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Polymer quantification using the Rock-Eval® device for identification of plastics in sediments

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ABSTRACT

In this work, artificial thermal degradation experiments using the Rock-Eval® device were performed on selected polymer microsphere samples (PE, PP, PE100, PA6, PA11, PFA and PET). The main idea of this work is first to create a database of different polymer standard responses using the specific Rock-Eval® FID/IR peak signals. Several specific Rock-Eval® parameters are now defined to characterize each polymer family. For instance, each polymer is characterized by specific quantified parameters like *Total HC_{polymer}*, *Total CO_{polymer}*, *TotalCO_{2polymer}*, *Tpeak_{polymer}*, among

others. This study attempts to demonstrate if this quick thermal degradation method can be also used to characterize the plastic contents (detection, type, and quantity) in sedimentary samples. Results indicate that each investigated polymer shows specific Rock-Eval® parameters that can be considered as useful characteristics of polymer families (mainly $T_{peak_{polymer}}$, $TOC_{polymer}$, $PC_{polymer}$, $RC_{polymer}$, total $HC_{polymer}$, total $CO_{polymer}$ and total $CO2_{polymer}$ parameters). Samples containing different mineral matrices (e.g. sand, shale, marl and carbonate) were also mixed with polymers at different concentrations varying between 0.2 and 4.2 wt.%. These composite samples were also analyzed in order to evaluate their thermal degradation comparing their specific Rock-Eval® FID/IR signatures. For example, most composite samples show an excellent linear correlation between TOC, PC, RC, total HC, CO and CO₂ parameters versus the amount polymer at different concentrations. Although more work is still needed, a methodology is here proposed to distinguish and quantify the presence of plastics in the environment applying the proposed polymer Rock-Eval® database.

Keywords: Plastics, Polymers, Sediments, Sand, Clay, Marl, Carbonate, Rock-Eval.

1. Introduction

Plastics are man-made, synthetic organic polymers, which are primarily derived from the polymerisation of monomers extracted from oil or gas (e.g. Derraik, 2002; Rios et al., 2007; Thompson et al., 2009), or more recently, could be derived from bio-monomers (e.g. Lambert & Wagner, 2017). The plastics industry has significantly contributed to the development of the present-day world, with a plastics production surpassing most of other man-made materials.

Although the first synthetic plastics appeared in the early 20th century, the very first studies on plastic occurrence and distribution in the environment were published only in the 1970s (e.g. Carpenter et al., 1972; Carpenter & Smith, 1972). Since these pioneer studies, the plastic pollution issues remained relatively confidential with only few scientific articles published per year until 2010. Since 2015, it became a relevant topic with an exponential increase in the number of scientific publications (e.g. Bellasi et al., 2021). National and international projects funding are also recently booming, as are government, regulators and other interested parties cogitation on regulations in terms of the use and monitoring of the plastics cycle in the environment. The capability to identify, and then to quantify plastics in the environment is therefore a current major issue.

Plastics can be found from soils to oceans and atmosphere, as well as digestive tracts of both vertebrates and invertebrates (e.g. Rochman, 2015; Auta et al., 2017; Ribeiro-Claro et al., 2017; Li et al., 2018; Prata et al., 2019). The types of sample thus include several matrix such as water,

sediments, air, tissues and cells of multiple organisms, requiring specific equipment and sampling strategies, as well as separation procedures (e.g. Masura et al., 2015; Silva et al., 2018; Lv et al., 2021). Samples collected from the environment commonly need pretreatment before separation to extract impurities and matrix (e.g. Klein et al., 2015; Miller et al., 2017; Felsing et al., 2018). Prepared samples are then analyzed for identification, using a relatively common analytical workflow and technologies whatever the origin of the sample, and researchers are currently working on unifying them (e.g. Masura et al., 2015; Metz et al., 2020).

The identification of microplastics is usually done by visual inspections, including macroscopic and microscopic observations. Staining microplastics with dyes could be used for easiest plastic recognition. Scanning electron microscopy (SEM) gives detailed information about the size and shape of a particle. Pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy are additionally used to obtain the chemical characterization of microplastics, and they also confirm the occurrence of plastic (e.g. Rocha-Santos & Duarte, 2015; Hanvey et al., 2017; Dümichen et al., 2017; Hermabessiere et al., 2018; Fortin et al., 2019). X-ray photoelectron spectroscopy (XPS) or nuclear magnetic resonance (NMR) could also be used for identification and quantification (e.g. Peez & Imhof, 2020). The final quantification step depends on measurements realized during the sampling procedure combined with results from the

identification step, that is intensive “time-consuming” and prone to human mistakes. How to extract all plastics (micro- and nano-) from an environmental complex matrix sample? How to determine both the type and the quantity of plastics in such samples? These are some of the main challenges that the scientific communities are currently facing. New and rapid technique for quantifying the amount of plastics without a major pre-treatment phase could be a significant trump for balancing plastic cycle in the environment.

