

Recognition of areas of anomalous concentration of potentially hazardous elements by means of a subcatchment-based discriminant analysis of stream sediments

M. Spadoni*, M. Voltaggio, G. Cavarretta

Consiglio Nazionale delle Ricerche, Istituto di Geologia Ambientale e Geoingegneria, via Bologna 7, 00138 Roma, Italy

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Abstract

The statistical technique of discriminant analysis associated with the calculation of an *information coefficient* has been applied to the concentrations of 37 chemical elements for calculating the mixing of stream sediments of different origin in the Mignone river basin.

Discriminant analysis has been based on *sample catchment basins* (SCBs), defined as the part of the drainage basin between two consecutive sampling points along the same stream branch, and on the identification of 4 different litho-geochemical groups. This approach, has been used to define the membership probability values for every sample by applying Bayes' rule and calculating posterior probability. The grade of uncertainty for each group assignment has been evaluated by using an *information coefficient*, based on a *classification entropy index*, and running a procedure analogue to that used for processing membership values in fuzzy analysis. The maximum theoretical concentration that can be expected in soils near the sampling point (*enhanced concentration*) has then been calculated from both the measured and the membership values by introducing a specific *enhancement function*. Theoretical background concentrations at every sampling point have been also calculated by weighting the average value of concentration in each group with the membership values for each sample. These have been successively compared with the measured and enhanced concentrations to identify anomalous areas.

The distribution maps of Arsenic and Vanadium in the Mignone River basin (central Italy) have been drawn accordingly to this technique, leading to the identification of areas of potential risk for human health.

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1. Introduction

Active sediments collected along a stream (stream sediments, Salminen et al., 1998) can be genetically considered as a mixing between grains and particles of different nature originated from erosive processes within a catchment basin. Consequently, the geochemical

characteristics of each sample can be considered as a function of the composition of different geological materials and sediments of anthropogenic origin transported along the hydrographical network (Meyer et al., 1979; Bölviken et al., 1986; IGS, 1978; Webb et al., 1978; Lahermo et al., 1996). Their composition can be described by means of weighted averages of different factors such as geological setting and history, slope, vegetation, pedogenesis, industrial activities. These factors are hardly quantifiable in detail, even when an

* Corresponding author. Tel.: +39 0649914660; fax: +39 064468632.
E-mail address: massimo.spadoni@igag.cnr.it (M. Spadoni).

accurate knowledge of the natural processes and economic activities in the whole drainage basin is available.

Understanding the complex nature of stream sediments and estimating the geochemical inputs rising from different sources is of fundamental importance in environmental geochemistry, especially when investigating the background concentrations and the presence of natural and man-induced anomalies. For this purpose multivariate statistics approaches, such as discriminant and cluster analysis, can help in identifying subtended environmental processes, assigning each sample to different statistic ‘groups.’ Among these techniques, fuzzy c-means cluster analysis has recently spread in the field of environmental sciences for its capability to give answers in terms of membership, allowing to appreciate gradual changes among clusters (i.e. Hanesch et al., 2001; Kramar, 1995). It has also been successfully applied to stream sediments to identify local enrichments of geochemical concentrations (Rantitsch, 2000). In general, fuzzy c-means studies are directly based on the algorithm given by Bezdek et al. (1984) and are used to give a membership value, variable between 0 and 1 for each case, in order that the sum of all membership values is 1.

As an alternative to the fuzzy c-means analysis, in this paper we suggest the use of a simple discriminant analysis associated with the measurement of the conditional and posterior probability, measured with the Bayes’ theorem, to identify areas of anomalous enrichment of potentially harmful elements. We also show how this information can be used to draw operative maps in a GIS in order to better circumscribe areas of risk for the health of population and to plan further detailed surveys.

2. Data processing

Sample Catchment Basins (SCB) can be described as the part of the drainage basin between two consecutive sampling points along the same stream branch (Spadoni et al., 2004). The sediments are expected to be more homogeneous when SCBs are of low rank (close to the watershed line) and, above all, when a homogeneous geological setting (i.e. same bedrock) is recognizable in them. In this kind of catchments, named ‘index SCB’ (iSCB), we can reasonably associate the measured concentrations with specific and well defined geochemical sources. However, even when considering different catchments extended over the same bedrock, i.e. two iSCBs extended over the same geological unit, a natural geochemical variability has to be expected as well.

