ORGANIC POLLUTANT UPTAKE BY VEGETABLE PROBES AND BIOMONITORING OF MOSS-LINKED METALS IN REGIONS OF NORTHERN ITALY.

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ABSTRACT

A biomonitoring survey to evaluate the atmospheric deposition of the elements Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Ti, V and Zn was carried out by the moss *Hypnum cupressiforme* in the Aosta Valley and Piedmont. An assessment was also made of the element concentrations in soil samples taken from under the moss. The moss and soil concentrations were investigated using Principal Components Analysis (PCA) and the Geographic Information System (GIS). These analysis resulted in visual representations of the metal distribution in the moss and soil, and the recognition of sites polluted contemporaneously by different metals. Literature data of uptake by various plants have been collected and studied by multivariate analysis (PCA) and QSAR (Quantitative Structure-Activity Relationships) modelling. The combined analysis and modelling allows greater insight into the information obtained using plants as biological probes of chemical environmental distribution.

INTRODUCTION

The emergency created by environmental pollution, caused by human activities (both industrial and domestic), means that tools are needed to determine the quality and quantity of pollutants in the environment. Recording system are necessary to identify appropriate strategies of reduction of pollutants emitted and to verify, afterwards, the effectiveness or the inadequacy of measures taken. Technological research has provided and improved instrument systems to record air, soil, water and biota pollution. Since these instruments are often characterized by high cost just few of them are usually applied; moreover being these techniques projected to record only certain substances, they are unable to detect the presence of new pollutants. In order to complete the information given by the technical instruments there is a spreading use of living organisms to detect the presence of pollutants and to determine their effect on live communities.

MATERIALS & METHODS

Data of uptake by plants (*Azalea indica, Chicorium endivia, Daucus carota, Fagus silvatica, Hypnum cupressiforme, Lactuca sativa, Parmelia sulcata and Picea abies*) for 44 substances (pesticides, PAHs, PCBs, etc.), have been collected from the literature [1-6] and used to develop predictive QSAR models for the BioConcentration Tendency (BCT).

Multiple Linear Regression analysis and variable selection were performed by the software MOBY DIGS using the *Ordinary Least Square Regression* (OLS) method and GA-VSS (*Genetic Algorithm-Variable Subset Selection*) [7].

Internal validation procedures: *leave-one-out* (LOO) BOOTSTRAP (*boot*) and responses randomisation (Y-scrambling)

Chemical domain of applicability: verified by the l*everage* approach

External validation [8] performed on validation set obtained by splitting of the original data set into a training set of 26 molecules and a validation set of 18 chemicals by applying Kohonen Artificial Neural Networks (K-ANNs) using the *KOALA* software [9].

Principal Component Analysis

Molecular Descriptors were calculated by the software *DRAGON* Ver. 5.2:

OD: Constitutional descriptors.; 1D: Empirical, Functional groups, Properties, Atom-centred fragments descriptors.; 2D: Autocorrelations, Topological, Molecular walk counts, Galvez topological charge indices, BCUT descriptors.; 3D: Geometrical, WHIM, GETAWAY, Charge descriptors. [10].

RESULTS & DISCUSSIONS

BIOCONCENTRATION TENDENCY (BCT)

The Principal Component Analysis (PCA) of the experimental and predicted log BCF (BioConcentration Factor) of 44 compounds in plants allows the ranking of the chemicals according to their tendency accumulation in leaves or in roots. A **BioConcentration Tendency** is obtained from the linear combination of log BCF data (PC1 score, E.V%=61.2%, in Fig.1).

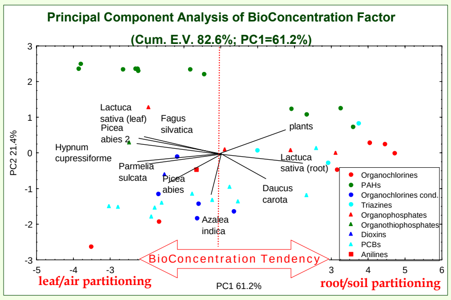


Figure 1

The chemicals on the right are the most accumulated in the root while those on the left are the most accumulated in the leaf .

The PC1 score was modelled by theoretical molecular descriptors, to have a fast method to rank the compounds according to their bioaccumulation tendency in roots or leaves.

