

Soil structure and organic matter repartition as controlling factors of PAH-type compounds availability in a former industrial soil

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Past industrial activities associated to coal exploitation such as coking plants or steel industries have left huge areas of wastelands. These industrial sites are particularly contaminated by persistent organic pollutants (POP) including polycyclic aromatic hydrocarbons (PAH). Those contaminants, recognized for their toxic and carcinogenic properties and occurring in all environmental compartments (air, soil and water) must be treated. In opposition with classical treatment techniques (thermal desorption, chemical oxidation...) the phytoremediation is an emerging biological technology using plants more environmentally friendly.

However, the efficiency of such bioremediation treatments in these old industrial soils is limited due to the low availability of the targeted organic contaminants including PAH. Both accessibility due to localization in the soil structure and extractability controlled by sorption to organic matter (OM) and minerals strongly control this availability. In this context, my Ph-D focuses on the characterization of these factors on a former coking plant soil contaminated by PAH. The objectives are to (i) describe soil structure; (ii) identify and localize the different OM types present in the soil size fractions; (iii) define the respective contributions of these different OM types to the soil structure; (iv) link these results to PAH availability and its evolution.

The methodology proposed is based on an extensive chemical characterization of soil fractions obtained by gentle water granulodensimetric fractionation after selective OM pre-extractions (dichloromethane, *n*-hexane and hot water) or none. Dichloromethane (DCM) extraction is supposed to remove all the extractible organic matter (EOM), the macromolecular extractible organic fraction (asphaltene) remains with *n*-hexane extraction and the hot water removes labile OM. A comparison between untreated and pre-extracted soil shall give clues on the types of organic fractions controlling soil structure. For untreated and pre-extracted soils and for each size fractions (200-2000 μm , 50-200 μm , 20-50 μm , 2-20 μm and 0-2 μm), EOM was characterized at molecular and spectroscopic level. Specific molecular fingerprints as well as concentration of 16 US-EPA PAH were determined by GC-MS (Gas Chromatography – Mass Spectrometry). Complementary structural information on EOM was also determined by FTIR (Fourier Transformed Infrared spectroscopy).

Results show that the granulodensimetric distribution of the untreated soil is dominated by coarse sands (more than 55%). PAH are distributed mainly in two major fractions: coarse sands and fine silts. Though less abundant in weight than coarse sand, fine silts (~12%) contribute significantly to the overall PAH content of the soil due to higher concentration. Among the 16 PAH, two isomers (phenanthrene and anthracene) are frequently used to determine organic sources. Phenanthrene is considered as a kinetic compound, preferentially produced at low temperature during geologic time, suggesting a fossil origin,

such as coal. On the contrary, anthracene, a thermodynamic compound, is preferentially produced at elevated temperature, and reveals an industrial origin such as coal tar. Here, coarse particles are more enriched in phenanthrene (phenanthrene/anthracene > 1) than silts. Coarse fractions (sands) are thus characterized by a coal signature whereas fine fractions (silts) exhibit a coal tar signature. Moreover, no significant natural contributions to OM were evidenced by molecular characterization.

Hot water extraction did not significantly affect the granulodensimetric distributions of the soil. The *n*-hexane treatment led to a decrease of the biggest particles proportion and an increase of the fine fraction. Such evolution could be explained by a disaggregation of the coarse particles. On the contrary, the dichloromethane treatment led to an increase of the coarse sand fraction and decrease of the finest particles proportions. It seems that DCM extraction allows the preferential removal of coal tar particles found in the fine fractions. The IR spectra from these fine particles are characterized by a relative increase of the aliphatic bands intensity consistent with a preferential removal of an aromatic rich OM such as coal tar.

Thus, the combination of granulodensimetry and chemical analysis reveal the almost exclusive anthropogenic origin of the OM in the former coking plant soil studied and the specific role of the fine silt fraction both as the main sink for PAH and highest reactive fraction. Complementary characterization will be carried out including Scanning Electron Microscopy observations and organic petrography in order to estimate the tar particles proportion and repartition in the different granulodensimetric fractions. In a second step, the effect of recent organic matter incorporation in the former soil and especially its consequences on the organic contaminant repartition, availability and reactivity will be studied.