The open-system, programmed pyrolysis and oxidation instrument known Rock-Eval® is a technology widely used to characterize the thermal properties of sedimentary source and reservoir rocks, organic matter concentrates, oils, soils, and sediments using different thermal methods (including both pyrolysis and oxidation steps). This device was primarily developed to investigate the source rock potential for petroleum systems (e.g. Espitalié et al., 1977; Espitalié et al., 1986, 1987; Lafargue et al., 1998; and others). Furthermore, to improve the source rock characterization, a specific Rock-Eval® Shale Play™ method was proposed in 2014, including a new pyrolysis program and associated parameters for evaluation of in-situ liquid hydrocarbons (e.g. Romero-Sarmiento et al., 2014b; 2016a; b and references therein). The Rock-Eval® device has also been used and developed for many different matrices to detect and quantify the total organic carbon (TOC) and the mineral carbon (MINC) contents. This analytical technique has been used increasingly in other geoscience

applications including: (1) the characterization of organic matter in soils (e.g., Di-Giovanni et al., 2000; Disnar et al., 2003; Hetényi et al., 2005; Sebag et al., 2006; Saenger et al., 2013); (2) the study of recent lacustrine sediments (e.g., Campy et al., 1994; Di-Giovanni et al., 1998; Jacob et al., 2004; Sanei et al., 2005); (3) the evaluation of recent marine sediments (e.g., Peters and Simoneit, 1982; Hussain and Warren, 1991; Calvert et al., 1992; Ganeshram et al., 1999; Tribovillard et al., 2008, 2009); (4) the study of past climate changes and global carbon cycle (e.g. Baudin et al., 2007, 2010; Rohais et al., 2019), and many other applications.

Nevertheless, the Rock-Eval[®] device has not been tested to identify and to quantify human made polymers in the environment. For these reasons, a comparative and quantitative approach is proposed here using the 5 thermograms obtained by: (1) the Rock-Eval[®] analyzes carried out on the pure polymer samples quantifying the total hydrocarbon (HC), carbon monoxide (CO) and carbon dioxide (CO₂) signals, (2) the Rock-Eval[®] analyzes performed on natural mineral matrices (e.g. sand, clay, marl and carbonate) and (3) Rock-Eval[®] analyzes performed on artificial samples composed by mixtures of natural samples (e.g. sand) with polymers at different concentrations. In this study, an improvement on the identification and quantification of polymers present in samples containing different mineral matrices is provided. This comparative methodology between pure polymers and samples contaminated by plastics could be also used to

determine the percentage (%) of each polymer family present in a natural contaminated sample (e.g. beach sand + residual plastic detritus).

2. Materials and methods

2.1 Materials: Polymer, mineral matrix and composite samples

In this study, seven different synthetic polymer standards were first tested in order to characterize the corresponding polymer properties as a function of the thermal degradation. Analyzed polymers include polyethylene (PE), polypropylene (PP), polyethylene 100 (PE100), polyamide 6 (PA6), polyamide 11 (PA11), perfluoroalkoxy (PFA) and polyethylene terephthalate (PET). Regarding the elemental composition, PE, PP and PE100 polymers are characterized by significantly higher carbon and hydrogen contents whereas PA6, PA11, PFA and PET polymers also show lower to higher oxygen contents.

Furthermore, one representative mineral matrix from natural sand, shale, marl and carbonate samples were selected as follow: (1) a natural sand sample was taken from the typical Fontainebleau Sandstone group located in the southern part of the Île-de-France, about 60 km southeast of Paris (France), (2) a representative shale sample mainly dominated by clays located in Saint-Germain-en-Laye, about 20 km west of Paris (France), (3) a marl containing variable amounts of carbonates and clays was sampled from a borehole located in the Gulf of Corinth, on the western coast of Greece,

and (4) a calcite (CaCO_3) sample was selected from the typical Upper Cretaceous chalk succession located in the eastern part of the Paris Basin (France).

In order to reproduce a real sample contaminated by plastics from a natural environment, artificial composite samples were finally created mixing the selected mineral matrices (e.g. sand, shale, marl, carbonate) with amounts of polymers at different concentrations varying between 0.2 and 4.2 wt.%.

2.2 Methods: Rock-Eval[®] device and protocols

A Rock-Eval[®] 6 device operating at the IFP Energies Nouvelles (France) was used here to develop a specific procedure to identify and quantify plastics in sediments. The Rock-Eval[®] 6 device is equipped with two ovens dedicated for pyrolysis and combustion processes, respectively. During the pyrolysis step, all hydrocarbon compounds generated are monitored by a Flame Ionization Detector (FID) whereas the non-hydrocarbon compounds like CO_2 and CO released during both pyrolysis and oxidation stages are monitored by an infra-red (IR) detector (Espitalié et al., 1986; Lafargue et al., 1998; Behar et al., 2001). In this work, 3 Rock-Eval[®] pyrolysis methods (Figure 1) were tested including the Basic/Bulk-Rock and the Pure Organic Matter methods described in Behar et al. (2001) as well as the Shale Play[™] method described in Romero-Sarmiento et al.

