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GEOBASI: The geochemical Database of Tuscany Region (Italy)

GEOBASI: Il Database geochimico della Regione Toscana

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Keywords: *geochemical data, database, statistical analysis, geographical information system, geostatistics.*

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Riassunto: In questo lavoro sono illustrate le varie fasi di attività svolte da un gruppo di lavoro costituito da ricercatori e funzionari delle università toscane (Firenze, Pisa e Siena), del CNR di Pisa (Istituto di Geoscienze e Georisorse), dell'ARPAT (Agenzia Regionale per la Protezione dell'Ambiente della Toscana), del Consorzio LAMMA (*LABoratory for Monitoring and Environmental Modeling for the Sustainable Development*) e del Sistema Informativo Territoriale e Ambientale della Regione Toscana; il lavoro ha avuto come obiettivo la realizzazione del Database Geochimico Regionale (DBGR), chiamato GEOBASI.

GEOBASI si propone come uno strumento in grado di raccogliere tutta l'informazione di natura chimica (composizionale e isotopica) di differenti matrici geologiche, solide, liquide o gassose campionate nel territorio toscano. L'obiettivo è di contribuire ad uno sviluppo strutturato delle conoscenze dei processi geochimici alla base della variabilità chimica dei materiali geologici.

Nella prima fase del progetto le attività sono state orientate a favorire la piena fruizione di dati disaggregati già disponibili tramite una potente interfaccia Web-GIS e ad implementare l'utilizzo di strumenti grafico-numerici di analisi statistica esplorativa mediante i quali: 1) comprendere la variabilità del fenomeno oggetto di studio; 2) individuare la posizione geografica di classi di valori o di singoli campioni; 3) confrontare gli esiti di diverse metodologie analitiche sperimentali per uno stesso analita; 4) estrarre dati relativi ad un determinato periodo temporale e/o area e 5) verificare l'impatto della presenza di informazione numerica con valore inferiore al limite di rilevabilità strumentale.

Lo sviluppo del progetto prevede la definizione di regole e strumenti finalizzati a una continua e progressiva implementazione controllata del database, al fine di evitare il danneggiamento dell'informazione già presente, anche in previsione di un utilizzo interattivo della risorsa da soggetti esterni.

E' inoltre in corso uno studio di dettaglio dell'area di Scarlino-Follonica con l'obiettivo di potenziare i metodi grafico-numerici di analisi statistica e geostatistica, avvalendosi di *software open source* (QGIS e R), al fine di supportare il processo d'individuazione della così detta "*geochemical baseline*" per un dato analita.

Abstract: *In this study the new Regional Geochemical Database (RGDB), called GEOBASI, is presented and illustrated in the framework of a joint collaboration among the three Tuscan universities (Florence, Pisa and Siena), CNR-IGG (Institute of Geosciences and Earth Resources of Pisa), ARPAT (Regional Agency for the Environmental Protection), LAMMA (Environmental Modelling and Monitoring Laboratory for Sustainable Development) Consortium and S.I.R.A.*

(Territorial and Environmental Informative System of Tuscany). The database has permitted the construction of a repository where the geochemical information (compositional and isotopic) has been stored in a structured way so that it can be available for different groups of users (e.g. institutional, public and private companies). The information contained in the database can in fact be downloaded freely and queried to correlate geochemistry to other non compositional variables.

The first phase of the project was aimed at promoting the use of the geochemical data already available from previous investigations through a powerful Web-GIS interface to implement the exploratory statistics graphical-numerical tools used to: 1) analyse the spatial variability of the investigated context, 2) highlight the geographic location of data pertaining to classes of values or single cases, 3) compare the results of different analytical methodologies applied to the determination of the same element and/or chemical species, 4) extract the geochemical data related to specific monitoring plans and/or geographical areas, and finally 5) recover information about data below the detection limit to understand their impact on the behaviour of the investigated variable.

Developments of this project will be focused on the definition of rules and standardized methods in a way that external users could also interactively pursue the RGDB. Furthermore, a detailed investigation of the Scarlino-Follonica plain will permit the improvement and test of statistical and geostatistical methods, using open source software (QGIS and R) to support the process of evaluation of the geochemical baseline.

Introduction

The identification of the natural geochemical baseline for chemical elements or compounds is a fundamental step to understand how natural processes work and to identify perturbations due to anthropic factors. This knowledge is useful to guide political decisions concerning the management of environmental problems (e.g. quality of drinkable water, reclamation of polluted sites).

Notwithstanding the developments in this field of investigation, due to the pressure on the use of natural resources, a shared protocol from field sampling to statistical analysis, has not yet been clearly adopted. One of the difficulties is to relate the results of the scientific research published on peer-reviewed journals to application studies whose results are reports of public agencies not widely diffused in the scientific community. The consequence is that, as discussed in Gałuszka (2005, 2006, 2007), the terms baseline and background do not have a commonly accepted definition. In fact sometimes they are used interchangeably, while at other times background is used to describe only “natural” conditions, meaning those that are a result of the local conditions such as geology, climate, hydrology, without reference to the influence of anthropogenic activity (Reimann and Garrett, 2005; Rodrigues and Nalini Júnior, 2009). The definition used in the FOREGS (Forum of European Geological Surveys) project refers to the baseline as the concentration at a specific point in time of a chemical element, species or compound in a sample of geological material (Salminen et

al, 2005; De Vos et al. 2006; Johnson and Ander, 2008). Recently several authors have spoken about a baseline study as simply defining the “pre-operation exposure” conditions for the set of indicators that will be used to assess achievement of the outcomes and their impact expressed in the program’s logical framework (Ander et al., 2013; Levitan et al., 2014). When compared with the condition of the same indicators at some point during implementation (mid-term evaluation) and post-operation implementation (final evaluation) the baseline study forms the basis for a “before and after” assessment or a “change over time” assessment. Without baseline data to evaluate pre-operation conditions for outcome and impact indicators it is difficult to establish whether change at the outcome level has in fact occurred.

In the last twenty years public institutions devoted to the monitoring of the surficial Earth have focused their attention of this theme with the aim to recognise, prevent and reduce the pollution of the environment (e.g. US EPA, www.epa.gov; EEA European Environment Agency, www.eea.europa.eu/; FOREGS, Forum of European Geological Survey, <http://wepi.gtk.fi/publ/foregsatlas/ForegsData.php>). In this framework particular attention has been devoted to the protection of hydrological resources whose chemistry is attributable to natural water-rock interactions. The importance of this research has long been recognised by the Italian authorities so that it has been formalised through specific acts (Law n. 752, 6 October 1982). The first formal project dates back to 1996 when the Italian National Research Council (CNR) constituted an ad-hoc Commission for geochemical cartography (ordinance n. 14021, September 1996), followed by strategic long-term plans also financed at Ministerial level. Through the contribution of these projects a dynamic National Geochemical Archive (NGA) was created with the aim to associate under the same framework the geochemical properties of elements and compounds with geolithology and any other information about the territory (Ottonello and Serva, 2003). The validation and integration of the geochemical data collected under the NGA concerning Tuscany Region has formed the starting point for the development of the GEOBASI project (Bottaini et al., 2011; Buccianti et al., 2011; Buccianti et al., 2014).

