detritus | Multidisciplinary Journal for Waste Resources & Residues

CISA

Environmental Forensic

TOTAL PETROLEUM HYDROCARBON: A CONTROVERSIAL MACRO-PARAMETER IN ENVIRONMENTAL FORENSIC

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In environmental forensic practice, values measured for chemical parameters, such as chemical concentration in a specific matrix (soil, wastewater, air, waste), are crucial for the assessment of possibly occurred pollution. If these values exceed regulatory limits and if it can be demonstrated that they are the result of a deliberate release from anthropic activities, an environmental crime can be supposed.

"Macro-parameters" are widely used in many environmental fields; examples are Total Organic Carbon (TOC) in wastewater; Particulate Matter (PM) in atmospheric air andTotal Petroleum Hydrocarbons (TPH) in soil. In these cases, the parameter does not refer to a specific compound but it quantifies the presence of a larger class of chemicals characterized by a common property.

In a forensic investigation, the aim is to identify the potential cause of the presence of the chemicals. Due to this, these macro-parameters, if analysed stand-alone, may be misinterpreted and be a source of bias. This is because they quantify substances that could have either natural or anthropogenic origin.

In this context, a simple and direct use of these macro-parameters could generate the so called "confirmation bias" (Newman, 2018). This is described as where individuals have the "tendency to gather evidence to confirm hypotheses rather than objectively weighing the merits of all plausible hypotheses" (Newman, 2018). The primary, and usually the only considered assumption, is that the measured concentration is due only to the related anthropogenic activities. Consequently, the conclusions derived from this conservative hypothesis could be considered not realistic as it is supported by partial and non-scientific evidence. This simplistic approach should not be acceptable in correct environmental forensics practice.

A clear example is represented by the case of PM air pollution monitored in the Veneto Region (north-east of Italy), being one of the most polluted areas for air quality in Europe (Khomenko et al., 2021). Here, during the pandemic lockdown imposed between March and June 2020, specific emissions, such as those deriving from the vehicles traffic, almost completely ceased. Therefore, peaks of PM concentrations (i.e., exceeding regulation thresholds) were not expected during this period. However, some PM peaks were registered as caused by natural sand transported by the wind from Asian regions (Pivato and Cappai, 2021). In this case, the "macro-parameter" PM concentration includes the contribution of particulate matter generated from natural processes and unfavourable climatic conditions. Therefore, considering the number of yearly exceedances of particulate matter could represent a biased tool to support restriction measures aimed at improving air quality (e.g., traffic limitations).

A less known example is addressed by the authors in this column: the macro-parameter "Total Petroleum Hydrocarbons (TPH)".

The analytical determination of TPH allows to quantify the total presence in soils (e.g., through ISO, 2004) or waste (e.g. by EN, 2004) of a large family of different hydrocarbons, substantially corresponding to substances with C > 12. In particular, the measured values do not give information on compounds' molecular arrangement (i.e., linear, branched, cyclic, and/or aromatic), composition and related toxicity.

Considering the possible source, Vecchiato et al. (2017) stated that terrestrial plants can produce hydrocarbons as components of their epicuticular waxes to protect plant tissues from adverse environmental conditions. In particular, soils from woodland and protected areas (where anthropogenic activities are absent), exceeded the threshold limits or TPH at 50 mg kg^{-1} DW. As a paradoxical consequence, soils should have been remediated because of the presence of natural hydrocarbons such as leaf wax n-alkanes.

Considering the related human toxicity, TPH includes both human carcinogens and also non-carcinogens with low toxicity to humans. Due to this, regulations should refine the procedure for classifying a waste for carcinogenicity (HP 7) or mutagenicity (HP 11) by considering only the concentration values of the carcinogenic substances, the so-called "bio-markers", i.e., dibenzo[a,h]anthracene,

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Detritus / Volume 17 - 2021 / pages III-IV
https://doi.org/10.31025/2611-4135/2021.15150

benzo[a]anthracene, benzo[def]crhysene, Benzo[e]acephenanthrylene, benzo[e]pyrene, benzo[j]fluoranthene and benzo[k]fluoranthene.

TPH should also be considered when classifying a waste for ecotoxicity through the hazardous property HP 14. In this regard, TPH substantially corresponds to the parameter “Hydrocarbons C10-C40”, already classified within the Regulation 2008/1272/EC for Classification, Labelling and Packaging of products with the Hazard Statement Code H411 related with chronic aquatic toxicity. Therefore, according to the so-called “calculation approach", as established by the current Regulation 2017/997/EC, a waste containing high concentrations of Hydrocarbons C10-C40 could be classified as HP 14 Ecotoxic without any realistic assessment of its real impact on the ecosystem. This is the case, for example, of the dismantled conveyor rubber belts (see Figure 1) where the concentration of hydrocarbons “C10-C40” could be as high as 10% (w/w). In this case, the assumptions on considering all components quantified in this macro-parameter could overestimate the presence of effectively ecotoxic compounds.

To refine this overcautious waste classification, two possible approaches are proposed:

Similar to the refinement proposed for the HP 7 or HP 11, a list of substances already classified with HSCs related with aquatic toxicity can be proposed as “eco-markers” within those considered within the macro-parameter TPH or, equivalently, Hydrocarbons C10-C40;

Ecotoxicological testing represents, in these cases, the best tool to realistically assess the ecotoxicity of a waste sample and to consistently classify it. Also, it is worth mentioning that the results derived from the bioassays performed should always prevail over the classification judgement based on the chemical composition of the waste itself.

In conclusion, this column wanted to initiate a discussion on the way the use of values measured for macro-parameters can induce overprotective and unrealistic interpretation. Further, we highlighted the consequent need to go beyond their mere meaning by deepening the knowledge on the real constituents behind them.

FIGURE 1: Dismantled conveyor rubber belts.

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