(2014; 2016a,b). The Basic/Bulk-Rock method is characterized by a starting pyrolysis step at 300°C during 3 minutes and then the pyrolysis temperature increases from 300°C to 650°C at 25°C/min (e.g. Espitalié et al., 1986; Lafargue et al., 1998; Behar et al., 2001). The Pure Organic Matter method is also characterized by a starting pyrolysis step at 300°C for 3 minutes but the pyrolysis temperature increases from 300°C to 800°C at 25°C/min (e.g. Behar et al., 2001). The Shale Play™ method is characterized by a starting pyrolysis step at low temperature (100°C) then the pyrolysis temperature increases from 100°C to 200°C at 25°C/min. This last temperature is maintained for a plateau of 3 minutes. The temperature is raised again from 200°C to 350°C at 25°C/min. A plateau of 3 minutes is imposed at 350°C and finally the pyrolysis temperature increases from 350°C to 650°C at 25°C/min (Romero-Sarmiento et al. 2014; 2016a,b). Concerning oxidation conditions, it should be noticed here that the oxidation step is the same for these 3 standardized Rock-Eval® methods from 300°C to 850°C at 20°C/min (Figure 1).

For polymer (plastic) characterization, the analytical procedure proposed in this study is described as follow:

(i) First, samples were cut from polymer microspheres using a sharp scalpel to obtain thin fragments with dimension between 1 µm and 1 000 µm (= 1 mm). Rock-Eval® analyses were performed on these obtained micro-fragments of pure polymer samples at different mass varying between 0.1 to

2.5 mg. Pure polymer fragments were diluted with silica in Rock-Eval® crucibles in order to prevent saturation of both FID and IR detectors.

The aim of this first step was to create a completed database of different polymer standard responses using the Rock-Eval® FID/IR peak signals. As the investigated polymers mainly consist of organic polymers composed from carbon and hydrogen atoms with some heteroatoms such as oxygen, nitrogen and fluorine, it was possible to define specific Rock-Eval® parameters for plastic characterization. Using any Rock-Eval® method presented in Figure 1, Figure 2 illustrates the Rock-Eval® parameters defined in this work to characterize each polymer family. The corresponding equations are also shown in Figure 2. For each investigated polymer, the $Total\ HC_{polymer}$ provides the quantity of hydrocarbon compounds released during the total pyrolysis of the polymer. The $Total\ CO_{polymer}$ provides the quantity of the carbon monoxide released during both the total pyrolysis and oxidation of the polymer. The $Total\ CO2_{polymer}$ provides the quantity of the carbon dioxide released during both the total pyrolysis and oxidation of the polymer. $Tpeak_{polymer}$ parameter corresponds to the temperature at the FID signal reaches its maximum. $PC_{polymer}$ and $RC_{polymer}$ parameters represent the total amount of carbon content quantified during the pyrolysis and the oxidation, respectively. The $TOC_{polymer}$ corresponds here to the sum of both $PC_{polymer}$ and $RC_{polymer}$. Concerning the units, the $Total\ HC_{polymer}$, $CO_{polymer}$, $CO2_{polymer}$ are expressed en mg/g whereas $PC_{polymer}$, $RC_{polymer}$ and $TOC_{polymer}$ are expressed in wt.%. Finally, the $Tpeak_{polymer}$ is expressed en °C (Figure 2).

(ii) The second step of this protocol was focused to complete the Rock-Eval® FID/IR peak signals database performing individual Rock-Eval® analysis on the selected natural mineral matrices (e.g. sand, clay, marl and carbonate). Triplicate Rock-Eval® analyses were carried out on 60 mg of each powdered mineral matrix sample. These measurements were used to define the corresponding baseline for each mineral matrix.

(iii) The third part of this procedure was dedicated to acquire the proposed Rock-Eval® parameters for plastic characterization (Figure 2) on 60 mg of each composite sample (e.g. sand matrix previously mixed with amounts of polymers at different concentrations varying between 0.2 and 4.2 wt.%). These measurements were used to assess both the identification and quantification of polymers present in samples containing different mineral matrices.

3. Results and Discussion

3.1 Polymer properties as a function of the thermal degradation

Table 1 summarizes the Rock-Eval® parameters defined in this study for each polymer family (PE, PP, PE100, PA6, PA11, PFA and PET).