At the present time the determined baseline values are often compared with concentrations representing a contamination threshold. These reference levels have been defined at national level (D.Lgs. 152/06) and acknowledge European directives adopting USA and Canadian laws. By considering this, it is important to clearly define the concept of baseline and its link with the spatial distribution of the data as well as with the conceptual model of the processes affecting the territory. However, the starting point to achieve good results is related to the completeness of the numerical information about chemical concentrations of elements or compounds in different geological media and to its organisation in a dedicated dynamic repository. For this reason Tuscany Region’s S.I.T.A (Territorial and Environmental Information System of the Tuscan Region) has financed and organised a working group constituted by geochemists, geologists and hydroge-

ologists of the Universities of Firenze, Pisa and Siena and of the National Research Council, Institute of Geosciences and Georesources (IGG) with the aim of identifying a protocol for managing the geochemical information. This working group has also been joined by the researchers of the LAMMA Consortium thanks to their competence in Informatics and to the adequacy of their dedicated hardware and software resources. The participation of researchers of the Regional Agency for Environmental Protection has also been fundamental to understand the needs of public institutions called upon to handle emergencies concerning contamination problems.

In this framework the database GEOBASI was proposed as a direct access user service, accessible to different levels of users, whose contents could be freely queried and downloaded (<http://www506.regione.toscana.it/geobasi/index.html>). The aim was to give reference knowledge on the geochemical composition of different geological media, solid (soils and stream sediments), liquid (stream and ground waters, springs, lakes) and gaseous (natural emissions). In a first phase the work was oriented towards the aggregation of the information already available, but fragmented in several files, through a powerful Web-GIS interface and subsequently towards the use of univariate methods of statistical analysis to explore data behaviour. Following a guided path it is possible to immediately analyse the variability of a given element/species. In the database the different experimental procedures related to the determination of the same chemicals represent the most important source of heterogeneity, and box-plots are used to visualise the variability of the different analytical methods. In fact only after having chosen a specific analytical method, a histogram or a cumulative curve can be obtained and the spatial location of classes of values or single cases visualised. The procedure can be repeated transforming the data by using the logarithm function or choosing a delimited portion of the Region or a defined interval of time.

The project illustrated herein is the actual development of the NGA and the GEOBASI PRAA 2009, the latter financed by Tuscany Regional Government (Regional Plain of Environmental Action, Target E, Preservation of the hydrological resources, Bucciante et al., 2011). Starting from the obtained results it aims to organise and structure the geochemical information so that it can be used for several purposes. While updating and populating the database with old and new data from different sources at the regional scale, an area has been chosen as a case study for geochemical characterisation, implementation of the graphical-numerical tools and definition of a protocol to support the identification of the geochemical baseline. In this case study sampling, experimental analysis and statistical treatment were under control and followed shared paths among all the participants in the project. The area chosen by the working group is the coastal plain and the hydrographical basin of Follonica-Scarlino (southern Tuscany). For this portion of the regional territory both the old and the newly produced geochemical information were inserted into the database and associated with geological, hydrological and land use information, thus implementing the conceptual

(and numerical) model of the system as a whole. Comparisons with the regional context for the same geochemical variables have also been planned. The inclusion of old well-structured information in the repository has permitted an adequate new sampling strategy, with efficiency in time and costs

Materials and methods

Compilation of existing data and multi-source updating

One of the main requirements that we had to take into account was to obtain a complete collection of existing geochemical information. Old data collections were specifically recorded as metadata fields. Basically, the reference archives were:

- The National Geochemical Archive (NGA);
- The Geobasi project – Tuscany, Regional Plain of Environmental Protection - PRAA 2009 following Target E devoted to the safety of hydrological resources;
- Surficial and ground waters monitoring and sampling (MAT – Monitoring groundwaters and aquifers, and MAS – Monitoring internal surficial waters) carried out by ARPAT, the Regional Agency for the Environmental Protection.

As a first step all the different kinds of existing data were reorganised into the new database even though at the moment it is not completely available for further analysis, as the collection of more information about origin/generation of some samples is still pending. The problems arising from working with the incorporation of data from different archives has opened the question about how to plan the continuous updating of the dataset with new information if diverse sources are expected (Fig. 1). To answer this issue, integration methods and semantic test evaluation functions have been constructed in order to verify data compatibility between existing and new updated information. More specifically, the same approach followed for the download of a selection of the dataset has been applied, implemented with a graphical-numerical comparison procedure between the new information and that already contained in the GEOBASI repository.

The uploading procedure of a new dataset, currently being developed, is possible thanks to a format of interchange (CSV, Comma Separated Value) similar to that of the downloading, currently operational. Its implementation will be realised through the same interface, open source software and services of the Lamma Consortium geoportal (Gianecchini et al., 2013).

Data accessibility, analysis of the information and interoperability

The validation process and accessibility requirements work in a similar way during the query formulation phase on the web interface. With the aim of taking this duality into account, a specific design of the web interface was developed to handle the requirements of clients and non-database administrators on different access levels. Functions for using temporal and spatial dimensions were also implemented, thus allowing the analysis of the geochemical information in relation to

