UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

FACOLTÀ DI INGEGNERIA

DIPARTIMENTO DI INGEGNERIA IDRAULICA, GEOTECNICA ED AMBIENTALE

(D.I.G.A.)

Tesi di Laurea
in
Ingegneria per l'Ambiente ed il Territorio

Assessment of heavy metals in sediments of Prague creeks

RELATORE

CH.MO PROF. FRANCESCO PIROZZI
CH.MO PROF. MASSIMILIANO FABBRICINO

CANDIDATO

MARCO RACE
324000214

CORRELATORE

MGR. JANA NÁBĚLKOVÁ, PH.D.

ANNO ACCADEMICO 2011/2012

ABSTRACT

Sediments represent a fraction of considerable importance for the ecosystem; they play a significant role in the accumulation-storage of the pollutants, mainly heavy metals (HMs), derived from the water, and are responsible for HMs release to the water itself. The analysis of sediments is therefore extremely significative to characterize the quality of water bodies.

The objective of this elaborate has been to monitor the pollution of urban streams through sediments analysis.

The analysis has been carried out on sediments sampled from the following creeks located in the urban area of Prague (Czech Republic) that all are affluents of the Vltava River: Botic, Rokytka, Uneticky and Zatissky Creeks. Considered contaminats have been: cadmium(Cd), chromium(Cr), copper(Cu), nickel(Ni), lead(Pb), zinc(Zn).

The Botic and the Rokytka Creeks are the largest affluents of the Vltava River in Prague and, in the stretches studied, they are affected by Combined Sewer Overflows (CSOs) and Storm Water Drains (SWDs). The Zatissky Creek is affected by SWDs only and the Uneticky Creek is affected by a waste water treatment plant from Prague's airport.

Only recently the study of environmental pollution has been carried out through the sediments, so no standard procedure has been established, but nevertheless hardly any procedure can be defined as "the best", because sediments, such as soil, have origins, compositions and structures different from each other so they must be treated differently in order to extract the substance to be analyzed (e.g. HMs in this work).

The concentrations of heavy metals Cd, Cr, Cu, Ni, Pb and Zn, in watercourses sediments of studied creeks, have been regularly monitored.

Sediment samples have been frozen, freeze-dried and microwave digested by $HNO_3$and H_2O_2 (method USEPA 3051, 1994), before analysis with atomic absorption spectrometer with flame or graphite furnace atomization (FAAS or GFAAS). Each sample has been sieved for grain size distribution (fractions 200-600 mm, 63-200 mm, <63 mm), and has been specially analyzed for studying of binding behavior of HMs in sediments of different characteristics.

The amount of organic matter in the samples has been analyzed using thermo-gravimetry, better known as Loss on Ignition (LOI).

The sediments, with high concentrations of HMs, have been subjected to the sequential extraction procedures, through which it is possible to calculate the amount of HMs that are more or less bioavailable.
To consider uncertainties of analysis, two measurements (re-samples) of each sample were performed and the mean value and the relative standard deviation (RSD) were calculated. To better understand the influence of sediment quality on heavy metals' distribution in the sediment, Pearson's correlation analysis between the concentrations of heavy metals and grain size distribution and OM content was performed.

Analyzed concentrations have been compared with the Italian legal limits and with two American benchmarks (PEC: (Probable effects concentrations) and TEC (Threshold Effects Concentrations). The enrichment factor EF has been evaluated according to Malkoc et al, (2010), by it is possible to evaluate the level of loading (contamination categories). An estimation of bioavailability and hazard of HMs in sediment has been based with Distribution Coefficient (K_d), that is a ratio between pollutant concentration in sediment and its concentration in water.K_d gives information about what medium (water or solid phase) is crucial for the risk assessment (US EPA 402-R-99-004A, 1999).

The presence of pollutants varies from what is injected into the river: in Botic e Rokytka creeks arrive the contributions from CSOs and SWDs, so it is derived, for organic matter and for all HMs except for the Pb, that the SWD cause an increase in pollutant greater than the CSO. In Uneticky creek the WWTP of the airport can have a significant impact on concentrations of Cd; the encountered values may also suggest that there is some impact from the village. As follows from the analysis of the HMs and of the organic matter in the granulometric fractions, the content of HMs increases as grain size decreases.

These results concur with other studies where it was shown that the characteristics change with the particle size; in fact, when the particle size decreases, this increases the specific surface area and consequentially increases in absorption capacity and cation exchange (Shim 2003). This effect is mainly due to the porosity and surface area of the particular sample fractions. Fractions of a small grain size have a larger surface area, hence they contain a higher amount of HMs. However in most cases the real amount of pollutant is provided by the sieve fraction with a diameter> 0.2 mm; this is due to the fact that this fraction, compared with the other two fractions (sand end and pan, silt and clay), in almost all cases, is quantitatively much larger.