As thermal degradation proceeds, each investigated polymer shows a specific FID/IR signature that can be considered as a useful characteristic of polymer families. Figure 3 shows an example of Rock-Eval® FID thermograms showing the distinct $T_{peak_{polymer}}$ and $Total HC_{polymer}$

parameters associated to the thermal degradation of PFA and PET polymers. In general, results indicate that the investigated polymers can be mainly distinguished considering its specific Rock-Eval® parameters such as: $T_{peak_{polymer}}$, $TOC_{polymer}$, $PC_{polymer}$ and $RC_{polymer}$ (Table 1). Although the specific quantified parameters like $Total\ HC_{polymer}$, $CO_{polymer}$, $CO2_{polymer}$ show relatively high standard deviations, these parameters can be also used for polymer characterization (Table 1).

Figure 4 presents a normalized radar diagram using the seven main Rock-Eval® parameters defined in this study (Table 1). Three groups defined by specific radar envelops can be identified. The first group includes PET polymers characterized by the highest values in $Total\ CO2_{polymer}$, $Total\ CO_{polymer}$, and $RC_{polymer}$ and very low values in $T_{peak_{polymer}}$ and $Total\ HC_{polymer}$ (Figure 4). The second group includes PFA polymers characterized by the highest value in $T_{peak_{polymer}}$ and the lowest values in $Total\ HC_{polymer}$, $TOC_{polymer}$, and $PC_{polymer}$. The third group includes PE, PP and PA polymers characterized by intermediate to the highest values in $Total\ HC_{polymer}$, $TOC_{polymer}$, and $PC_{polymer}$ and low to very low $RC_{polymer}$, $Total\ CO_{polymer}$, $Total\ CO2_{polymer}$ and $T_{peak_{polymer}}$. PP polymers are characterized by the highest value in $Total\ HC_{polymer}$, $TOC_{polymer}$, and $PC_{polymer}$ in the third group. The relative values in $Total\ HC_{polymer}$, $TOC_{polymer}$, and $PC_{polymer}$, as well as $RC_{polymer}$ could also be used to distinguish between PE, PP and PA polymer types.

These results are in line with the works of Moldoveanu (2005) (see also La Nasa et al. (2020) for a complete review) suggesting that the molecular structures of polymers and their main related pyrolysis products seem to be the primarily controlling factors on polymer identification.

3.2 Comparison between polymer versus composite samples : Environmental implications

To validate the robustness of the Rock-Eval® methodology for plastic characterization, the proposed Rock-Eval® parameters were also calculated for each composite sample. This allows to compare and to find out the relation between polymers versus samples contaminated by the presence of plastics (polymers). For instance, Figure 5 illustrates the evolution of the calculated TOC values for artificial samples containing sand mineral matrices mixed with different polymers at different concentrations. Obtained correlation coefficients are near to 1 indicating that a linear equation describes the good relationship between the calculated TOC of composite samples and polymer contents varying between 0.2 to 4.2 wt.% (Figure 5). Furthermore, we demonstrated here that the slope of the most regression lines correspond to the $TOC_{polymer}$ value previously calculated for each investigated polymer (Figure 5; Table 1). By knowing the polymer type and the TOC of the composite or natural sample, we could thus quantify the plastic concentration.

Applying the same linear regression, a positive correlation between the TOC, PC, RC, total HC, total CO and total CO₂ parameters and the percentage (%) of each polymer was also observed for all the investigated composite samples containing different mineral matrices. Figure 6 shows an example of straight-line relationships between these parameters and the quantity of the PET polymer at different concentrations in different mineral matrices (e.g. sand, shale, marl and carbonate). In general, correlation coefficients are comprised between 0.74 and 0.99 indicating that all Rock-Eval[®] parameters can be considered highly correlated and these results confirm that they can be used to identify specific polymer families present in different mineral matrices from environmental samples (Figure 6). They should be preferentially used to quantify the polymer content. In low polymer content values (<1 wt. %), the matrix effect is globally less important so that a mean linear regression could be used to estimate the polymer concentration irrespectively to the matrix type (Figure 6). For a real case study (e.g. beach sand containing residual plastic detritus), the proposed approach comparing pure polymers with samples contaminated by plastics could be finally used to determine the percentage of each polymer family present in a natural contaminated sample.

4. Conclusions

An analytical methodology was proposed here in order to both identify and quantify the presence of plastics in sediments using the Rock-Eval[®]

device. It was mainly demonstrated that each investigated polymer shows specific Rock-Eval[®] parameters that can be considered as useful characteristics of polymer families (mainly $T_{peak_{polymer}}$, $TOC_{polymer}$, $PC_{polymer}$, $RC_{polymer}$, total $HC_{polymer}$, total $CO_{polymer}$ and total $CO2_{polymer}$ parameters). Correlation coefficients whose magnitude are between 0.7 and 0.9 indicate that all Rock-Eval[®] parameters proposed in this study can be considered highly correlated together with plastic content. This implies that this thermal degradation method can be also used to characterize the plastic contents in sediment samples. Although more work is still needed, a methodology is here proposed to distinguish and quantify the presence of plastics in the environment applying the proposed polymer Rock-Eval[®] database. It could be considered as an additional and rapid screening approach to more advance analytical workflow including SEM, Raman or FTIR technics.

