NATURE, ORIGIN AND EVOLUTION OF ORGANIC POLLUTANTS FROM TRANSPORTS IN AN URBAN SEDIMENTARY ARCHIVE

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Introduction

It is now admitted that Humans have emerged as the predominant force on geological and geochemical cycles (Zalasiewicz et al., 2015). The Anthropocene Working Group of the International Commission on Stratigraphy aims at defining the beginning and the stratotype of this new geological era. Within the Golden Spike project (BIOHEFECT, INSU-CNRS) we hypothesize that urban areas are potential targets for defining such a stratotype, because (1) tracers of anthropic activities (pollutants) are varied and concentrated and (2) sediments archiving those tracers potentially accumulate in specific areas. This would constitute a sedimentological record of the evolution of a large array of societal concerns (food, health, energy, transport…) in cities over the Anthropocene.

A 1.5m long sedimentary core of was drilled in a decantation tank that collects the unitary (wastewater WW and stormwater SW) sewer network of Orléans. Previous work showed that: 1) this core represents between 6 months and 1 year of sedimentation; 2) sediments are constituted of organic (in the lower half core) and mineral (in the upper half core) facies, originating from WW/SW inputs, respectively, under the control of precipitation events; 3) drugs and illicit drugs vary over the core, depending on facies, grain size, organic matter content and speciation rather than their production/consumption rates. In this context, our goals are to 1) explore the diversity of hydrocarbons in lipid extracts; 2) determine their sources (fuels, oils and bitumen); 3) identify factors controlling their presence and abundance in sediments.

Results

Two types of n-alkanes distributions were found. n-alkanes in organic-rich sediments that mainly derive from WW input show a strong odd/even predominance (high CPI) attesting a relatively fresh organic matter contribution from vascular plants. Reversely, n-alkanes with low CPI, which indicates a fossil fuel origin, are found in both mineral and organic facies. A series of hopanes pseudo-homologues with 17α,21β and 17β,21α configurations and R/S isomers was also detected in sediment samples but also in a bitumen freshly applied on a sidewalk in the Orléans CNRS campus. This bitumen could be a non-exclusive source of hopanes in the sediments.

Polycyclic Aromatic Hydrocarbons (PAH) were detected in low amounts in our samples. The fluoranthene/fluoranthene+pyrene (F/F+P) ratio (Yunker et al., 2002) was used to determine their source, with values < 0.4 corresponding to petroleum products (fuel, oil), values comprised between 0.4 and 0.5 to combustion of petroleum products and > 5 to biomass combustion. In our samples (4 analyzed for HAP), F/F+P values are lower than 0.4 in the lower half core and between 0.4 and 0.5 in the upper half. This is consistent with a SW input for the upper half core (oils, fuels and bitumen from roads and sidewalk leaching) but inconsistent for the lower half core. Onocerane I was detected in nearly all samples in varying concentrations. Its source is very likely petroleum Pearson and Obaje (1999). Onocerane I is systematically associated with a compound the mass spectra of which shows M⁺ 400 and abundant m/z 123.
This compound could be a nor-onocerane isomer derivative of onocerane I, although it has never been described before. These two compounds were detected in the sidewalk bitumen. Therefore, we suggest that Onocerane I and nor-onocerane could be tracers of sidewalks or roads bitumen. This must be ascertained by analysing more extensively these materials and more precisely defining the source petroleum.

Conclusion
This study reveals a large diversity of hydrocarbons archived in urban sedimentary archives. Some of their sources and significance could be determined, and their input from SW or WW addressed. Nevertheless, their presence/concentration with depth cannot solely be interpreted as a function of WW and SW inputs. The nature of sediment (organic matter and mineral content, granulometry) may play a significant role in their occurrence in sediments. This study also points to several questions on the transfer of hydrocarbons from sources to the sedimentary archive. Because road and sidewalk bitumen water leaching are considered inefficient, onoceranes and hopanes could be transported on sands and gravels on which we observed bitumen coatings in our samples.

References
Zalasiewicz et al., 2015. When did the Anthropocene begin? A mid-twentieth century boundary level is stratigraphically optimal. Quaternary International 383, 196-203.