Considering the Americans criteria TEC and PEC, in Botic (site B4) Pb and Cu is exceeded the TEC. In Rokytka there are the excess of Cu, Pb and Zn, because the TEC index is not respected, and some concentrations (referring to smaller fraction sizes) do not meet even the PEC index. In Zatissky there are no problems with limits, while in Uneticky, after WWTP of the airport, there are exceeded values for the Cd. The hazard assessment, performed by using of the index described above, showed interesting results. According to distribution coefficient the most available metal from the sediment is Cd, but also for other metals Kd value (<4) implies a possibility of easy releasing from sediment to liquid phase, which can happen during critical events (rain or accidental events). According to Kd value, Cr and Ni show higher availability (according to lower Kd) in all the courses, and Zn and Cu are the ones that tend to stick to the ground. Pb tends to be always released, except in Uneticky,where there is the influence of the WWTP.

Detected the concentrations' values that are considered dangerous for human health and environment, some sequential extractions have been carried out to see the bioavailability of HMs issue into the environment (Fig 1).

Cd analysis returns disturbing data, because in the first step (exchangeable and weak acid soluble fraction) a large Cd amount is released. These data justify the high presence of Cd fractions in water. For the others HMs is been observed that the most part is released in Oxidisable fraction (i.e. step 2), how it is also reflected in literature. (M. Pueyo et al. 2007).

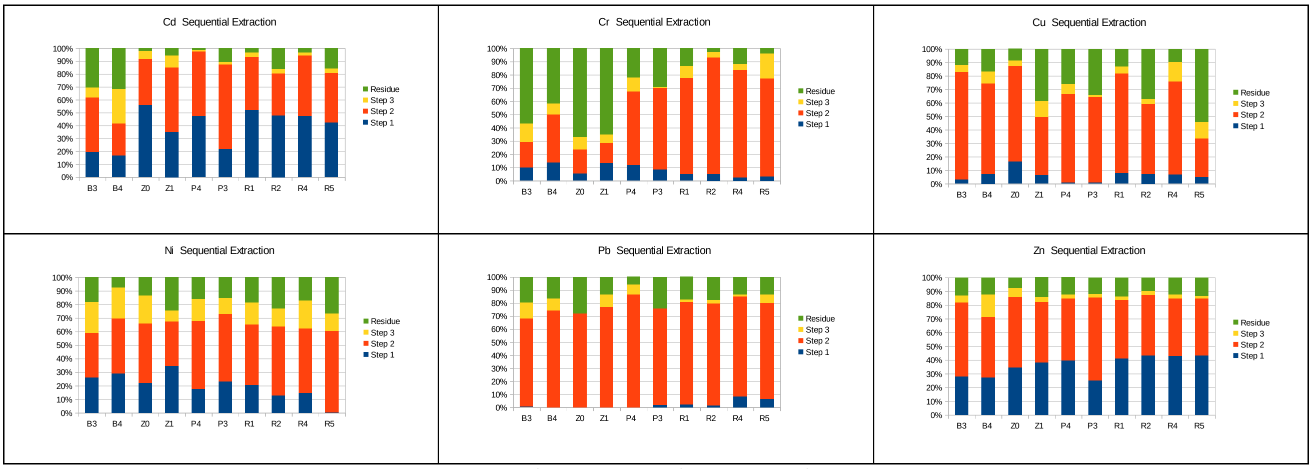

Fig 1 Percentages of concentrations for each step of sequential extraction
(step1: Exchangeable and weak acid soluble fraction, step2: Reducible fraction step3: Oxidisable fraction and residual)

This study showed that there is a real possibility of HMs release from sediment to water and a threat of a toxic impact on biota.

From studied metals Cd is the most available, but also other studied metals, according to Kd, imply a possibility of easy releasing from sediment to liquid phase. To date there has been no action taken yet, because this amount of HMs (sometimes in large concentrations), does not seem to make any damage to the larger stream where it enter (Vtava).

A feasible work of biological remediation in situ through the use of phytoremediation could be done exploiting plants ability to remove, immobilize, or transform inorganic (such as HMs) and organic compounds. Removing inorganic contaminants may be stabilizing (HMs by immobilizing the chemical bonds with substances produced by the roots, slowing or inhibiting the migration) or by extraction/accumulation (accumulate HMs in plant tissues).
The preferable way to follow is reducing concentrations of HMs in treatment plants, also because thinking about the future with ever decreasing drinking water, waste water from Combined Sewer Overflows (CSOs) and Storm Water Drains (SWDs), could be used for irrigation of agricultural land instead of using drinking water.

Checking the intake of cadmium from discharges, which increase P3 and P4 levels, is necessary; then presumably the amount of cadmium come from the airport is not supportable by the ecosystem. Therefore the wastewater plant treatment in Prague airport should be monitored and possibly undertake action about it.