Considering different iSCBs inside a wider catchment system, their geochemical variability can be efficiently modelled thanks to techniques of multivariate statistics. Cluster analysis is one of the traditional statistical techniques used in geochemistry to group multivariate objects (SCBs in our case) of similar characteristics. This approach demonstrates its effectiveness especially when litho-geochemical features of the surveyed areas are poorly known. On the contrary, when an accurate knowledge of the geological setting is available, as in our case, statistical analysis can be better oriented by establishing a priori the belonging of the objects to specific groups characterized by a specific field of variability. Discriminant analysis is the statistical technique that can be used: (1) to identify the geochemical variables and their linear combination that better characterize the differences between ‘groups’; (2) to assign ungrouped objects to the recognized groups at specified probability levels. This statistical technique requires that the predictor variables have multivariate normal distributions. Since geochemical variables usually show very skewed distributions (Reinmann and Filzmoser, 2000), the lognormal transformation should be used to fulfil the required assumption. Discriminant analysis approach allows to assign every sample to one group with a certain grade of probability. For each sample, the probability level to belong to the generic group n can be expressed in terms of *posterior probability* (P_n) that can be estimated, using Bayes’ rule, from the *conditional probability* (C_n) and the *prior probability* (G_n):

$$P_n = \frac{C_n \cdot G_n}{\sum_{n=1}^f C_n \cdot G_n} \quad (1)$$

where the G_n is an estimate of the belonging of a sample to a specific group when no information is available and the C_n is the probability associated to the membership score for the same sample when it is assumed to belong to a particular group.

The grade of uncertainty of each group assignment can be calculated, considering the associated posterior probabilities, by means of a *classification entropy index* (h , from Brown, 1998), calculated adapting the equation that was originally developed for managing fuzzy membership values:

$$h_x = \left| \frac{1}{\ln f} \sum_{n=1}^f P_{nx} \cdot \ln(P_{nx}) \right| \quad (2)$$

where P_{nx} is the posterior probability value for sample x in group n and f is the total number of groups.

Entropy values range between 0, when P_{nx} is in only one group, and 1, when P_{nx} is equally partitioned among all the groups. In our specific case, h_x can be interpreted as a measure of the mixing between sediments of different origin.

An *information coefficient* (Vistelius, 1967) has been introduced to be associated to every sample in order to make more evident the statistical inference:

$$I_x = 1 - h_x. \tag{3}$$

In this study we used I to measure the expected mixing between sediments of different origin. When I is high (up to 1) we assume that the information about the origin of sediment is maximum, i.e. the source of the sediment is quite homogenous and geologically identifiable. When I is low (up to 0) even the information is low because the sediment is a mixing between sediments of different nature and origin.

According to this approach we use I to identify land areas where geochemical concentrations are expected to be higher than the values measured in stream sediments samples and, at the same time, to identify possible geochemical anomalies. Measured concentrations can be modified taking into account mixing processes by introducing an *enhancement* function expressed as:

$$E_{ix} = Y_{ix} f e^{-I_x \ln f} \tag{4}$$

where Y_{ix} is the concentration measured for the target element i in the sample x , E_{ix} is its *enhanced concentration* (Fig. 1).

In terms of probability, E_{ix} values can be interpreted as the maximum concentrations that are likely to be expected around each sampling point under the extreme

hypothesis that the target element concentration originated from only one of the groups represented in the sediment while sediments from other groups act as diluents. According to Eq. (4) the maximum *enhanced concentration* can rise to f times the measured one.

Even if the hypothesis that an element could be concentrated only in one group can appear as unrealistic, however it is extremely functional for finding the *enhanced concentration* that is the maximum theoretical concentration that can be expected in soils surrounding the sampling point.

A *weighted background* (W_{ix}), defined as the expected background concentration for the element i in the sample x , can be calculated by:

$$W_{ix} = \sum_{n=1}^f B_{in} P_{nx} \tag{5}$$

where B_{in} is the average value of concentration in each group n calculated excluding outlier values, the latter considered as values exceeding $\bar{x} \pm \sigma$.