The next step will be to set up additional calibrations for each polymer, and even enlarging the polymer database including PVC and other plastic types. These first results show detection limit of around 0.2 up to 0.5 wt.% in 60mg of sediment sample. Sample pretreatments as well as the influence of natural organic matrix content should also be investigated in a near future.

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Figure captions

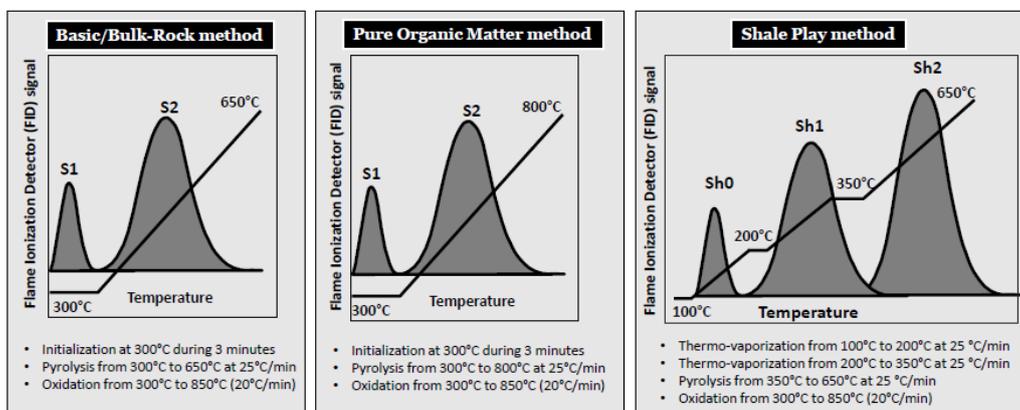


Fig. 1. Standardized Rock-Eval® methods showing the specific pyrolysis conditions (more details available in Espitalié et al., 1986; Lafargue et al., 1998; Behar et al., 2001; Romero-Sarmiento et al., 2014; 2016a,b; Romero-Sarmiento, 2019).

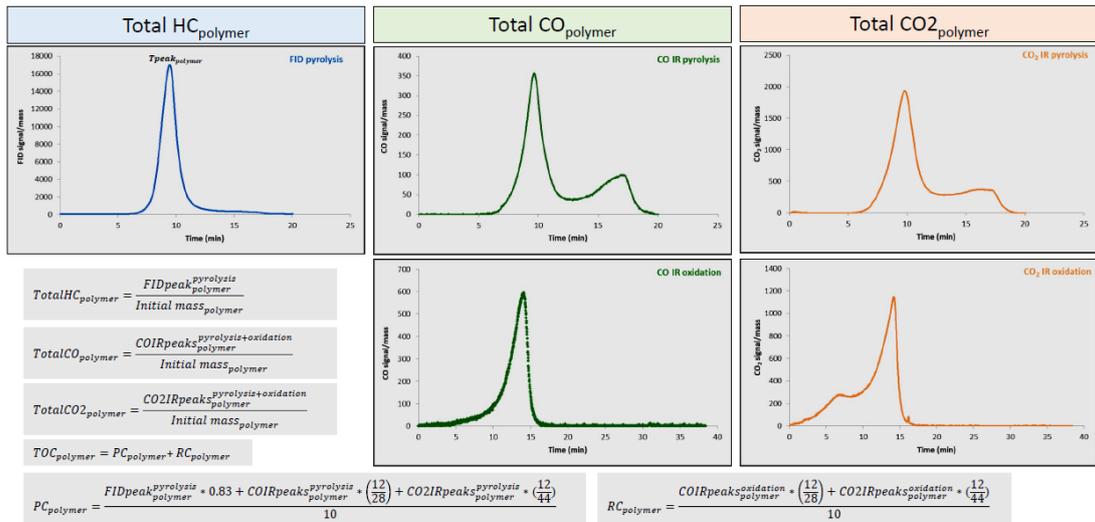


Fig. 2. Rock-Eval® thermograms and parameters defined in this work to characterize each polymer family (modified from Romero-Sarmiento et al., 2021a,b)