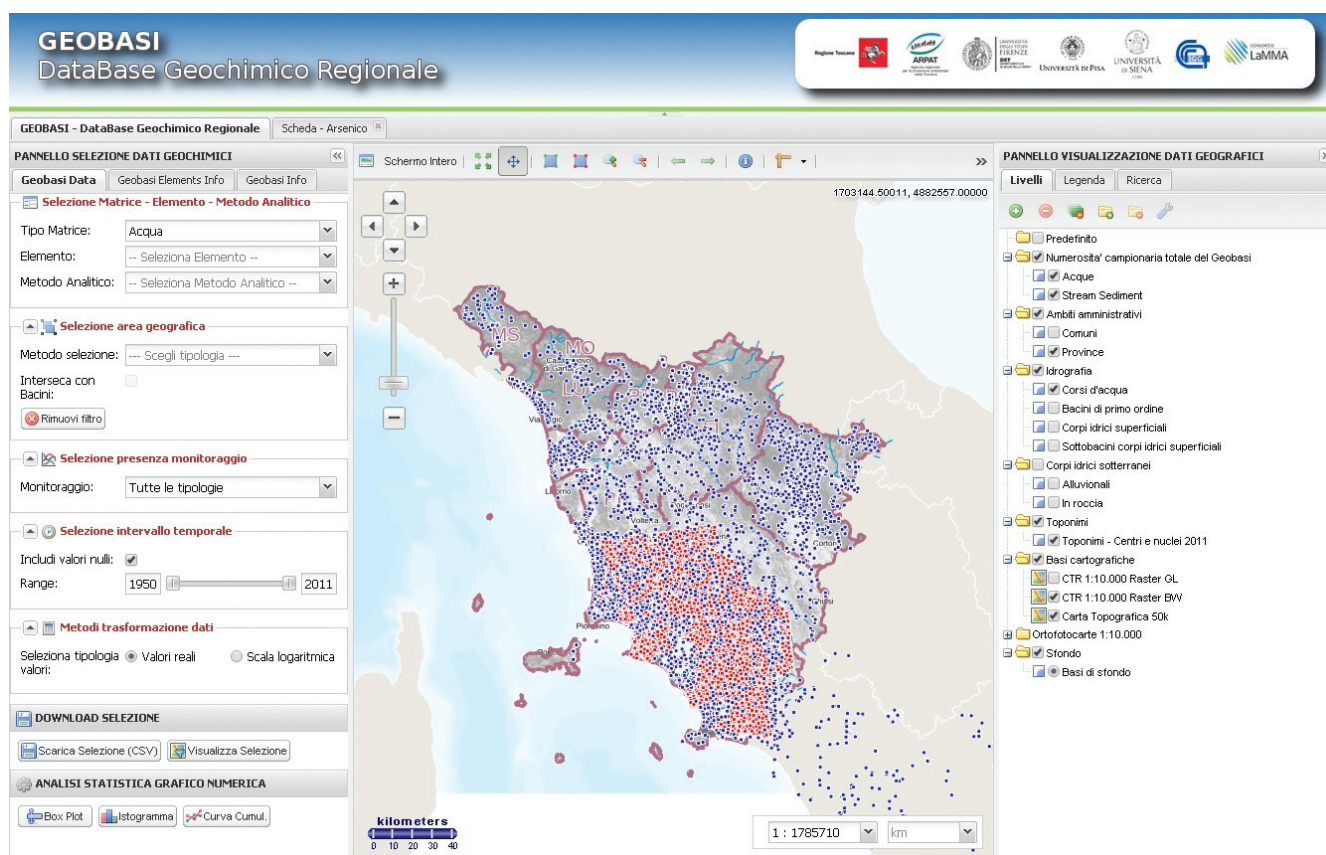


Fig. 1 - Visualisation of the user interface. Blue and red dots represent the available samples for water and stream sediment compositions.

Fig. 1 - Visualizzazione dell'interfaccia utente. I punti blu e rossi rappresentano rispettivamente i campioni disponibili per acque e sedimenti fluviali.

geology, land use, and the hydrological network, considering also accuracy and scalability requirements.

The web interface was constructed and implemented according to the Open Geospatial Consortium (OGC) standards (www.opengeospatial.org) focusing on research, query and view, then integrating these into a complex system where the comparison of the old information with the new uploaded one can be performed by the use of trigger procedures.

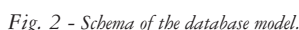
The analysis of the regionalised variables is in progress, evaluating the feasibility in a Web Processing Service (WPS) of analysing the uploaded information with the aim to discover errors and omissions in coordinates and in the metrical units of the geochemical data. In all phases particular attention was dedicated to underlining the presence of zero values (or negative values) instead of the respective analytical detection limit, to making comparisons among different analytical methods used to determine the same chemicals, to verifying the spatial coverage for the different geological media, and to integrating and linking together different information sources. As an additional feature, the surveyed data were distinguished from those derived from different geographical datasets.

On the whole, the core of the database is made up of primary chemical analysis, while derived information is useful for qualitative and functional evaluation in a territorial context.

It is important to stress here that all the problems encountered in the organisational phase of the database structure, as well as the strategies adopted for their solution, have allowed us also to define new tactics for future development (Fig. 2).

The web interface is compliant with the Inspire System which establishes an infrastructure for spatial information in Europe to support Community environmental policies, and for policies or activities which may have an impact on the environment (Fig. 3, <http://inspire.ec.europa.eu/>). As a matter of fact, the Geobasi interface adopts the Tuscany Regional Government OGC web services and uses this application for its own necessities and statistical processing, based on the Geoscopio, the Web-GIS tool by which the geographical data of Tuscany Region can be queried and visualised (<http://www.regione.toscana.it/-/geoscopio>). Thus orthophotos, topographic maps, geographical boundaries of administrative units, information about hydrological network, geology, land-use, pedology and all the other layers that constitute the Regional Database of Geographical Information are available. This operating schema highlights how the Geobasi project fits well into the general strategy of the Tuscany Regional Government to use an open data – open knowledge approach.

In figure 4 a general schema of the DB repository and the Web-GIS services interconnections is reported.



The integration between the geographical database and statistical analysis tools

Starting from the information store in the repository DB it is possible to query the behaviour of a chemical element or compound for a given geological media by the use of various univariate statistical graphical and numerical univariate tools. The results can be related to the regionalisation of the analysed data. Thus it is possible to link the chemical abundance of a chosen element in the different geological media with the geology, the land cover or the soil nature. Moreover, any other useful information about the behaviour of a given chemical element and sources (natural and anthropical as well as hazardous limits) is reported in a pdf file easily visualised or downloaded. Furthermore, the distribution of the element on a Europe scale can also be visualised thanks to a link with the maps of the FOREGS database (Salminen et al., 2005; De Vos et al., 2006) so that a comparison between the range of values reported in GEOBASI and those registered in Europe can be performed. At the moment this facility is activated for a limited number of elements but work is in progress.

When the GEOBASI portal is visited, it is possible to choose the appropriate geological material discriminating among solid (stream sediments) or liquid (waters and/or type of water) and, according to the selected variables, to generate comparative box-plots to identify the amount of variability attributable to different analytical methods, the most important source of heterogeneity of the repository. Then, after having chosen a specific analytical method a frequency histogram or a cumulative curve can be plotted visualising the spatial position of classes of values or single cases. The analysis can be repeated after having transformed the data by using the



Fig. 4 - Schema delle interconnessioni tra GEOBASI e input attraverso Web-GIS.

logarithm function or after having selected a specific portion of the Region or a defined time interval.

Examples for Ca^{2+} (mg/L) in water are reported in figure 5a. If the pdf file containing information about Ca is opened and visualised it is possible to see that this element belongs to group 2 of the periodic table, along with Be, Mg, Sr and Ba. It has an atomic number of 20, an atomic mass of 40, one oxidation state (+2) and six naturally occurring isotopes. Calcium generally has a high mobility and, except under strongly alkaline conditions, occurs in solution as dissociated Ca^{2+} ions. Concentrations generally grow with stream order as a result of increasing contact time between water and soil or rock. The main anthropogenic activity that would lead to an increase

of Ca in the drainage system is the long-established agricultural practice of liming land to correct for soil acidity. Other anthropogenic sources of calcium include cement factories, fertilisers and dust, although geogenic sources are much more important than anthropogenic ones in the environment (Reimann and de Caritat 1998). Calcium values in stream water of Europe range over three orders of magnitude, from 0.02 to 592 mg/L, with a median value of 40 mg/L (<http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php>, Salminen et al., 2005; De Vos et al., 2006) while in the GEOBASI values range from 0.7 to 952 mg/L up to 2000 mg/L if anomalous values are considered (median equal to 102 mg/L).

The diagrams of figure 5 have been implemented thanks

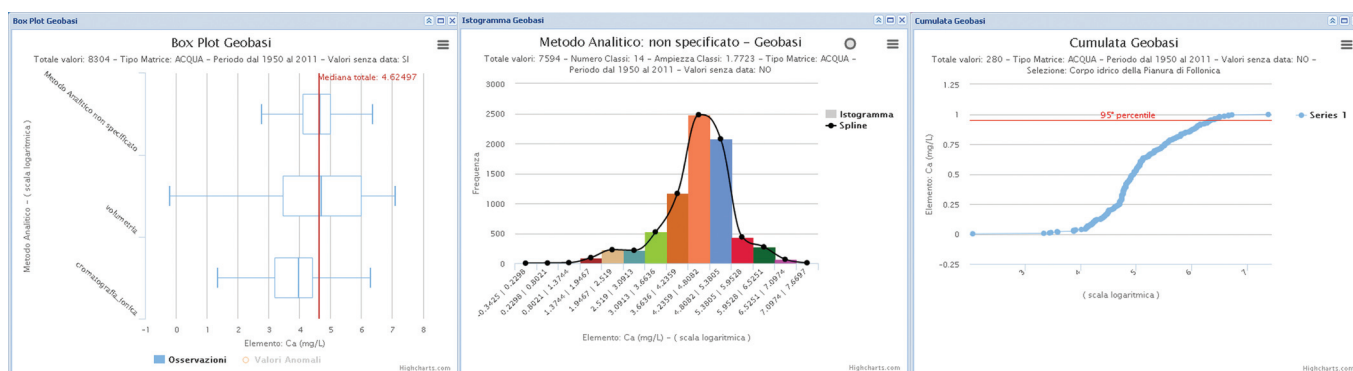


Fig. 5a - Left figure.