An *enrichment factor* can be defined for each sample as follows:

$$F_x = \frac{Y_{ix}}{W_{ix}} \tag{6}$$

and similarly can be defined an *enhanced enrichment factor* given by:

$$F'_x = \frac{E_{ix}}{W_{ix}}. \tag{7}$$

In general, when referring to *potentially harmful elements and species* (PHES), both F_x and F'_x values should be considered in order to identify areas of

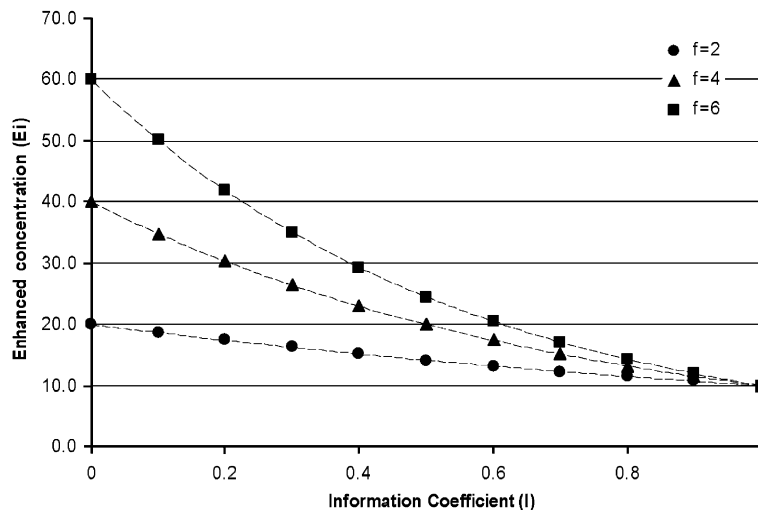


Fig. 1. Variation of the enhanced concentration value in function of f and I for a hypothetical measured concentration of 10.

potential geochemical hazard. F_x gives an indication of the scattering between measured and background values, while F'_x indicates the maximum potential scattering assuming the element as originated from only one group. The latter is an index of the hazard due to the possible presence of a high-PHES source of natural or anthropogenic origin.

3. Example of application: the Mignone river basin

3.1. Geological setting

The Mignone river basin area is placed in Latium (central Italy) between the Tyrrhenian margin, at west, and the Pleistocenic volcanic reliefs of the Sabatini and Cimino–Vicano Mounts (Fig. 2). Its quite complex geological setting includes the presence of many sulphide mineral ores linked to the upwelling of hydrothermal fluids.

3.1.1. Allocthonous succession (Cretaceous–Paleogene)

The sedimentary succession called *serie dei Flysch tolfetani e della Pietraforte* (Fazzini et al., 1972) outcrops over a considerable part of the drainage basin. It shows, at its bottom, a *clayey-calcareous* unit discontinuously overlapped by *polychrome manganese rich*

clay, that in turns includes the *Pietraforte* lens, and *calcareous-marly* units interbedded with the *Mignone formation*, compounded by polychrome shales with calcareous levels. At the top Oligocene sandstones outcrop. Tectonic contacts are likely between the different members of this succession.

3.1.2. Neoautocthonous succession and recent deposits (Neogene–Holocene)

It is compounded of three Neogene series and a quaternary one of marine origin (Fazzini et al., 1972), onlapping flysch units and discontinuously overlapped by quaternary continental sediments. Calcareous sandstones and molasse of Miocene age outcrop at the bottom of this succession. They are followed by a series compounded of reddish sandy conglomerates, gray clays with lens of gypsum, *Tarquinia limestone*, yellow sands and final conglomerates up to Upper Pliocene.

A further series of medium Pliocene age, consisting of dark clays and yellow sands, follows with partial unconformity, along with transgressive marine sediments of Sicilian and Tyrrhenian age, compounded by sediments of heterogeneous size mixed with volcanic products.

The succession ends with quaternary sediments of continental origin ranging from conglomerates to sands, to marshy sediments and travertines.