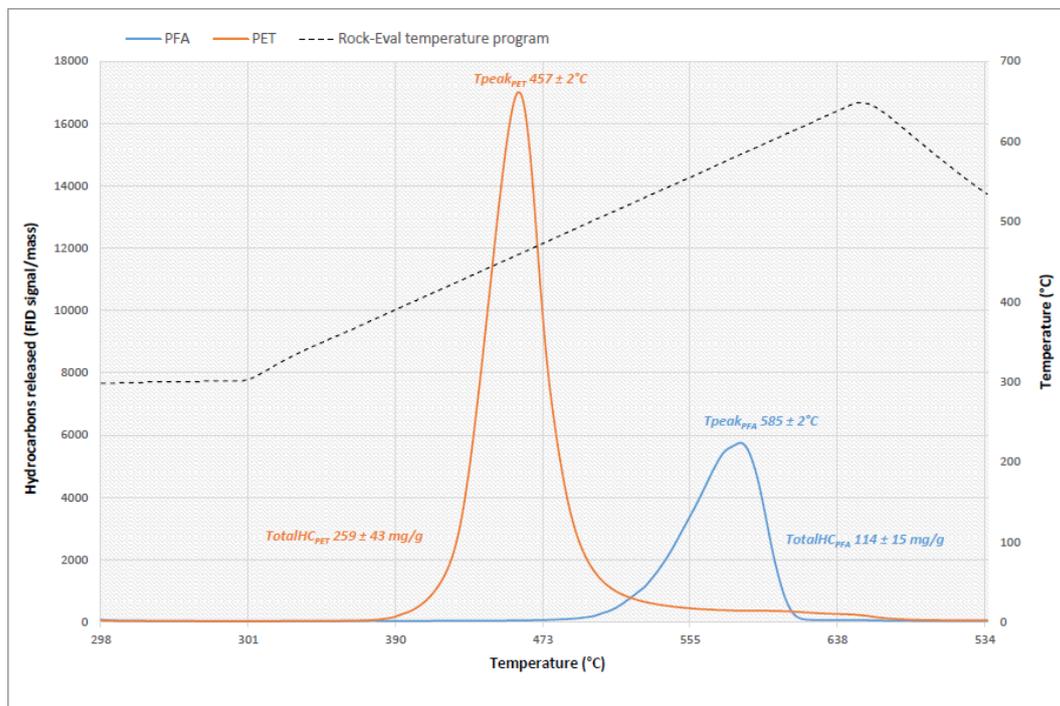


Fig. 3. Example of Rock-Eval® FID thermograms showing the distinct $T_{peak_{polymer}}$ and $Total\ HC_{polymer}$ parameters associated to the thermal degradation of PFA and PET polymers.

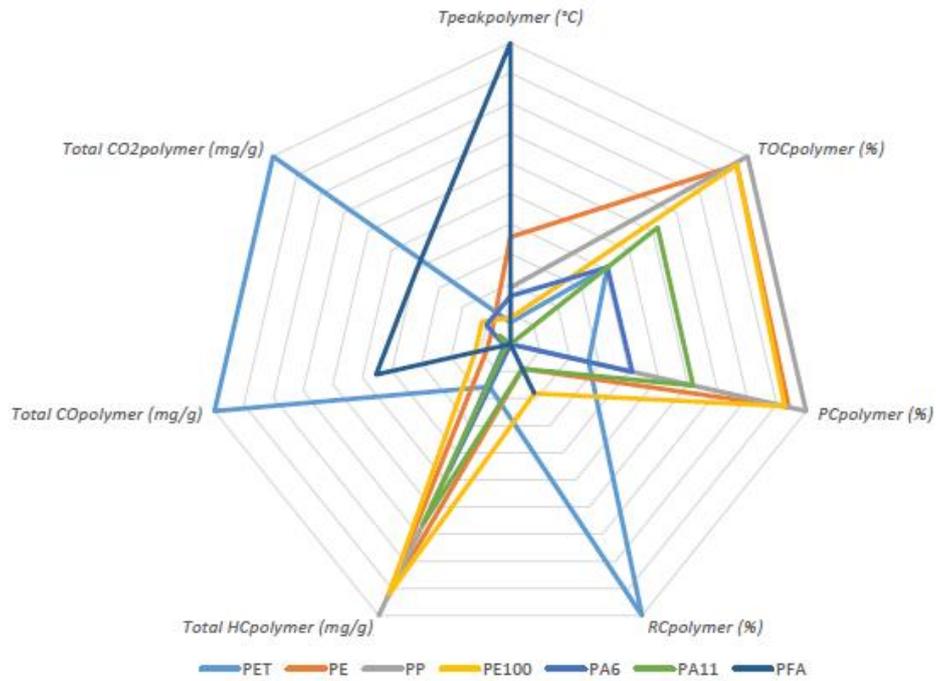


Fig. 4. Radar diagram using the 7 proposed Rock-Eval® parameters to distinguish polymer families.

