréter les grandes et complexes matrices de données que l'on peut obtenir pendant les opérations de suivi de la qualité de l'eau. En particulier le "cluster analysis", qui analyse les données selon les différentes classes de qualité plus ou moins voisines entre elles, a été à même de caractériser la qualité des eaux issues de différentiels dépurateurs. Enfin il a été possible d'individualiser plusieurs typologies des eaux dans les cours d'eaux superficiels dans le sous-bassin de Bologne et Ferrara.

Mots-clés: eaux ussées; cluster analysis; Spectrométrie d'émission ou plasma d'argon (ICP-OES)

Riassunto

La crescente scarsità della risorsa acqua unita al rapido incremento della popolazione, allo sviluppo di grandi città dovute alla rapida urbanizzazione sono diversi aspetti di un importante problema e la competizione tra i diversi utilizzatori dell'acqua aumenta le preoccupazioni per la protezione dell'ambiente e della salute. Il settore agricolo consuma la prevalente disponibilità dell'acqua e la gran parte dei progetti mondiali che trattano del suo riuso sono finalizzati al settore agricolo. Il riuso dell'acqua per l'irrigazione non può prescindere da alcuni rischi per la salute e l'ambiente che dipendono dalla qualità dell'acqua riciclata, dalle applicazioni, dalle caratteristiche del suolo e dalle condizioni climatiche. Le acque reflue urbane nel caso vengano separate da quelle industriali contengono concentrazioni di composti organici ed inorganici tali da presentare limitati problemi per la salute nel caso di riutilizzo irriguo. Sulla base di tali considerazioni in questo lavoro vengono prese in esame numerose caratteristiche di acque reflue provenienti da alcuni depuratori urbani e di corpi idrici superficiali appartenenti al Bacino padano orientale ed in particolare alle Province di Bologna e Ferrara. L'applicazione di approcci statistici multivariati può permettere di interpretare grandi e complesse matrici di dati analitici che si ottengono durante le campagne di monitoraggio. In particolare la "cluster analysis"

che discrimina i dati in base a diverse classi di qualità più o meno vicine tra loro è stata in grado di caratterizzare la qualità delle acque reflue dei diversi depuratori. Inoltre è stato possibile discriminare diverse tipologie delle acque dei corpi idrici superficiali dei sottobacini della Provincia di Ferrara e Bologna.
Parole chiave: acque reflue; Cluster analysis; Spettrometria in emissione al plasma (ICP-OES)

Introduction

Water, from an agronomic point of view, is one of the main factors of production, and surface waters (rivers and lakes) are those most commonly exploited for agricultural use, but in the areas where the farming activity is more intensive they are frequently integrated with subterranean waters (Wang *et al.,* 2007). In some arid and semi-arid regions the re-use of urban wastewater for irrigation is widespread (Mendiguchia *et al.,* 2007). The main factors involved in the quality of such water, making it sustainable for recycling purposes, are the content of pathogens, the salinity, and low rates of specific toxic ions, trace elements and nutrients; drip irrigation provides the highest levels of health safety, as well as a high potential of water conservation (Angelakis *et al.,* 1998).
The purpose of this study is to assess the composition of macro and micro elements in wastewater from five treatment plants and of the respective surface water bodies into which the wastewaters are emitted. The eastern Po basin contains rivers such as those in the Province of Bologna and in particular the River Santerno and the River Idice into which the treatment plants of the towns of Imola (Imola-Santerno) and Castenaso discharge their wastewater, as well as artificial canals of the drainage network of the Burana-Po di Volano Basin which receive wastewaters from the treatment plants of the Province of Ferrara (Codigoro, Copparo, Tresigallo) (ARPA, 2004).. Moreover, the composition in terms of macro and micro elements was tested in water collected both upstream and downstream of the points of discharge.

Materials and methods

Water sampling. Monthly samples were taken of water from the treatment plants of Castenaso and Imola (Province of Bologna) and of Codigoro, Copparo and Tresigallo (Province of Ferrara) and from the surface waters into which the plants discharge the treated wastewater. In the water bodies such as the River Idice and the River Santerno, samples were collected both upstream and downstream of the point of discharge, and similarly in the drainage canals of the Consorzio di Bonifica ferrarese I Circondario.

Samples were also taken from the Canale dei Molini and the Canale Emiliano Romagnolo, artificial constructions used for irrigation. At each station, samples were collected in acid-washed polyethylene containers. To provide reliable and accurate trace metal data, specific cleaning techniques were used for handling and analysing the samples. All materials coming into contact with the samples were acid washed and stored in double polyethylene bags until required. The samples used for the detection of dissolved traces of metals were acidified with high-purity HNO_3 (Suprapur, Merck, Germany). The samples thus treated were stored at 4°C for three months and then analysed (APAT and IRSA-CNR 2003).

