Speciation of metals in refinery emissions particles

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The Bay of Algeciras is a well documented industrial pollution hot spot, with relatively high concentrations of metals such us Ni, V, Cr and La in PM10 and PM2.5, being attributed to both industry (de la Rosa *et al.,* 2010) and shipping emissions (Pandolfi et *al.,* 2010). These metal releases inevitably impact on the local ecosystem and surroundings populations. They were identified in the cocktail of pollutants emanating from different emissions stacks from San Roque refinery complex located in the Bay of Algeciras by Sánchez de la Campa *et al.,* (2011). V and Ni are related to the refining of crude oil and processing of its downstream products in the petrochemical complex, while La is specifically used in the form of La-concentrates in zeolitic fluid catalytic cracking units (FCC) which crack heavier crude oil distillation fractions into lighter compounds (LPG) (Moreno *et al*., 2010).

The goal of this work is to evaluate the bioavailability of the main metal content emitted from refinery including V, Cr, Co, Mo, La, Ce and Pb, The study deals with the size distribution and chemical characterization of particulate matter emitted by the most polluting emissions stack in the refinery complex: sulpholane (V, Cr, Ni in particles with diameter < 0,33µm), HDS (V in particles with diameter < 10 µm, Cr and Ni in particles with diameter < 0,33µm, La 2-10µm) and FCC (Cr, Ni and La in particles with diameter 0,3-10 µm). For this aim, four steps Tessier sequential procedure modified by Fernández Espinosa *et al.,* (2006) was applied to airborne emissions refinery samples.

This speciation scheme determines the chemical form in which the metals are present: 1st step: soluble and exchangeable metals, 2nd step: carbonates, oxides and reducible metals, 3rd step: bound to organic matter, oxidizable and sulphidic metals and 4rd step: residual metals. The dissolved metals in the first matrix (H_20 Milli-Q) are the most potentially toxic for the human health. Moreover, the metal bioavailability was studied depend on size particles. Four cut off stage diameter (>17 µm, 5-14 µm, 0,67-1,3 µm, < 0,33µm) were used. The final solutions, obtained of each step extraction, were analyzed by ICP-MS.
Figure 1 show the metal extraction percentage obtained in H_20 Millli-Q matrix from FCC stack emissions samples.

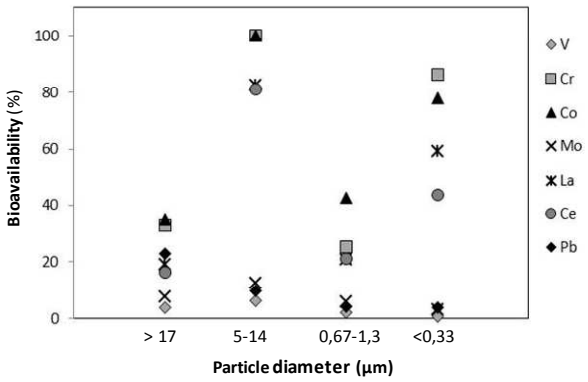

Figure 1.Bioavailability (%) vs. particle diameter (µm) from FCC particulate matter emissions.

V, Mo and Pb show a low extraction percentage (below 25%) of the soluble chemical forms in all the size particle modes. However, the rest of the elements present a different bioavailability depend on size distribution.
The great bioavailability of Cr (86), Co (78%) and La (59%) in the smallest particle mode (< 0,33 µm) is remarkable. Therefore, these metals can been considered hazardous pollutants to human health due to their high residence time and wide dispersion to be easily inhaled and assimilated by our organism.

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de la Rosa, J.D. et al., (2010) *Atmospheric Environment* **44**, 4595-4605.
Fernández Espinosa A.J. et al., (2006) *Inter. J. Environ. Anal. Chem*. **86**, 641-651.
Moreno, T. et al., (2008) *Environmental Science Technology*, **42**, 6502-6507.
Pandolfi, M. et al., (2011) *Environmental Science Pollution Research*, **18**, 260-269.
Sánchez de la Campa, A.M. et al (2011) *J. Environ. Monit.*, **13**, 1276-1287.