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Size fractionation highlights the mobility of copper from urban stormwater to river

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Copper is an ubiquitous essential element but also toxic to aquatic organisms, Environmental Quality Standards being $1 \mu\text{g}\cdot\text{L}^{-1}$ for surface water (annual mean concentration). Rivers and estuaries are mainly concerned by copper accumulation in sediments and in organisms. Copper can originate from various manufactured products (antifouling painting, vineyards fungicides, brake linings...) and anthropic activities (industrial, landfills...). As a result, copper French median concentration in oysters is about $200 \text{ mg}\cdot\text{kg}^{-1}$ DM (Ifremer, 2017).

Transportation, especially road transport, is the main French source of copper air emissions (92% of total emissions) (CITEPA, 2019). Then, urban areas, mainly impervious, constitute a major non-point source of copper from abrasion of brake pads and tires, and fuels. This contaminant is released from the road surfaces through stormwater runoff directly to water bodies or after collection in sustainable urban drainage systems (SUDS). As the epuration performance of SUDS for copper was shown to be low, this study is carried out to evaluate if copper mobility can be explained by its physical speciation. The distribution of copper among dissolved, colloidal and particulate fractions is studied by size fractionation, assuming that the mobility of copper is related to a high dissolved and colloidal occurrence.

The study site is a retention-infiltration basin collecting the runoff waters of the main bridge of Nantes (France; about 90 000 vehicles/day), and overflowing to the Loire river . Size fractionation by in series filtration and ultrafiltration was performed on stormwater runoff and surface waters sampled within the basin. Five fractions were analyzed for major and trace elements: $> 8\mu\text{m}$], $8\mu\text{m} ; 1,2\mu\text{m}$], $1,2\mu\text{m} ; 0,45\mu\text{m}$], $0,45\mu\text{m} ; 5\text{kDa}$] and $< 5\text{kDa}$]. Among these fractions $> 8\mu\text{m}$] correspond to particulate copper, $8\mu\text{m} ; 1,2\mu\text{m}$], $1,2\mu\text{m} ; 0,45\mu\text{m}$], $0,45\mu\text{m} ; 5\text{kDa}$] to colloidal copper and $< 5\text{kDa}$] to dissolved copper. Size fractionations were implemented for 8 samples with 2 replicates for each sample and over 1 year. $0.45 \mu\text{m}$ filtrations were also conducted as a reference.

The total copper concentration in runoff was around $100\mu\text{g}\cdot\text{L}^{-1}$, which is in the upper part of the concentrations observed in the area of Nantes in SUDS. The results of the size fractionation are as follows : 1) for the stormwater runoffs, particulate copper is about 70% of the total amount, colloidal copper is present for 20% and 10% of dissolved copper is measured. Thus 30 % of copper are mobile; 2) for the surface waters in the basin, the distribution of copper among the dissolved, colloidal and particulate fractions, is respectively 20 %, 70 % and 10 %.

We concluded that 1) the concentration of copper is 100 times higher the regulation value for natural environment, and 2) particulate fractions of copper are trapped at the entrance of the basin, and an high content of mobile copper (dissolved and colloidal fractions) is observed in the basin that could either be overflowed or infiltrated in the sub-soil of the basin.