Analytical procedures. In order to measure acid-extractible metals bound to suspended particles and to preserve samples, the latter were adjusted to pH 2 with ultra-pure 69.5% nitric acid (Suprapure, Merck, Germany). The macro- and microelements were determined by Spectros (Circular Optical System CIR.O.S.[CCD]) Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES). The ICP-OES setting followed multi-standard solutions (CPI-International-Amsterdam) that reproduce the matrix effect present in samples and allow the lowering of Detection Limits (DL). Instrument response was assessed by measuring a standard sample (CRM 609 - Community Bureau of Reference - BCR). The analytical method was validated by repeating the measures of concentrations present in the different standards used for ICP-OES setting. Ag, Ba, Cd, Co, Cu, Li, Mg, Mn, Mo, Ni, Ti, V and Zn concentration values showed variability coefficients (VC%) lower than 1%, while the elements Al, B, Cr and Sr fell within the interval between 1 and 2% and As, Ca, Fe, Na, Pb, Se, and Si between 2 and 5%. Hg, Sb and Sn were not considered as they displayed a high coefficient of variation caused by the considerable interference of emission spectra.

Statistical procedures. The large number of elements determined would have made it difficult and time consuming to thoroughly analyse the data one variable at a time (univariate analysis). Multivariate analysis is useful for reducing the number of components in a database by identifying the relationship between variables (Wunderlin et al., 2001). To analyse our own data we used cluster analysis, an exploratory multivariate statistical technique that is useful for the purpose of classifying multivariate data. The main objective of this technique is to separate cases (monitoring stations in this study) into groups, or clusters, so that the degree of association is strong between members of the same cluster. The idea is that a cluster describes, in terms of the data collected, a "class" to which its members belong. The experimental data were normalized to zero mean and unit variance in order to avoid misclassifications arising from the different order of magnitude of both the numerical values and variance of the parameters analysed and non-parametric methods of classification were used. In all clustering algorithms discussed in this paper, the squared Euclidean distance was used to measure similarity among clusters while Ward's method was used as an agglomeration

technique. The results of a cluster analysis (CA) are usually summarised using a dendrogram.

Results and discussion

The results of the analysis of the wastewater samples from the five treatment plants of Castenaso and Imola-Santerno (Province of Bologna) and Copparo Codigoro and Tresigallo (Province of Ferrara) were submitted to multivariate statistical analysis. Figure 1 shows the dendrogram obtained from a cluster analysis of the macro and micro elements present in the wastewaters.
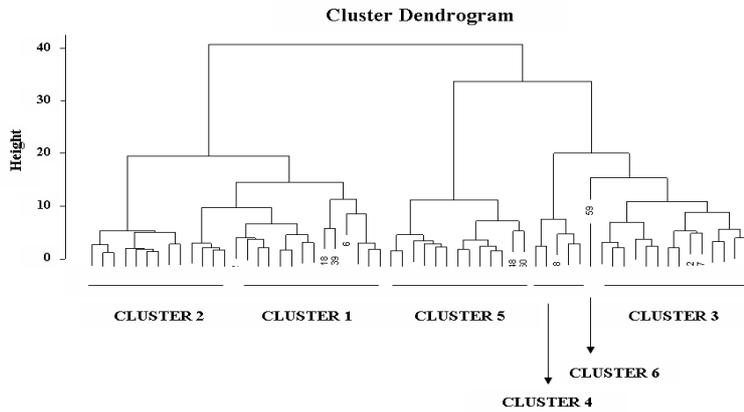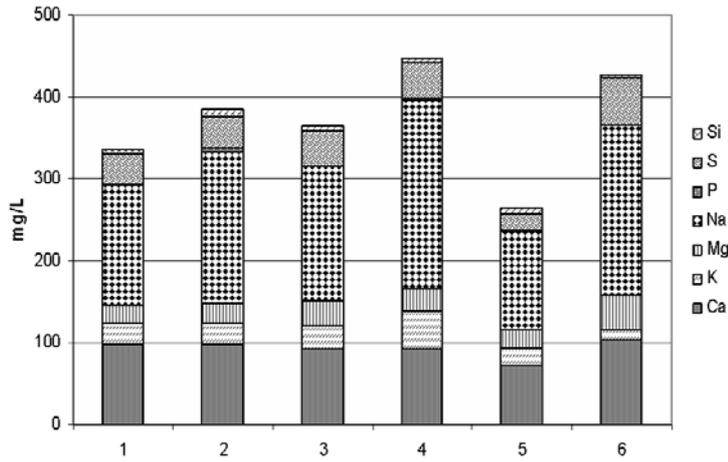