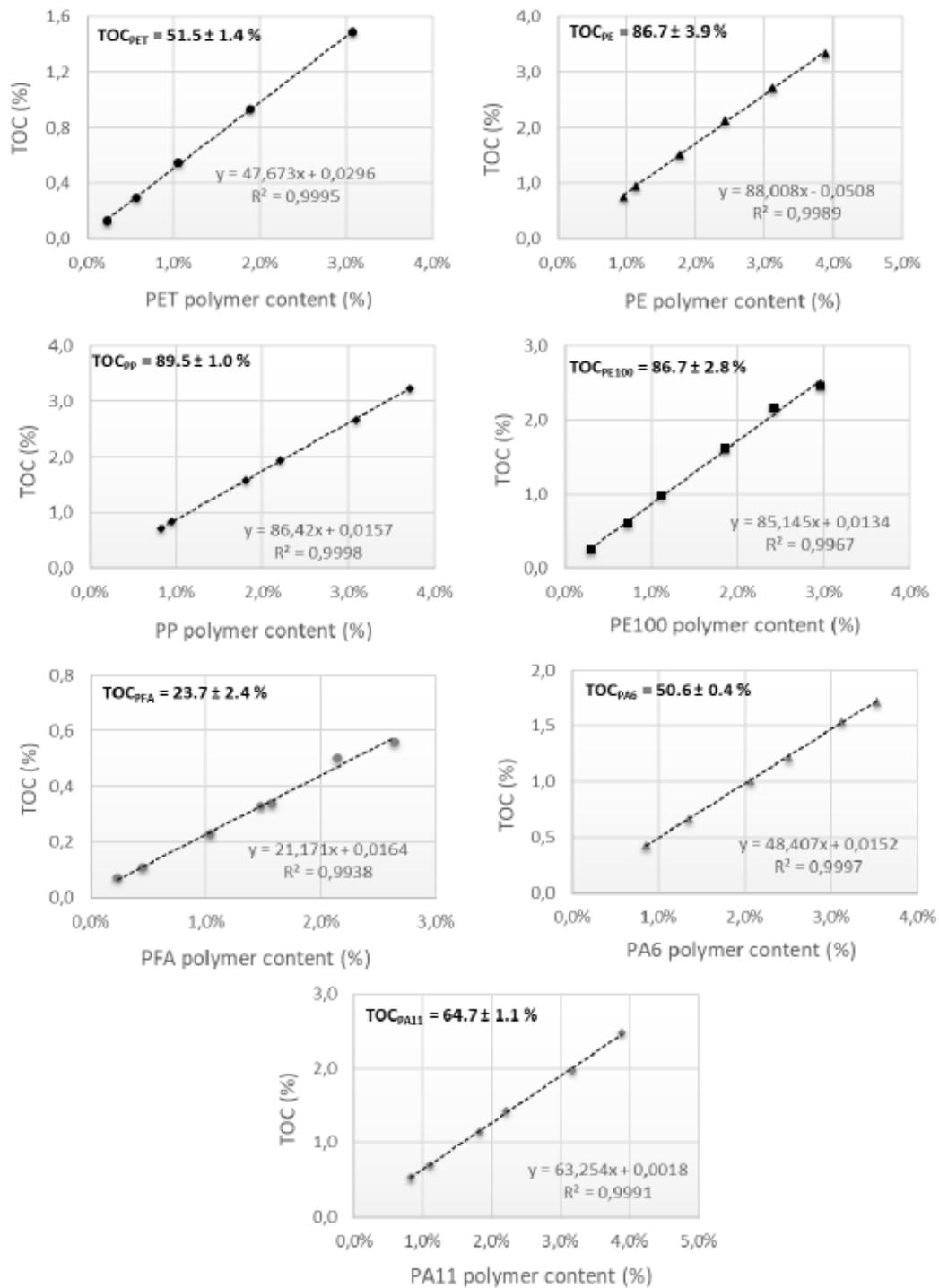


Fig. 5. Calculated TOC values for samples containing sand mineral matrices mixed with different polymers at different concentrations.