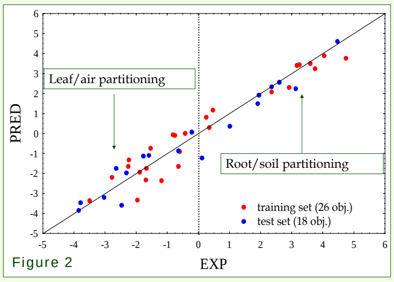


Figure 2

The "best model" (Fig.2), selected by the Genetic Algorithm, was verified for its stability and predictivity by internal and external validation.

PC1score=7.04-0.02(±0.0007) Whete

Stable and predictive model!!!

R^2	Q^2	Q^2_{ext}
0.94	0.93	0.95

Whete is a topological descriptor (Wiener-type index from electronegativity weighted distance matrix).

CONCLUSIONS

- A new predictive linear model for **BioConcentration Tendency** is proposed.
- This model is based only on theoretical molecular descriptors.
- Genetic Algorithm is applied for Variable Subset Selection.
- Internal and external validations demonstrate the stability of the models.
- BCT values also for new chemicals can be predicted.

MATERIALS & METHODS

Data: Soil and mosses samples were collected in 41 sites in Piedmont and in 20 sites in Aosta Valley.

The methodology adopted for the samples analysis was applied according to the A.N.P.A. method [11].

The heavy metals Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti, V, Zn e Hg were investigated.

Principal Components Analysis (PCA): linear combinations of the input variables (metal concentration in this case) to new uncorrelated variables, called principal components, which account for the variance in the data. The first PC explains the main part of the variance of the original data set.

Geostatistical Methods and Mapping: each data set was transformed in logarithmic units. The heavy metal levels were shown on contour maps using the coordinates of sampling sites. Maps were obtained using an universal kriging interpolator [12].

RESULTS & DISCUSSIONS

Principal Components Analysis (PCA) of metal concentrations in Aosta Valley and Piedmont mosses and soils was performed in order to have a multivariate view and a graphic representation of the overall metal distribution in mosses and soils in the studied sites (Fig.3) identifying the most polluted zones. The normalization of the concentration values of heavy metals in soils and mosses, considering Al as the conservative element, allows the discrimination between anthropogenic and natural heavy metals' sources using the following formula: Enrichment Factor (EF)= [(X moss/Al moss)/(X soil/Al soil)]

EF<10 : heavy metals' concentrations observed in moss are related to their concentration in soil and/or substrate (natural sources);

EF≥10 : heavy metal's concentrations observed in moss could be originated by anthropogenic activity and/or natural events such as volcanic eruptions and large forest fires.

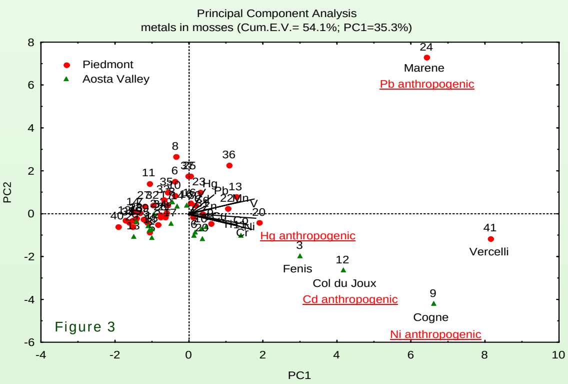
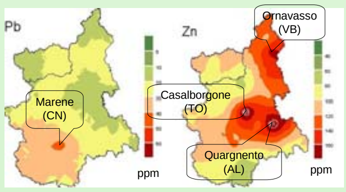


Figure 3

The GIS approach was adopted to distinguish the sites characterized by high concentration of Cd, Cu, Hg, Ni Pb and Zn in Piedmont and in Aosta Valley. The results are presented in the form of coloured maps reported below.



road traffic
non-ferrous metal industries

textile and engineering industries,
electric power plants, waste incinerators

Figure 4 - **Pb and Zn in mosses**

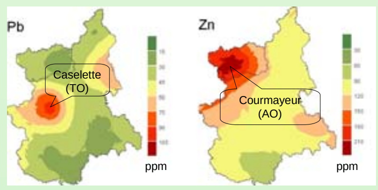


Figure 5 - **Pb and Zn in soils**

CONCLUSIONS

- Mosses are good indicators of atmospheric pollution by heavy metals useful for the monitoring at a regional scale, for the estimation of the actual contamination or of the temporal changes in contamination.
- PCA performed on heavy metals concentrations measured in Piedmont and Aosta Valley sites, identified the most polluted sites and the similarity in pollution typology.
- GIS mapping is useful for immediate visualization of metal distribution and contamination level in a region.

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