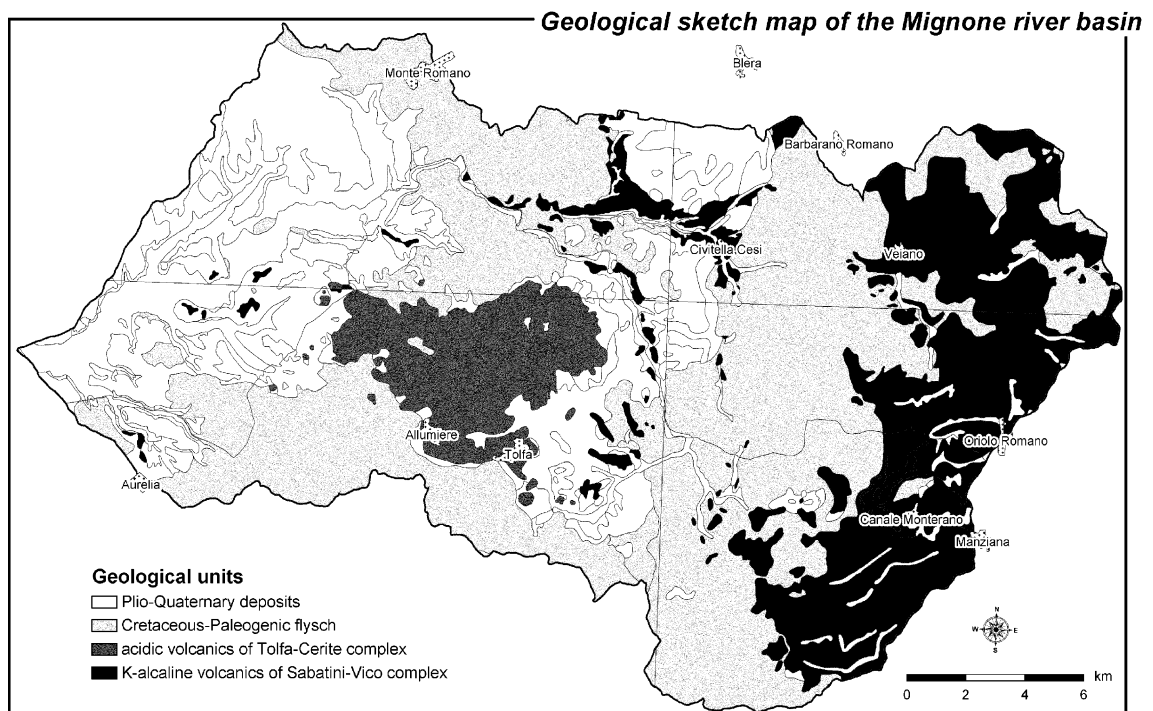


Fig. 2. Geological sketch map of the Mignone river basin.

3.1.3. Volcanic unit of the Tolfetano–Cerite complex (Pliocene)

This unit extensively outcrops in the central part of the Mignone basin and is represented by acidic ignimbrites and lavas compounded by quarzolatites, liparites and latites. These volcanites are the most ancient outcropping in northern Latium erupted about 4.2–2.3 Ma ago (Fornaseri, 1985).

3.1.4. Volcanic units of the Vicano and Sabatino Complex (Pleistocene)

These rocks outcrop in the eastern and south-eastern part of the Mignone basin. The oldest unit, known as *tuffo rosso a scorie nere*, is made of pomiceous black

scoriae in an alkaline–trachitic matrix, with radiometric age of 0.43–0.49 Ma (Evernden and Curtis, 1965). The pyroclastic flow of *Bracciano unit*, compounded by pyroclastic deposits of tephritic–phonolitic composition (De Rita et al., 1993) and aged 0.177–0.09 Ma, is partially overlapped on the previous unit. Finally the Vico volcanic complex units outcrop at the north-eastern edge of the basin. These are known as *tuffo rosso a scorie nere vicano*, and have a composition similar to the products from the Sabatini complex, consisting of ignimbrites with black tephritic–fonolitic scoriae in a reddish cineritic matrix (Locardi, 1965) aged 0.155–0.01 M.Y. (Borghetti et al., 1981; Sollevanti, 1983). Some fall deposits of stratified policrome tuffs of Vico

Table 1

Descriptive statistics of the 37 chemical elements measured in the stream sediments of the Mignone river basin