Fig. 5a - Figura sinistra.

Fig. 5a - Central figure.

Fig. 5a - Figura centrale.

Fig. 5a - Right figure.

Fig. 5a - Figura destra.

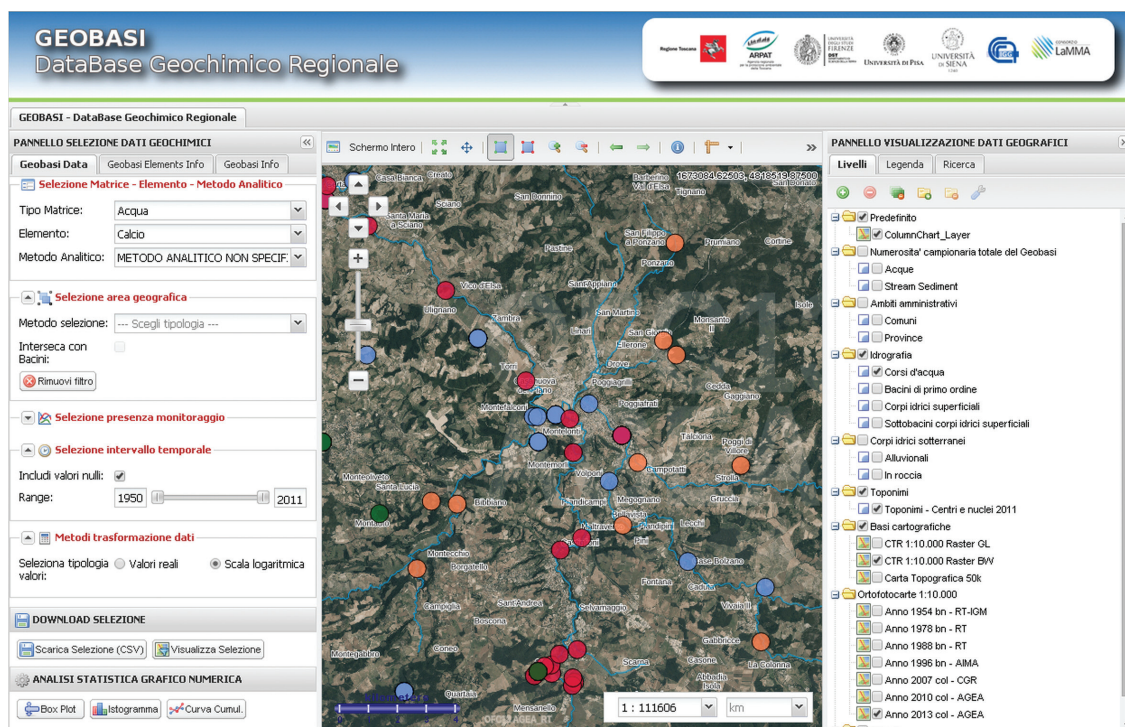
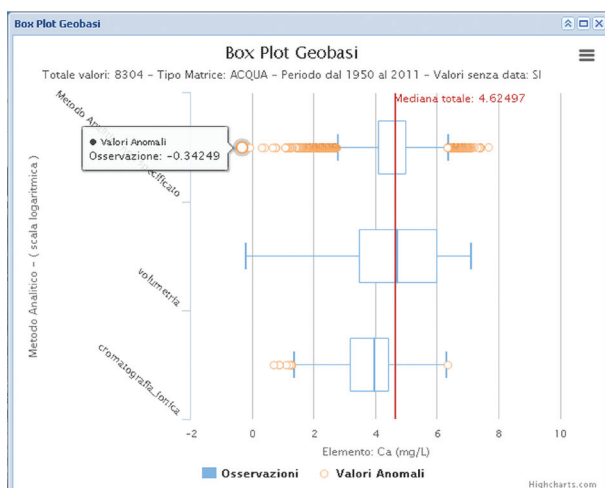


Fig. 5a - Interaction between statistical tools and Web-GIS interface. Box-plot, frequency histogram and cumulative curve are the fundamental tools to investigate the behaviour of a geochemical variable. Interactively the spatial position of the data pertaining to each class of the histogram can be visualised with dots of the same colour as the bars. Examples concern the abundance of Ca^{2+} (mg/L) in water.

Fig. 5a - Interazione tra strumenti statistici grafico-numerici ed interfaccia Web-GIS. Diagrammi a scatola, istogrammi di frequenza e curve cumulative sono strumenti fondamentali per studiare il comportamento di una variabile geochimica. La posizione spaziale dei dati appartenenti ad ogni classe dell'istogramma può essere interattivamente visualizzata sulla mappa. L'esempio riguarda il contenuto di Ca^{2+} (mg/L) nelle acque naturali.

to the use of the open source libraries of Highcharts (<http://www.highcharts.com>) written in pure JavaScript, offering an easy way of adding interactive charts to web site or web application. As we can see, when a chemical variable and a geological media is chosen, comparative box-plots (Fig. 5a, left) give us information about which type of analytical methods were used, the total number of available observations, the metric unit and the median for the whole data set. If some detailed choice was previously performed selecting an area of the regional territory or a specific time interval, the plot report will include these indications. When an analytical method is selected, a frequency histogram can be plotted (Fig. 5a, central). As we can observe, the classes of the histogram, obtained following Sturge's rule, are coloured differently, and by maintaining this colour discrimination their geographical visualisation is obtained. In this way it is possible to see immediately if the modal class is diffused or spatially clustered