Figura 1

Dendrogram of groups obtained by Cluster Analysis of macro and microlements in wastewater

The cluster analysis produced six groups: groups 1 & 2 refer to the wastewater of the Castenaso treatment plant, the wastewater of the Imola-Santerno plant is characterised by groups 1, 3 & 4, that of Codigoro by groups 3, 5 & 6, that of Copparo by groups 4 & 5, and finally the wastewater of the Tresigallo plant belongs just to group 5. Group 2 refers solely to the Castenaso plant and is characterised by a high concentration of phosphorus, boron and zinc (Figures 2 & 3). The concentrations of groups 1 & 3 are similar, while group 4 characterises the wastewaters of the Imola-Santerno plant. It can in fact be seen that, the Imola and Copparo grouping presents higher concentrations of Na as far as the macro elements are concerned, and of Fe, Li and Mn for the micro elements, highlighting some of the substances that characterise industrial wastewater.

Figure 4, on the other hand, shows the dendrogram obtained from the cluster analyses of the macro and micro elements detected in the water bodies into which the wastewaters are emitted.

Seven groups are obtained. Group 1 refers to samples taken from the River Idice upstream and downstream of the point of discharge of wastewater from the Castenaso plant, group 2 features samples taken from the River Santerno upstream and downstream of the point of discharge of wastewater from the Imola-Santerno plant.
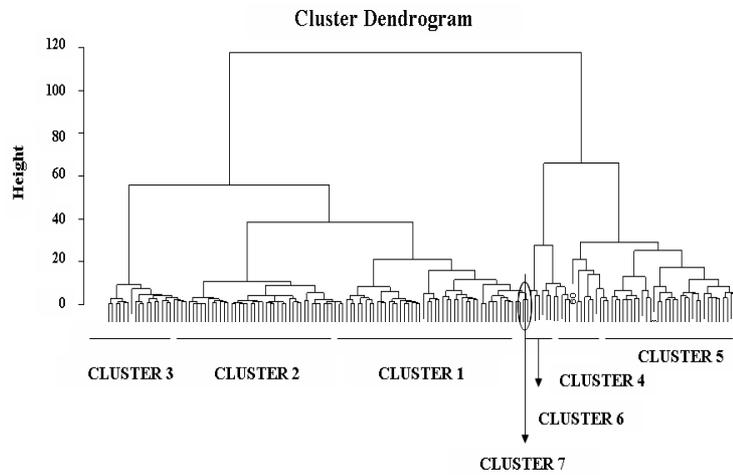
Figura 2

Macro elements concentration (mg L⁻¹)in groups obtained by Cluster Analysis in wastewater
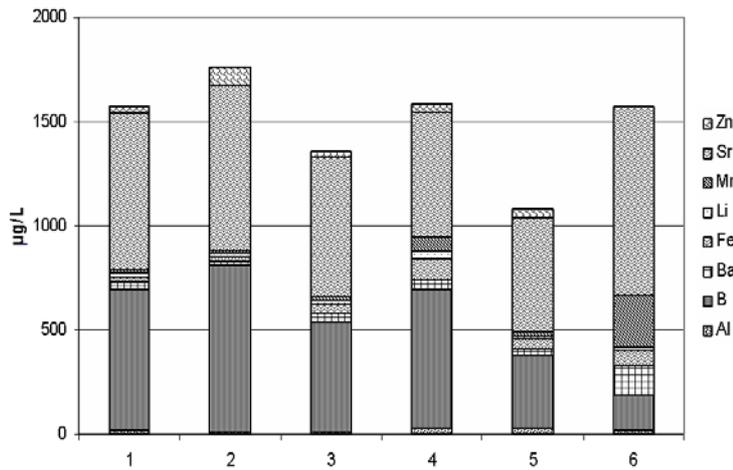
Figura 3

*Micro elements concentration (µg L⁻¹) in groups obtained by Cluster Analysis in wastewater*

Figura 4

Dendrogram of groups obtained by Cluster Analysis of macro and microlements dataset in fresh water (Idice and Santerno rivers, Canal of Molini, Emiliano Romagnolo canal, Burana-Po di Volano canals).

Figures 5 & 6 show the characteristics in terms of macro and micro elements of the groups obtained from the cluster analysis of the surface water samples. It can be seen that the Canale Emiliano Romagnolo presents lower concentrations of macro and micro elements than all the other surface water bodies; this is probably due to the phytodepuration action of the waters after the derivation from the Po.