	Range	Min	Max	Mean	σ	σ^2	Skew.	Kurt.	K–S test
Ag ppm	0.6656	0.001	0.666	0.067	0.077	0.006	4.87	30.02	
Al %	5.04	0.43	5.47	2.25	1.16	1.35	1.04	0.37	nor/log
As ppm	662.9	2.6	665.5	44.8	105.1	11,040.5	4.80	23.90	log
Au ppm	0.5455	0.0001	0.5455	0.0098	0.0482	0.0023	10.36	114.14	–
B ppm	68.8	1	69	9	7	51	4.63	36.44	log
Ba ppm	2049.3	70.2	2119.5	377.2	344.1	118,382.6	2.09	5.56	log
Bi ppm	6.73	0.11	6.84	0.60	0.76	0.58	5.64	40.56	log
Ca %	20.33	0.06	20.39	6.06	4.46	19.91	0.64	0.04	nor
Cd ppm	1.05	0.02	1.07	0.22	0.15	0.02	3.37	14.85	log
Co ppm	106.1	0.7	106.8	19.1	11.2	125.4	3.94	27.18	log
Cr ppm	82	7.8	89.8	37.8	12.5	157.5	0.66	1.75	nor/log
Cu ppm	118.74	6.24	124.98	32.66	18.69	349.33	2.17	6.70	log
Fe %	13.5	0.75	14.25	3.13	1.47	2.16	3.57	23.33	log
Ga ppm	14.1	1.7	15.8	6.5	3.2	10.1	1.09	0.45	log
Hg ppb	99.982	0.017	99.999	2.162	8.988	80.775	9.71	104.35	log
K %	0.99	0.07	1.06	0.36	0.17	0.03	1.57	3.13	log
La ppm	221.9	1.6	223.5	40.8	41.2	1696.3	1.68	2.65	log
Mg %	1.08	0.03	1.11	0.45	0.21	0.04	0.90	1.10	nor/log
Mn ppm	11,451	25	11,476	1168	1122	1,258,398	6.16	52.47	log
Mo ppm	7.08	0.29	7.37	0.87	0.87	0.75	5.61	38.01	log
Na %	0.4	0.008	0.408	0.052	0.050	0.002	3.68	20.53	log
Ni ppm	111.1	2.2	113.3	33.7	16.6	274.1	2.63	10.04	–
P %	0.372	0.012	0.384	0.073	0.043	0.002	3.30	19.80	log
Pb ppm	318.5	10.0	328.5	44.0	40.4	1630.6	3.22	17.45	log
S %	1.278	0.01	1.28	0.09	0.17	0.03	4.99	27.93	–
Sb ppm	125.62	0.14	125.76	3.64	11.85	140.48	8.41	83.48	log
Sc ppm	12.7	1.4	14.1	5.0	2.1	4.2	1.08	2.66	nor/log
Se ppm	1.38	0.1	1.4	0.4	0.3	0.1	1.57	3.75	–
Sr ppm	1568.3	31.6	1599.9	341.0	240.8	57,971.6	2.27	8.54	nor/log
Te ppm	1.216	0.01	1.22	0.10	0.11	0.01	7.43	68.58	log
Th ppm	67.1	2.8	69.9	16.7	16.9	286.5	1.57	1.64	log
Ti %	0.4048	0.001	0.405	0.058	0.089	0.008	1.77	2.15	log
Tl ppm	15.83	0.05	15.88	1.07	1.77	3.13	5.90	43.60	log
U ppm	15.8	0.1	15.9	2.9	3.2	10.4	1.87	3.07	log
V ppm	279	19	298	76	52	2657	1.62	2.66	log
W ppm	4.26	0.1	4.3	0.5	0.7	0.5	2.58	9.08	–
Zn ppm	1107	9.6	1116.6	93.1	103.9	10,797.8	7.54	70.09	–

The last column shows the results of one-sample Kolmogorov–Smirnov test after comparing the observed cumulative distributions function with normal and lognormal theoretical distributions. “Nor” and “log” respectively means that the null hypothesis of normal and lognormal distributions of the population has not been rejected for $p < 0.01$.

centre are also interbedded in them (Mattias and Ventriglia, 1970).

3.2. Detection of potentially anomalous areas and mapping

Very helpful information is obtained when concentrations exceeding admitted limits (*lim*) for human health safety are coupled with values exceeding *n* times the weighted background. In the following discussion we assumed *n*=2.

Maps can be obtained using Boolean operators between raster data in a GIS according to these relationships:

$$Y_{ix} > \text{lim}_i \text{ and } F_x > 2 \quad (8)$$

$$E_{ix} > \text{lim}_i \text{ and } F'_x > 2. \quad (9)$$

The two maps can be compared to highlight areas of potential hazard that could not be evidenced using the simple concentration values. Some examples about As and V distribution using geochemical data from stream sediments of the Mignone River Basin in central Italy are discussed below.

A geochemical survey has been run on stream sediments of the Mignone river basin, collecting 138 samples and measuring the concentration of 37 chemical elements extracted in aqua regia by ICP-MS. In Table 1 the descriptive statistics associated with each of these elements is summarized.

Samples collected in the μ SCBs (see Introduction), have been then used to identify the characteristic average composition of four litho-geochemical groups:

- Group 1. Plio–Quaternary deposits;
- Group 2. Cretaceous–Paleogenic flysch;
- Group 3. Acidic volcanics of Tolfa–Cerite complex;
- Group 4. K-alkaline volcanics of the Sabatini and Vico districts.

