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How Useful Classical Chemometrical Approaches Can Be In Environmental Assessment? A Case Study About Source Identification for Dioxins and Furans in an Urban-Industrial Coastal Area

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Abstract

Data about presence of dioxins and furans from different types of matrices - namely atmospheric powders, soils, industrial emissions and ash - were collected for samples coming from the coastal urban - industrial area around the city of Trieste (NE-Italy). Classical pattern recognition techniques, as principal component analysis and hierarchical cluster analysis, have been applied in order to identify fingerprints of industrial sources and to highlight origin of unknown environmental samples. Since we are chemometricians, we discuss about undesired chemical reactions that occur within industrial processes generating such pollutants and possible technological remediation.

Introduction

Persistent Organic Pollutants (POPs) represent a well known environmental global problem, since they are hardly decomposed, they can bioaccumulate and exert various toxicological actions; international conventions and resolutions try to deal with this criticality, as the UNEP Stockholm convention written in 2000 and entered into force in 2004. Polychlorinated dibenzo-dioxins (PCDDs) and -furans (PCDFs) belong to the list of dangerous POPs and some of them have been recognized as carcinogens for humans. Also at local scale these compounds can represent a problem, and authorization of economical activities by local authorities requires often measurements of PCDDs and PCDFs, for instance for building commercial and recreational sites on soils, or on industrial emissions from industrial plants as waste incineration plants, steel plants or cement industry. Relative abundance of isomers and congeners of such compounds in a sample can be considered as conservative parameter, being typical for the process that produced the contaminants and thus as marker or "fingerprints" of the sources.

In recent years several data sets on PCDDs and PCDFs have been produced during monitoning campaigns within the province of Trieste (NE Italy); an integrative study has been started on such evidences in order to show patterns and assess and manage such environmental risk. The methodological approach that is being used is presented in this study, showing the complementary information that is provided by data pre-treatment, hierarchical cluster analysis and factorial models.

Materials & Methods

A data set containing both environmental input measurements and industrial output (emissions) has been built, where fifteen PCDDs and PCDFs are the variables. Industrial emission data refers to the sinter-plant operating within local steel works and to different incineration lines of the active waste thermovalorization plant; environmental inputs are data about composition of atmospheric particles sampled in 2002 and 2006 campaigns, of ashes from a dismissed disposal site and from contaminated top soils. All data have been produced by experienced sampling teams and laboratories, following thorough QA/QC practices. Statistical analysis have been performed using the SPSS 11.01 package or routines written for the MATLAB 6 environment.

Results

The issue of pre-treatment is addressed, in order to cope with data from different environmental matrices and unit of measurements (as concentration in air and soils): molar fractions and row scaling are considered. Principal components analysis, followed by Varimax rotation, is used to study correlations between isomers and congeners and to visualize discriminating power of groups of dioxins and furans. Results from hierarchical cluster analysis using squared euclidean distance and Ward method as linkage algorithm are shown in figure 1. Three main cluster are shown, the first one grouping samples of incineration ashes (shown as G*v*), contamined top soils (TSB*w*) and air particles close to waste treatment site (SSM*x*); the second collects most of air particles and the third one emissions from the sinter plant (E5*y)* and air particulate from the site closer to it (MSP*z*). Profiles of centroids from the clusters can be used to identify main tipologies of contamination in the area. Cluster one shows predominance of perchlorinated dioxin ("incineration type" profile), while in cluster three there is abundance of highly chlorinated furans ("steel work" type profile).

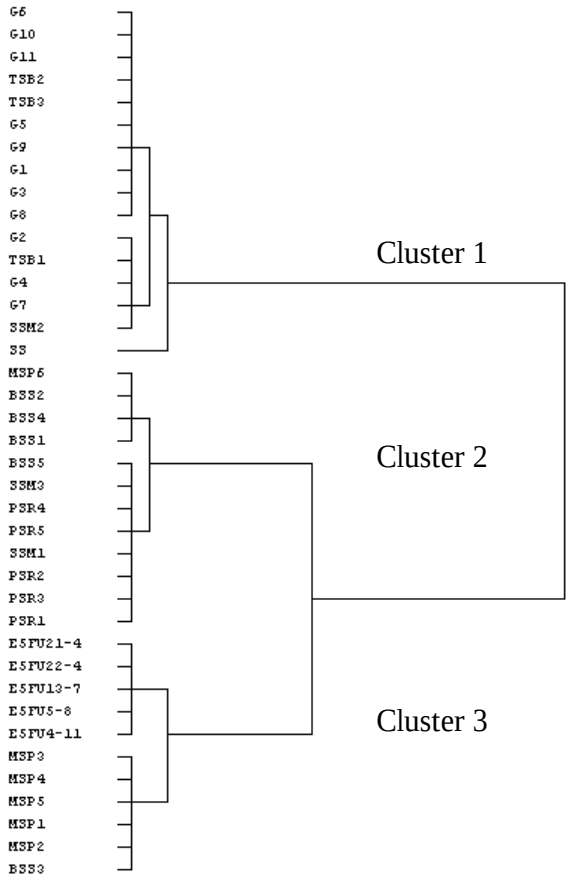

Fig. 1; Dendrogram obtained by Ward method from PCDDs and PCDFs profiles of industrial emissions and environmental samples collected in the province of Trieste.

Conclusions

Principal component analysis and hierarchical cluster analysis show (another time) to perform well as pattern recognition tools able to cope with complex - even if relatively small - data set, formed in our case by more subsets produced at different times by different laboratories on different matrices. The fingerprints of the two sources identified upto now (steel works and waste incineration) can be explained by reactions proposed in literature as happening at specific stages of the industrial processes, namely "*de novo*" synthesis of POPs occurring in sinter plants of steelworks[1,2] and dioxin condensation from precursors in waste incineration, for instance by means of Ulmann reaction [3,4].

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