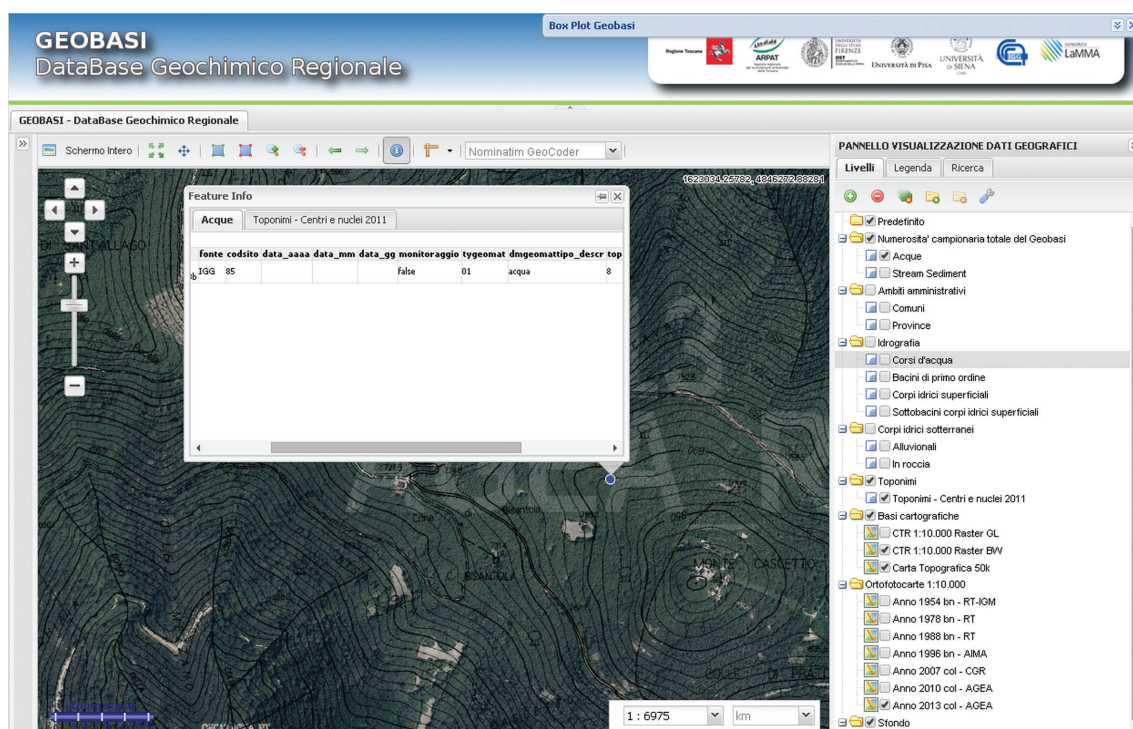
and if the less populated classes of the tails are related to specific portions of the regional territory. Dispersed and localised spatial processes can be consequently identified. A spline connects the mean value of each class giving us an idea about the continuous changes in the frequency density thus helping in the identification of complex multimodal phenomena.

The cumulative curve on the right of figure 5a-right is useful to identify the presence of anomalous data, comparing their values with the 95th percentile line reported above (red line). The analysis of the slope changes in the curve is also useful to verify if the behaviour of the investigated chemicals is fragmented and if multimodality better represents the investigated phenomena.

The previous graphical-numerical analysis can also be performed after having transformed the data by using the natural logarithm conversion in order to better visualise their structure. The identification of anomalous values as well as their spatial location is thus facilitated (Fig. 5b).

Fig. 5b - Anomalous low values for Ca^{2+} (mg/L) in water identified on box-plot for a specific analytical method (left, logarithmic scale) and their position on the map.

Fig. 5b - La posizione spaziale dei valori anomali bassi per il contenuto di Ca^{2+} (mg/L) relativi ad uno specifico metodo analitico e identificati mediante il diagramma a scatola (sinistra, scala logaritmica) può essere visualizzata su una mappa.



In the future the same graphical analysis will be implemented by using libraries of the open source R software (<http://www.r-project.org>) since these also contain fundamental tools for the development of geostatistical analysis. Innovative graphical and numerical tools will also be developed by taking into account the nature of compositional data as reported by Aitchison (1986). Compositional data are in fact vectors of positive values quantitatively describing the contribution of D parts of some whole, which carry only relative information. Due to these features, the Euclidean geometrical approach to the statistical analysis of compositions may give misleading results since compositional data pertain to the simplex sample space and not to the Real one (Egozcue and Pawłowsky-Glahn, 2006; Buccianti and Magli, 2011; Buccianti, 2013). The simplex sample space is governed by the Aitchison geometry, and has all the properties of a (D-1) dimensional Euclidean space (Egozcue and Pawłowsky-Glahn, 2006). To work in these unconstrained conditions, compositions need to be expressed as vectors of values that belong to such a space. To obtain these new vectors a family of log-ratio transformations can be used. Several improvements will have to be made to GEOBASI following this new perspective, as a natural way of representing regionalised compositions.

Preliminary results and discussion

With the aim to probe the efficiency and validity of the functions developed in the GEOBASI project for the uploading of new information from a controlled source, a case study area was selected where ground waters were collected, analysed and new numerical data produced. The Follonica-Scarlino plain was chosen and, in particular, the aquifer of the area as well as the network of surficial waters and stream sediments. The integration of the previously available numerical data and the new one was performed in tandem with the production of the experimental data by the IGG-CNR of Pisa (water samples) and Siena University (stream sediments).

It has to be stressed here that the new experimental data was collected within a planned sampling design concerning springs, groundwater, stream waters and stream sediments. In this phase the old knowledge stored in the database permitted the evaluation of where to collect new samples using the stored indications on the range of values for different chemicals and the area covered. The Follonica-Scarlino plain presents a peculiar interest on a regional scale, due to the presence of both point and diffuse sources of pollution whose origin is attributable to both natural and anthropic factors. Consequently, these conditions also make the area potentially representative of the problems that it is possible to encounter when the baseline of a chemical has to be defined. Finally, since a limited portion of the territory is investigated, the application of geostatistical methods can be evaluated in terms of verifying the presence of spatial continuity, with the aim to constrain the behaviour of geochemical variables in space and to set the boundary conditions of the conceptual model.

More specifically the area was chosen as the 'case study' for the following reasons: 1) the hydrographical basin dimension-

ally limited; 2) a geological context where the water-rock interaction processes modifying the water chemistry could be identified; 3) the possibility to calculate the mass-balance for elements and compounds on the basin scale; 4) the presence of important natural and anthropic phenomena able to perturb the most frequent and diffused compositions (hot springs, acid drainage from mines, dispersion of waste products due to pyrite manufacturing, presence of well developed soils); 5) the availability of a significant number of wells for drinkable water; 6) the past knowledge about geological and hydrogeological framework as a starting point.

Based on the derivation of existing geochemical information (about 500 records stored in the GEOBASI database) and on its chemical variability and spatial dispersion of samples, the sampling strategy was planned to assess the future application of an appropriate geo-statistical approach for estimation. The discussion on this item represented also the occasion to define a joint protocol for the management of the experimental phase.

The sampling campaigns permitted the measurement of the phreatic surface level for 128 locations and to collect 105 samples of surficial waters (Pecora river, Allacianti canal, and Gora delle Ferriere stream), 65 of groundwaters and more than 10 from the Fiora aqueduct. Measures of pH, temperature, electrical conductivity (EC), alkalinity, as well as of the abundance of Fe^{2+} and Fe_{tot} (with dedicated kit) were determined on site, repeating the measurements for metals also in laboratory.

In particular, the temperature, pH, and EC were measured using Eutech Instruments PCD650 multiparametric probe. Total alkalinity was determined by acidimetric titration using HCl 0.1 N as titrating agent and methylorange as indicator.

Laboratory analyses have permitted to obtain the concentrations of the main constituents such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , of the nitrogen and minor species, NO_2^- , NO_3^- , NH_4^+ , F^- , H_4SiO_4 and of some metals (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl, V and Zn). In particular: (i) anions were determined using ion-chromatography (Dionex DX-100), whereas, F^- was measured using the specific electrode method (Orion Research EA920); (ii) major dissolved cations and trace metals were determined by AAS Perkin Elmer mod. 3110 and ICP-OES (Perkin Elmer Optima 2000DV), respectively; (iii) silica was analysed by molecular spectrophotometry using the heteropoly blue method (spectrophotometer Jasco V-530) and (iv) nitrogen species were analysed by molecular spectrophotometry (spectrophotometer Jasco V-530).