Multivariate discriminant analysis has been run using log-transformed concentration data in order to fulfill the required assumptions after using the Kolmogorov–Smirnov test to identify the cumulative distribution type of each variable (Table 1). The goal of 100% of correct classification of the original grouped cases can be reached running a discriminant analysis over a selection of 13 variables (i.e. Ti, Mg, Ba, Cu, Ag, B, Ga, Ni, Mn, P, Sr, Fe, Al). However, a reduced number of a different set of variables has been preferred (Ti, Mg, Ga, Ba, Mn, Fe, K, P, Al) in spite of the lower

score of correct classification (85.3% — Table 2), for the better suitability of these elements both to represent background values independently from local abundance of mineral ores (hydrothermal mineralizations) and to match the mathematical assumption required by discriminant analysis.

The posterior probability for the samples to belong to each group has been automatically calculated by the SPSS statistical software programme.

The application of our method led to the identification of the weighted background and of the enrichment factors. These variables have been mapped for As and V, two of the elements of environmental interest that had shown clear tendency to exceed the limit imposed by the Italian law (Figs. 2 and 3). Mapping has been obtained using a simple Inverse Squared Distance interpolator in a GIS environment (Webster and Oliver, 1990). This has been preferred to the use of a more complex ordinary kriging interpolator on log-transformed data that had not shown any significant improvement of accuracy in terms of diminution of Root Mean Square error in the cross-validation tests.

Since Italy has no specific regulation about the concentration limits of chemical elements in stream sediments, we used, as a reference, the limits introduced by the Italian law DM 471/99 (Gazzetta Ufficiale, 1999) regulating the use and the reclamation of urban and industrial soils, also assuming that most of the stream sediments are made of particles that rise from soil erosion.

3.2.1. Arsenic

In several cases the measured concentrations exceed the limit of 20 and 50 mg/kg introduced by the Italian National law, respectively for urban and industrial soils.

Table 2
Classification score of discriminant analysis with 9 variables (Ti, Mg, Ga, Ba, Mn, Fe, K, P, Al) on grouped samples (samples collected from μ SCBs)

	Predicted group membership (%)			
	1	2	3	4
Group 1	77.78	22.22	0.00	0.00
Group 2	7.14	92.86	0.00	0.00
Group 3	16.67	16.67	66.67	0.00
Group 4	0.00	0.00	0.00	100.00
Ungrouped	29.81	39.42	12.50	18.27

85.3% of original grouped cases correctly classified

The classification score for the originally ungrouped samples has also been shown.

