# Chemical sequential extraction of trace metals in sediments of the Var River, France: Partition and origin

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The Var River catchment represents the main water supply of the Côte d'Azur (south-eastern France). Sediments play an important role in groundwater systems both as a filter and a source of contaminants. In a chemical speciation study of trace elements (As, Cd, Cu, Li, Mo, Pb and Zn), a sequential extraction method was developed and applied to a sediment core (950 cm) of the Var River. This method corresponds to a modification of the BCR procedure [1]. Two steps with weak reagents, (fraction A: water; fraction B: nitric acid 0.001M), were added before the first step of BCR (carbonate fraction) in order to better detect anthropogenic components. A pseudo-total acid digestion of solid residues by microwave assisted was also added in order to allow the assessment of trace metals recoveries. The 6-steps extraction method was tested on certified reference material IAEA-433, with recovery values ranging from 80 % (As) to 106 % (Cu)
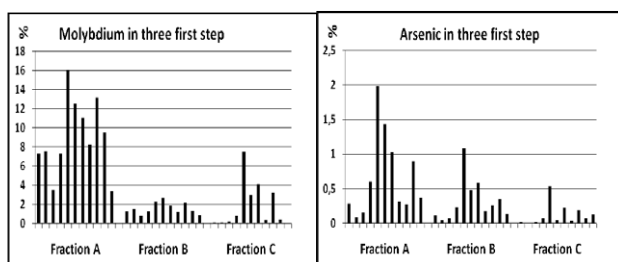


**Figure 1:** Chemical fractionation (percentage of total) of Mo and As in 11 samples (from top to bottom) of core sediments from the Var River. Fraction A, hydrosoluble; fraction B, acidosoluble; fraction C, carbonate.

Results show a higher percentage of Mo and As released in fraction A and B, than in the carbonate fraction (fraction 1 of BCR), revealing a high bioavailability of these two metals (not visible by BCR) that are not mostly included in carbonates. Cd exhibits great mobility and bioavailability, probably indicative of anthropogenic sources. Li, Cu, Pb and Zn are mostly released in the residual fraction respectively 99%, 71%, 99%, and 85% of total concentration. Therefore, these two fraction added (A and B) appear necessary for detecting and understanding anthropogenic or natural contaminations.

[1] Thomas (2001) *Analytica Chimica Acta* **286**, 42.

# Heavy metals contamination in urban alluvium soils – Loures Valley, Lisbon, Portugal

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## Spatio-temporal stochastic modelling

The input of heavy metals in soils of alluvium environment shows high variability in both space and time domains [1], hence the estimation of the measured metals (Co, Cr, Cu, Ni, V e Zn) should account for either dimension. Furthermore, it is also a non-stationary process, because spatial/temporal variability depends strongly on the distance to pollution sources and the amount of precipitation. The methodology presented herein deals with the application of kriging with external drift as an interpolation procedure [2]) for the measured heavy metals elements, in a generalised space-time domain. The definition of an auxiliary variable is based on the description of the processes involved [3].

## Discussion of Results

In this case study, the heavy metals input in soils of alluvium environment, shows high variability in a space-time domain. The soils pollution is more pronounced during the wet seasons than during the dry seasons. Estimation is a problem involving non-stationarity, controlled by the distance from the nearest pollutant source and the amount of precipitation which were used for the definition of an external variable through a linear multiregression model, defined in a generalised space-time domain. Kriging with such an external drift, was applied to the metals concentration estimation performance, and can be checked out from the cross-validation results as well as from the observation of the corresponding, estimated maps.

[1] Silva (2003) *Impacto ambiental da actividade agrícola e industrial na Várzea de Loures, Hidrosfera e Pedosfera*, PhD thesis, University of Lisbon. [2] Wackernagel (1995) *Multivariate Geostatistics*. Springer-Verlag, Berlin, 256pp. [3] Figueira *et al*. (1999) in Gómez-Hernández, Soares & Froidevaux (eds) Geoenv II, Kluwer Academic Publishers, Dordrecht, pp.53-64