In order to have indications about the hydrological cycle of the water fluxes, the hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotopic ratios were determined through mass spectrometer analysis by Delta Plus XP (ThermoFinnigan). Analytical precision was better than 0.10‰ and 1‰ for $\delta^{18}\text{O}$ ‰ and $\delta^2\text{H}$, respectively. For a selected number of samples the determination of the tritium content, able to indicate the age of the recharge of the different reservoirs, was also performed. Tritium was analysed through measurement of β^- decay events in a liquid scintillation counter. Direct liquid-scintillation counting has

a precision of 7 TU. For tritium contents lower than 20 TU, increased precision is gained through concentration by electrolytic enrichment of ^3H in the water before counting, thus reaching a precision better than 0.8 TU.

The availability of a detailed stratigraphy for about 200 locations has allowed us to reconstruct the permeability levels for the multistrata aquifer, by estimating their relative volumes thus contributing to constrain the conceptual model of the geochemical system.

In figure 6 the limits of the hydrological body of the Follonica-Scarlinò plain are visualised. The coloured dots correspond to the different classes of the frequency histogram referring to the Ca abundance (mg/L) in groundwater as reported on the right.

In figure 7 some of the other features of the GEOBASI project are illustrated considering, as an example, the spatial distribution of As (mg/L) in the waters of the Follonica-Scarlinò plain for the already available data. Arsenic, along with P, Sb and Bi, is a chemical element belonging to group 15 of the periodic table. The element has an atomic number of 33, an atomic mass of 75, three main oxidation states (-3, +3 and +5) and one naturally occurring isotope (^{75}As). The chemistry and geochemistry of As is most similar to that of Sb. Arsenic is strongly chalcophile, and is partitioned into a variety

of sulphide and sulpharsenide minerals, notably arsenopyrite FeAsS , but also realgar AsS and orpiment As_2S_3 . Even if As minerals and compounds are readily soluble, As migration is greatly limited, because of strong sorption by clays, hydroxides and organic matter; the latter may have a marked influence on the measured As concentration (Reimann et al. 2003). Arsenic values in stream water of Europe range from <0.01 to 27.3 $\mu\text{g/L}$, over three orders of magnitude, with a median value of 0.63 $\mu\text{g/L}$ (<http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php>). The arsenic distribution in Europe resembles generally the distributions of Mo, Sb, Se, U and V, although concentrations in alkaline stream water in the Mediterranean region tend to be enhanced. The distribution of As in stream water is most similar to patterns of major ions and associated elements, controlled mostly by exogenic and less geogenic factors, but also to felsic element patterns explained by geogenic sources of As in central and southern Europe.

As we can see (Fig. 7), the spatial visualisation of selected classes of a complex frequency distribution, for example A, B and C, can be performed. Moreover, it is possible to evaluate if the classes of the histogram contain or not some reference values, as for example those proposed by ARPAT for the As natural background (VNF = valori fondo naturale) and the admissible background (VFA = valori di fondo ammissibili)

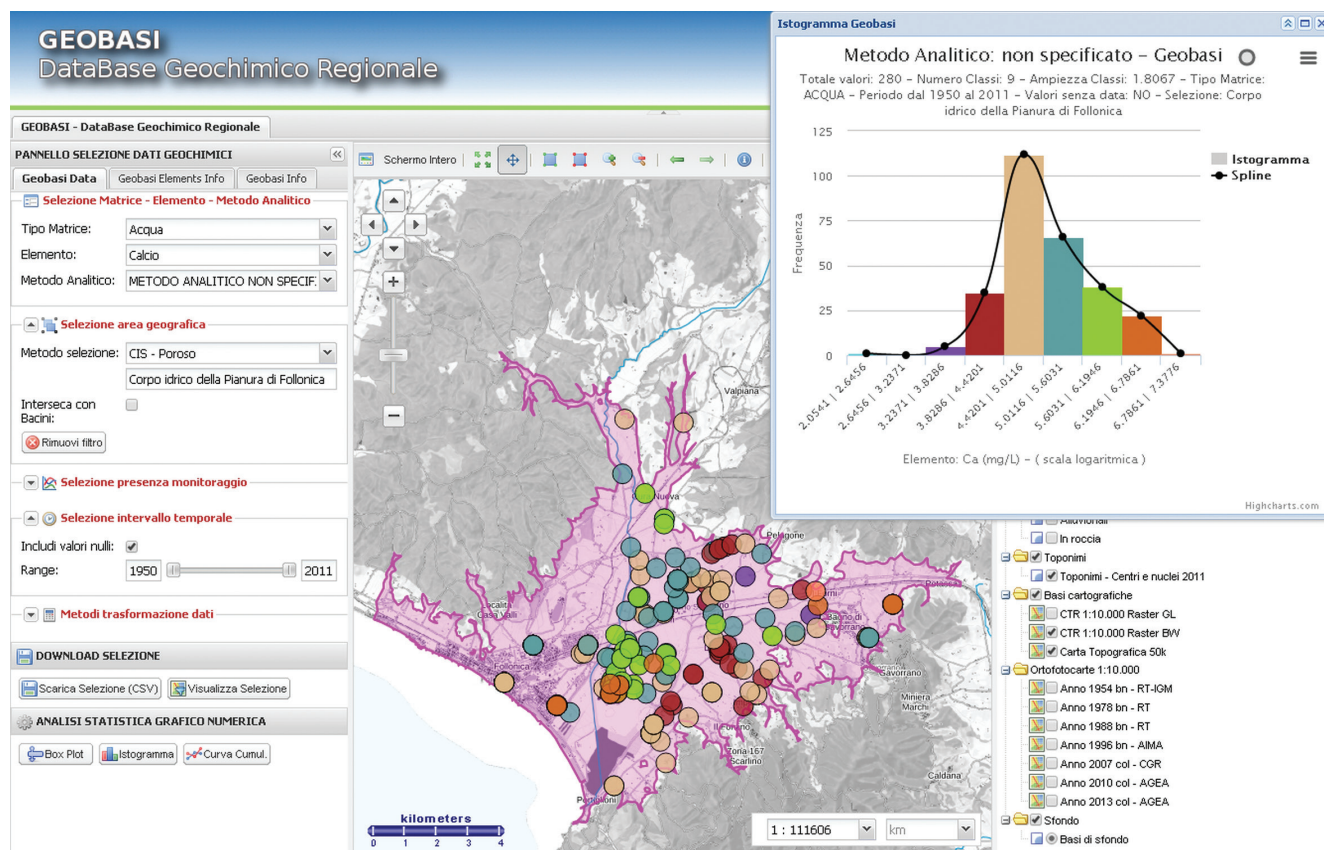


Fig. 6 - Case study area of Follonica-Scarlinò plain. Dots in different colours are related to the different classes of the frequency histogram for Ca^{2+} abundance (mg/L) for the available water data.

Fig. 6 - Caso studio dell'area della piana di Follonica-Scarlinò. I punti con differenti colori sono associati alle diverse classi dell'istogramma di frequenza per il contenuto di Ca^{2+} (mg/L) per i dati disponibili per le acque naturali.

values. For example in figure 7 the upper values of classes A and B are lower than $VNF = 5.5 \mu\text{g/L}$ and $VFA = 23 \mu\text{g/L}$, respectively, and the samples are spatially distributed. On the other hand, class C apparently contains point sources to be related with local phenomena.