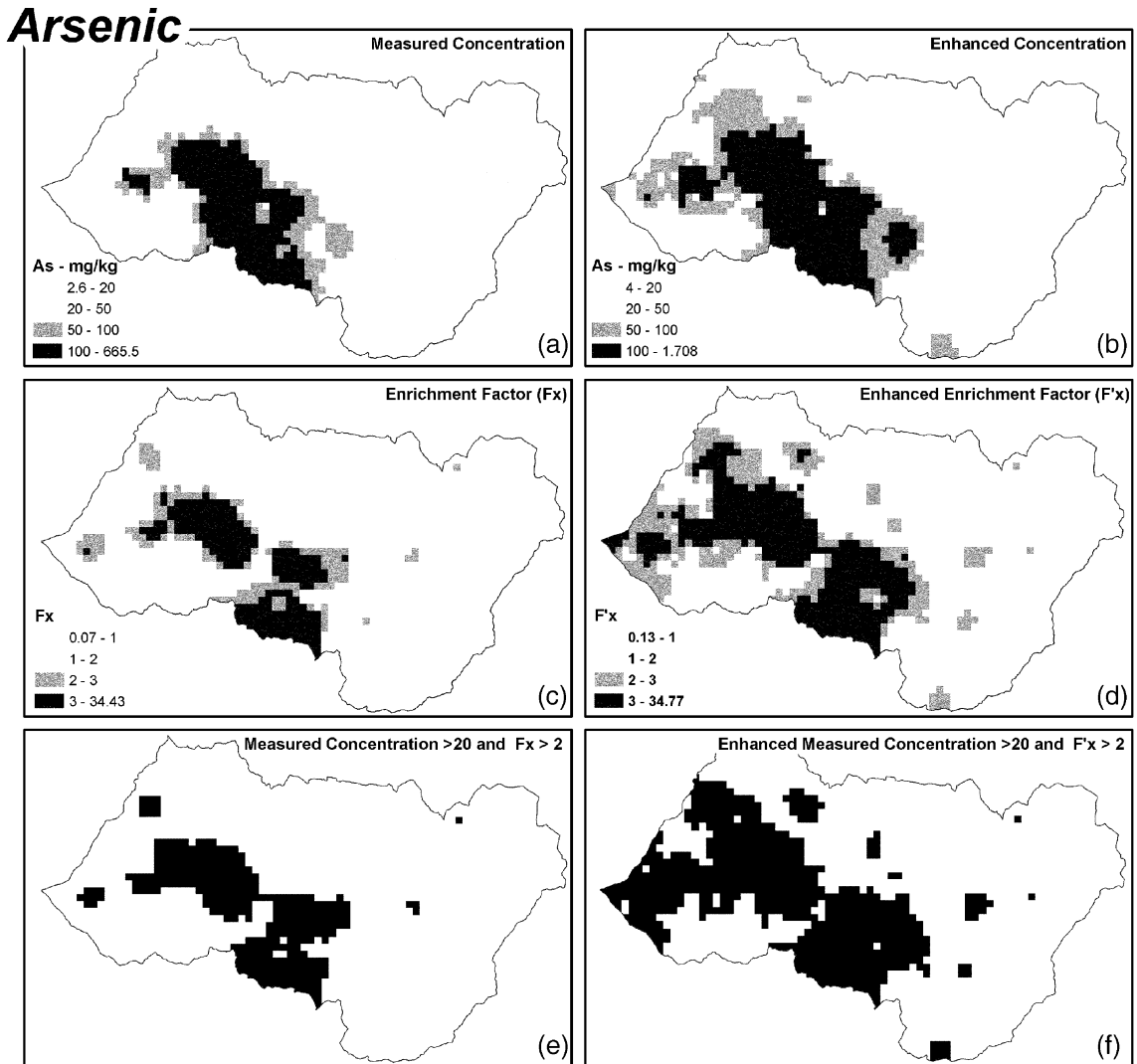


Fig. 3. Distribution maps of Arsenic in the Mignone river basin drawn using Inverse Squared Distance interpolator.

The highest concentrations are found in areas surrounding Tolfa and Allumiere, towns where mining industry, linked to the presence of sulphide ores, has been active up to few years ago (Fig. 3a).

Small areas of highly anomalous concentration can be evidenced in the western part of the Mignone river, apparently unconnected with mineralized areas.

When considering the enhanced concentrations, areas of high anomaly widen towards areas with low values of information coefficient, i.e. where mixing between sediments from different sources originated the dilution of possible remarkable concentrations (Fig. 3b).

Comparing the distribution of enrichment factor with the enhanced enrichment factor, the same process is made more evident and the highly anomalous areas extend to the whole final tract of the Mignone River

and its alluvial plain (Fig. 3c,d). A central-eastern area with high concentrations is also evidenced where sediments of all the lithologic groups occur.

Fig. 3e and f are an example of how the potentially anomalous areas can be operatively evidenced by means of the imposition of two constraints (concentration > 20 ppm and $F > 2$ for Fig. 3e, enhanced concentration > 20 ppm and $F' > 2$ for Fig. 3f). The potentially anomalous area has increased 135% towards areas with low information coefficient correctly addressing further surveys to better define areas of risk mitigation interventions.

3.2.2. Vanadium

In the eastern part of the Mignone river basin, where K-alkaline volcanics outcrop, the measured concentra-

tions often exceed the limit of 90 mg/kg fixed by the Italian National law for urban soils (Fig. 4a).

When considering the enhanced concentrations, the largest part of the river basin exceeds the above mentioned limit concentration value (Fig. 4b). The enrichment factor map shows as the anomalous values are actually comparable with the background ones (Fig. 4c). On the contrary the enhanced enrichment factor map identifies three noticeable areas where values could be found as anomalous and, thus, further surveys should be hoped for (Fig. 4d).

Maps in Fig. 4e and f clearly show how the use of the enhanced concentration and of the enhanced enrichment factors bring to identify intervention areas for vanadium mitigation that could not be highlighted

using the “normal” concentrations and enrichment factors as constraints in the Boolean equations.

In conclusion, the association among concentration values higher than the admitted limit allows to define priorities in detailing land knowledge by means of further survey and analysis. At first, these actions should be run in SCBs of lower rank where sediments collected at their edge are mainly of local provenance respect to sediments collected in SCBs of higher rank placed downstream.