Figura 5

Macro elements concentration (mg L⁻¹)in groups obtained by Cluster Analysis in fresh water

Figura 6

Microelements concentration (μg L⁻¹) in groups obtained by Cluster Analysis in fresh water
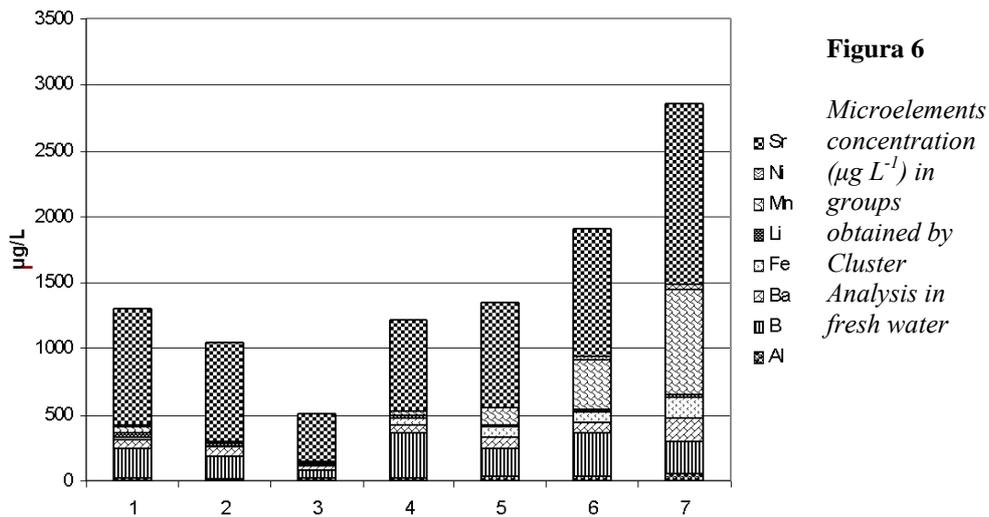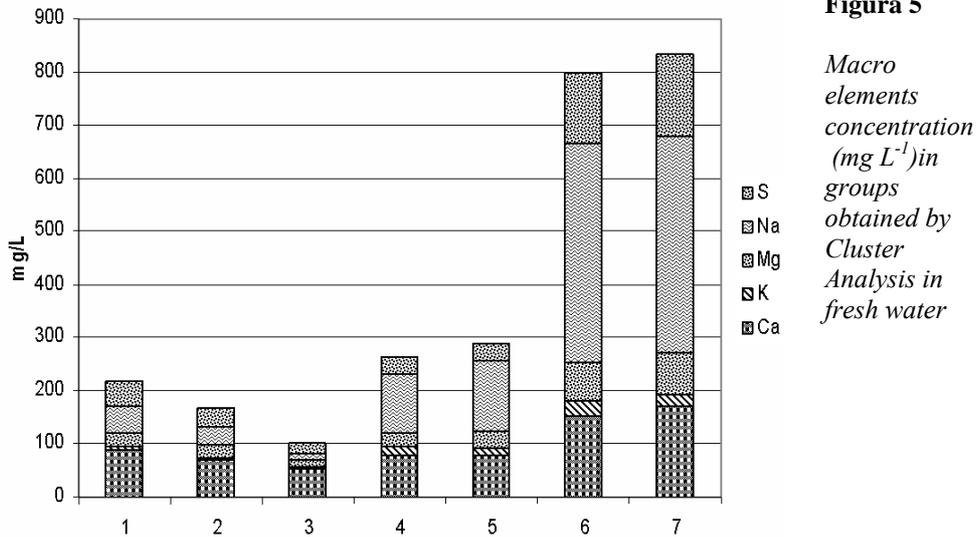
The samples with the highest levels are those belonging to the catchment basins at Codigoro called Acque alte and Acque basse; in particular there is a station at Codigoro with numerous pumps that discharge the waters of the network into the Po, which then carries them to the sea. Acque alte gathers the

water from the artificial drainage canals of the territories that are less morphologically depressed, while Acque basse gathers the waters from the artificial drainage canals that belong to the network of waters from the territories that are morphologically more depressed, situated below sea level.

The concentration of sodium is very high and characterises the waters of the groups of canals of the Burana-Po di Volano Basin, the greatest concentration being in the stations of Acque alte and Acque basse, which are affected by the infiltration of the salt wedge moving inland from the sea.

The concentration of micro elements confirms the diversity of the above-mentioned groups. The Canale Emiliano Romagnolo has the lowest concentration of micro elements, while Acque alte and Acque basse have the highest concentrations, in particular of barium, iron, manganese, nickel and strontium.

Conclusions

The results obtained show a good aptitude of the wastewaters, as far as macro and micro elements are concerned, to be re-used for irrigation, especially if compared to the drainage network of the Burana Po di Volano Basin. Of particular note is the good quality, in terms of macro and micro elements, of the water of the CER, an artificial irrigation canal, also thanks to the characteristics of the concrete structure and the presence of exclusively authorised collection points, which reduce the contact with potential sources of pollution.

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