As a further step, methods to analyse the spatial dimension of geochemical phenomena will be developed and implemented creating and/or executing R scripts for geostatistical analysis in QGIS, a free Open Source Geographic Information System (www.qgis.org). The aim is to focus the attention on the identification of a possible baseline whose significant identification cannot be performed without the analysis of the spatial continuity of the investigated phenomena.

Conclusions and future developments

The widespread use of hazardous substances in several anthropic processes (e.g. industry and agriculture), legal or illegal, has compromised the use of the territory and of its resources both in developed and underdeveloped countries

of the world. For this reason knowledge about the distribution of dangerous elements or compounds is fundamental and different public institutions on international and national scale have attempted to control this problem through specific acts and laws. The starting point is however related to the organisation and management of the available geochemical information and to the possibility of integrating it with geographical, geological and hydrogeological complements. Several types of geological media (e.g., waters, soils, stream sediments, gases) are in general the subjects of a great number of research products or public monitoring plans, on different scales. Often the quality of the measurements may be different but all the works have as a common aim to give a picture of the state of the investigated environment. If this available information can be integrated and validated in a dedicated dynamical repository, as well as updated in time, our knowledge about geochemical processes, their frequency and spatial distribution will increase. Furthermore, if the repository is constructed in order to correlate the geochemical records with

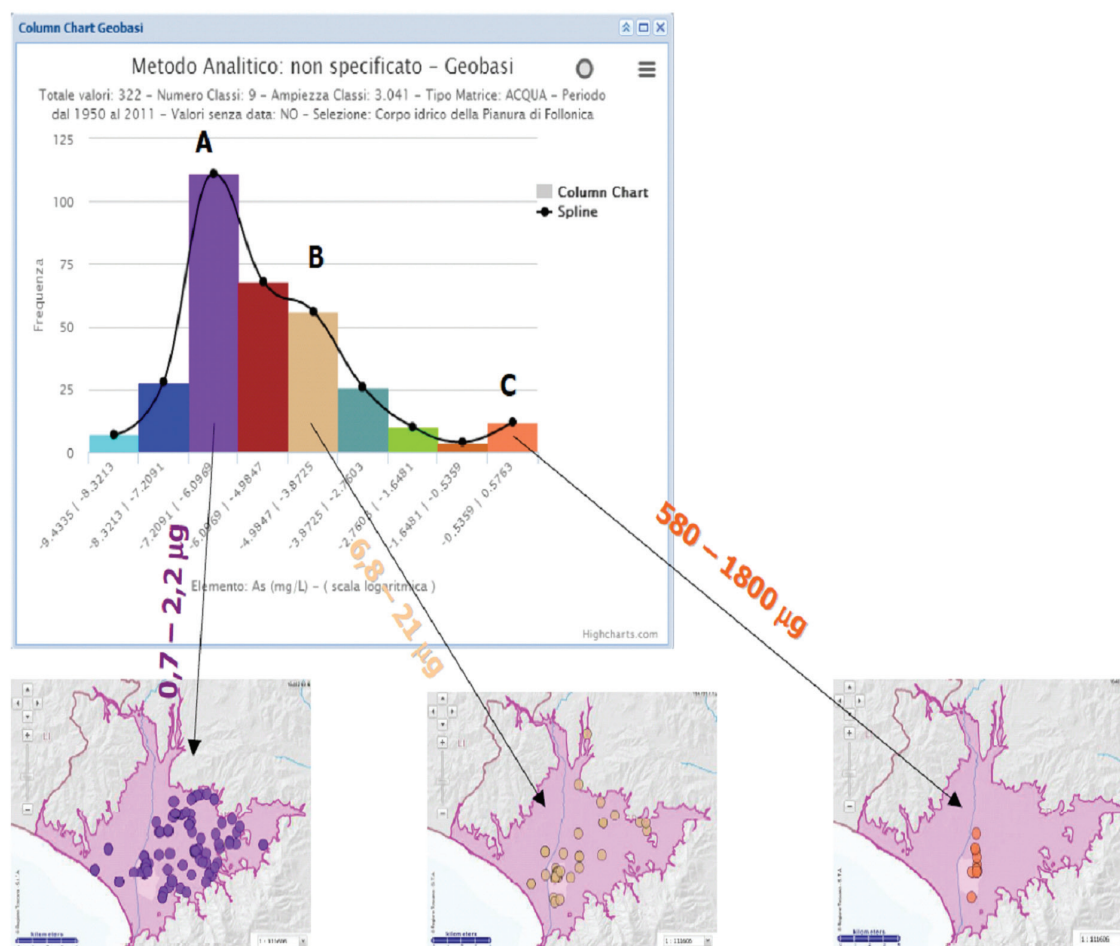


Fig. 7 - Application of the GEOBASI tools for the pilot area of the Follonica-Scarlino plain. The frequency distribution of As (mg/L) in waters is analysed and the spatial distribution of data of selected classes visualised. The upper values of classes A and B are lower than the ARPAT proposed $VNF = 5.5 \mu\text{g/L}$ and $VFA = 23 \mu\text{g/L}$ values (VNF = natural background values; VFA = admissible background values).

Fig. 7 - Applicazione degli strumenti del GEOBASI per l'area pilota della piana di Scarlino-Follonica. E' analizzata la distribuzione di frequenza dell'As (mg/L) e visualizzata la distribuzione spaziale dei dati presenti nelle varie classi dell'istogramma. I valori superiori delle classi A e B sono inferiori ai valori di fondo naturale ($VNF = 5.5 \mu\text{g/L}$) e di fondo ammissibile ($VFA = 23 \mu\text{g/L}$) come proposti da ARPAT.

other types of information paralleling and standardising the statistical and geostatistical analysis, the possibility to define baseline values will be facilitated giving us a concise and realistic reading of what is occurring in the environment.

By taking into account all the previous indications, the main aim of the development of the GEOBASI database has been to have a dedicated informatics support to manage all the present validated geochemical knowledge available for Tuscany Region, giving the opportunity to integrate it with other geographical, geological and hydrogeological information on different scales, regional and/or limited to a specific portion of the region. Most of the information was obtained from research works and monitoring plans of universities and public institutions initially collected, structured and organised inside the National Geochemical Archive (NGA) project.

At the current phase of development it is possible to query the database with the aim to receive information about the available geochemical knowledge of the regional territory for different geological media and compounds, including hazardous ones. An initial spatial distribution of the data as well as relationships with geology, land use and the hydrological network can be already obtained, as well as information about the different analytical methods used for the available experimental data. Plans are scheduled to associate explicative notes to each element or compound so that indications about the geochemical behaviour, source materials, reference law terms and effects on health can be obtained and downloaded. This work is in progress as well as the uploading of the new experimental data of the samples drawn from the pilot area of the Follonica-Scarlino plain, when the analytical phase is concluded. Their statistical and geostatistical analysis within the database will be the test-bed for the integration of old and new information but it will also permit the identification of the problems that it is possible to encounter when the geochemical baseline for some chemicals has to be defined. The problem-solving procedure will be useful to finalise the upcoming work and to draw up a shared protocol to map geochemical variables and to evaluate their baseline.