4. Conclusions

A technique based on the application of discriminant analysis to geochemical concentrations in stream sedi-

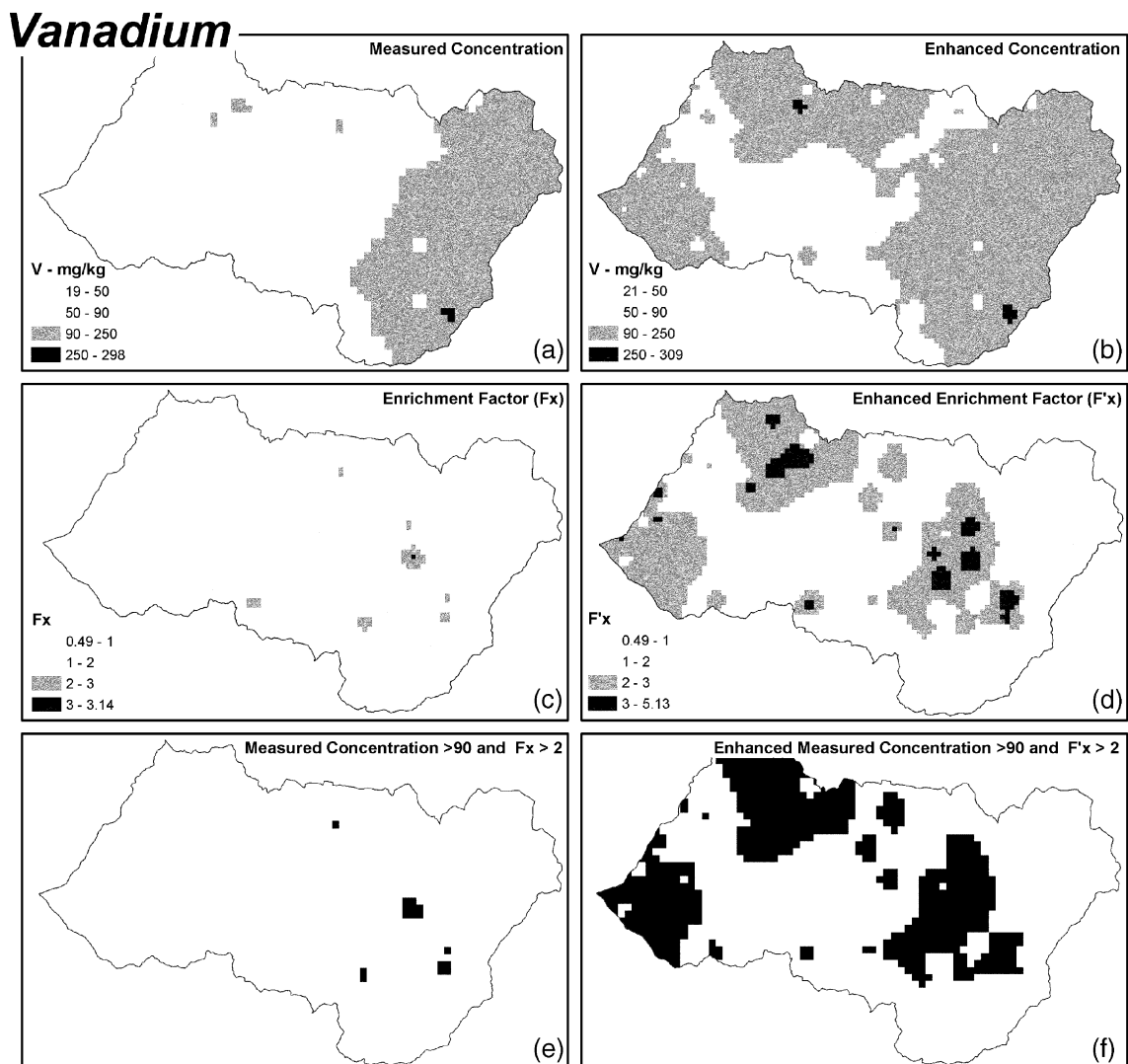


Fig. 4. Distribution maps of Vanadium in the Mignone river basin drawn using Inverse Squared Distance interpolator.

ments, associated with the calculation of an information coefficient for every sample, has been proposed to identify areas of theoretical maximum concentration (enhanced concentration). Discriminant analysis has been run taking into account the principle of sample catchment basins (SCBs). Enhanced concentrations have been referred to background values, calculated by weighting the concentrations measured in the index sample catchment basins (μ SCBs), to identify areas of possible anomaly.

This approach has been tested in the Mignone River Basin (central Italy) where geochemical concentrations have been measured on samples rising from the mixing among stream sediments of different geological origin and, thus, carrying a very poor amount of information (low values of the information coefficients). Here, areas of potential risk, due to the achievement of relatively high load of As and V, have been identified and mapped in a GIS.

In general, this technique demonstrated its utility in defining survey priorities during the preliminary phase of land planning activities in order to prevent possible risks for human health.

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