Summarising it is possible to say that the two main ambitious targets of GEOBASI are: 1) to collect all the geochemical information available for the Tuscany region under the same structured framework for free public access, and 2) to define a shared protocol among all the participants of the project, starting from the sampling design and the analytical methods for experimental data to the statistical and geostatistical analysis of the numerical information (Isaaks and Srivastava, 1989; Cressie, 1993). The basic idea is that geochemical maps can be used to evaluate natural phenomena and baseline concentrations only if some main directives have been followed starting from the field phase to the restitution of the results.

In the design of a before and after evaluation, baseline studies are a critical element in the formula for measuring change over time. A baseline study is required for every type of operation in an environmental context. However, the rigor of the methods used to establish baseline conditions varies according to the type of operation being implemented. A com-

promise must be reached between the need for robust, precise data to establish pre-operation exposure conditions and the cost of collecting such data in terms of resources (financial, human and time). National Programs that are focused on development should invest more resources and, as a result, conduct more rigorous baseline studies. However, initiatives like GEOBASI could provide significant assistance and reduce the associated costs by furnishing an integrated platform for the utilisation of the entire body of existing data and the optimised design and planning of new measurement campaigns.

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REFERENCES

- Aitchison J. (1986). The statistical analysis of compositional data, Reprint by The Blackburn Press, New Jersey, USA, 2003.
- Ander E.L., Johnson C.C., Cave M. R., Palumbo-Roe B., Nathanail C.P., Murray Lark R. (2013). Methodology for the determination of normal background concentrations of contaminants in English soil. *Science of the Total Environment* 454-455(1): 604-618. DOI:10.1016/j.scitotenv.2013.03.005.
- Bottaini N.J., Buccianti A., Di Lella L.A., Macera P., Marini L., Nannoni F., Protano G., Raco B. (2011). Testing of innovative approaches in geochemical mapping: the experience of the Geobasi Toscana project, VIII forum Italiano di Scienze della Terra, Geitalia 2011, Torino, 19-23. Poster. *Epitome* 4, 04-0330, pg. 90.
- Buccianti, A., Magli, R. (2011). Metric concepts and implications in describing compositional changes for world river' chemistry. *Computer & Geosciences* 37(5): 670-676. DOI:10.1016/j.cageo.2010.04.017
- Buccianti A., Macera P., Marini L., Protano G., Raco B. (2011). Progetto: GeoBasi - Toscana Piano Regionale di Azione Ambientale - PRAA 2009 Obiettivo E – Tutela della Risorsa Idrica, Relazione Finale, Dicembre 2011: 1-176 pp.
- Buccianti, A. (2013). Is compositional data analysis a way to see beyond the illusion? *Computer & Geosciences* 50: 165-173. DOI:10.1016/j.cageo.2012.06.012
- Buccianti A., Nisi B., Raco B. (2014). Compositional background for groundwater chemistry: the experience of the Geobasi project, Tuscany region (central Italy), GeoMap Workshop proceeding 17th-20th June, Olomouc, Czech Republic.
- Cressie N.A.C. (1993). *Statistics for Spatial Data*. Revised version, Wiley series in Probability and Mathematical Statistics, John Wiley & Sons, New York, 900 pp., isbn: 0-471-00255-0.
- De Vos W., Tarvainen T., Salminen R., Reeder S., De Vivo B., Demetriades A., Pirc S., Batista M. J., Marsina K., Ottesen R. T., O'Connor P. J., Bidovec M., Lima A., Siewers U., Smith B., Taylor H., Shaw R., Salpeteur I., Gregorauskiene V., Halamic J., Slaninka I., Lax K., Gravepe P., Birke M., Breward N., Ander E.L., Jordan G., Duris M., Klein P., Locutura J., Bel-Lan A., Pasieczna A., Lis J., Mazreku A., Gilucis A., Heitzmann P., Klaver G. and Petersell V. (2006). *Geochemical Atlas of Europe. Part 2. Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications*. Geological Survey of Finland, Espoo, 690 pp. – isbn: 951-690-956-6.

- Egozcue J.J., Pawłowsky-Glahn V. (2006). Simplicial geometry for compositional data, in: Buccianti, A., Mateu-Figuera G., Pawłowsky-Glahn V. (Eds.), *Compositional Data Analysis in the Geosciences: from theory to practice*. Special Publications n. 264, Geological Society, London, 12-28.
- Gałaszka A. (2005). The chemistry of soils, rocks and plant bioindicators in three ecosystems of the Holy Cross Mountains, Poland, *Environmental Monitoring and Assessment* 110: 55–70. DOI:10.1007/s10661-005-6290-1
- Gałaszka A. (2006). Methods of determining geochemical background in environmental studies. *Problems of landscape ecology*, Polish Association of Landscape Ecology, Warsaw (in Polish with English summary) XVI/1: 507–519.
- Gałaszka A. (2007). A review of geochemical background concepts and an example using data from Poland, *Environmental Geology*, 52: 861–870. DOI:10.1007/s00254-006-0528-2.
- Giannecchini S., Mari R., Corongiu M., Bottai L., Fibbi L., Pasi F. (2013). Geoportale del Consorzio LaMMA, *Rivista Geomedia*: 5: 12-16 – issn: 1128-8132.
- Isaaks E.H., Srivastava R.M. (1989). *Applied Geostatistics*, Oxford University Press, 561 pp., isbn: 0-19-505013-4
- Johnson C. J., Ander E. L. (2008). Urban geochemical mapping: How and why we do them. *Environmental Geochemistry and Health* 30: 511–530. DOI:10.1007/s10653-008-9189-2.
- Levitan D.M., Schreiber M.E., Seal R.R., Bodnar R.J., Aylor J.G. (2014). Developing protocols for geochemical baseline studies: an example from the Coles Hill uranium deposit, Virginia, USA. *Applied Geochemistry* 43: 88-100. DOI:10.1016/j.apgeochem.2014.02.007.
- Ottonello G., Serva L. (2003). *Geochemical Baselines of Italy*, Pacini Editore, Pisa, 294 pp., isbn: 88-7781-532-9.
- Reimann C., de Caritat P. (1998). *Chemical elements in the environment-factsheets for the geochemist and environmental scientist*. Berlin, Germany Springer-Verlag, isbn: 3-540-63670-6.
- Reimann, C., Siewers, U., Tarvainen, T., Bityukova, L., Erikson, A., Gilucis, V., Gregorauskiene, V., Lukasev, V.K., Matinian, N.N., Pasieczna, A. (2003). *Agricultural Soils in Northern Europe: a Geochemical Atlas*. *Geologisches Jahrbuch Sonderhefte Reihe D Heft 5* Stuttgart.
- Reimann C., Garrett R.G. (2005). Geochemical background-concept and reality. *Science of the Total Environment*, 350(1-3): 12-27. DOI:10.1016/j.scitotenv.2005.01.047.
- Rodrigues A.S.L., Nalini Júnior H.A. (2009). Geochemical background values and its implications in environmental studies. *REM (Revista Escola de Minas, Ouro Preto)* 62(2): 155-165.
- Salminen, R., Batista M. J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., Mrnkova J., O'Connor P. J., Olsson S., Ottesen R.-T., Petersell V., Plant J. A., Reeder S., Salpeteu I., Sandström H., Siewers U., Steenfelt A. and Tarvaine T. (2005). *FOREGS Geochemical Atlas of Europe. Part 1. Background Information, Methodology, and Maps*. Geological Survey of Finland, Espoo. 525 pp., isbn: 951-690-913-2 (Electronic publication, URL address: <http://gtk/publ/foregsatlas>, March 15, 2005).