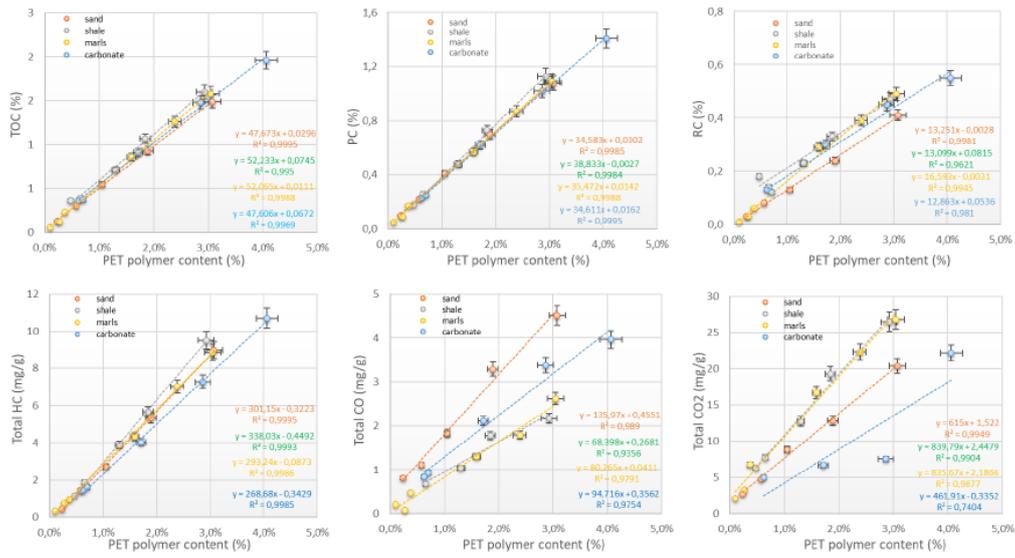


Fig. 6. Example of straight-line relationships between TOC, PC, RC, total HC, CO and CO₂ parameters and the quantity of PET polymer at different concentrations in different mineral matrices (e.g. sand, shale, marl and carbonate).

Table captions

Table 1. Rock-Eval® parameters proposed for each investigated polymer sample.

<i>Polyme r</i>	<i>T</i> _{peak} _{polyme} <i>r</i> (°C)	<i>TOC</i> _{polyme} <i>r</i> (%)	<i>PC</i> _{polyme} <i>r</i> (%)	<i>RC</i> _{polyme} <i>r</i> (%)	<i>Total</i> <i>HC</i> _{polyme} <i>r</i> (mg/g)	<i>Total</i> <i>CO</i> _{polyme} <i>r</i> (mg/g)	<i>Total</i> <i>CO</i> ₂ _{polyme} <i>r</i> (mg/g)
<i>PET</i>	457 ± 2	51 ± 1	39 ± 3	12 ± 2	259 ± 43	172 ± 17	836 ± 184
<i>PE</i>	496 ± 3	87 ± 4	85 ± 5	2 ± 1	979 ± 82	32 ± 19	151 ± 82
<i>PP</i>	473 ± 3	90 ± 1	89 ± 2	1 ± 1	1038 ± 36	20 ± 15	94 ± 60
<i>PE100</i>	459 ± 2	87 ± 3	84 ± 3	3 ± 1	965 ± 58	38 ± 18	183 ± 74
<i>PA6</i>	469 ± 2	51 ± 0	49 ± 0	1 ± 0	543 ± 15	23 ± 6	169 ± 45
<i>PA11</i>	447 ± 5	65 ± 1	63 ± 2	2 ± 1	727 ± 26	22 ± 7	129 ± 41
<i>PFA</i>	585 ± 2	24 ± 2	21 ± 3	3 ± 0	114 ± 15	89 ± 18	387 ± 101

CRediT author statement

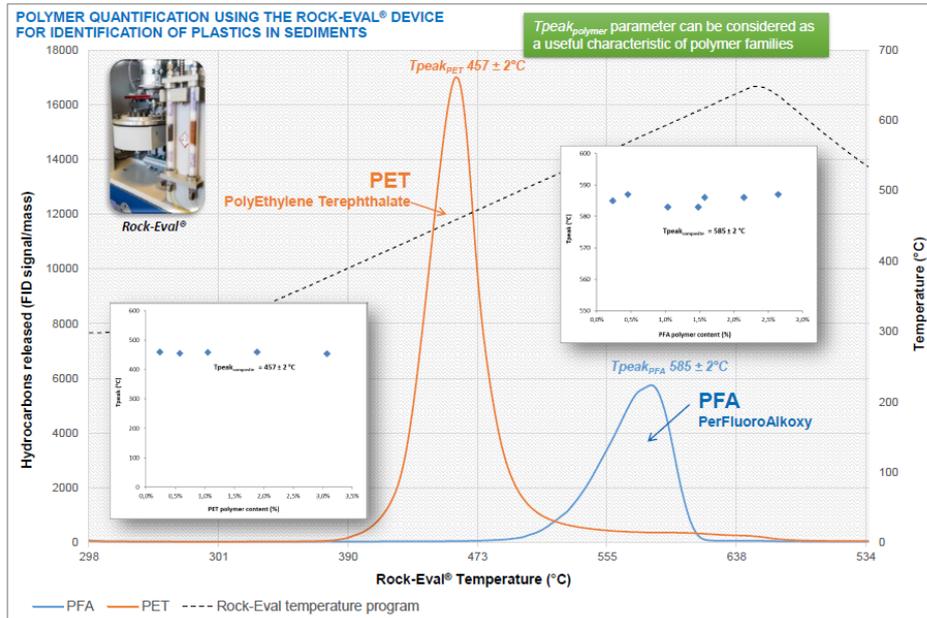
Maria-Fernanda Romero-Sarmiento: Conceptualization, Methodology, Investigation, Data curation, Writing- Original draft preparation. Herman Ravelojaona: Conceptualization, Methodology. Daniel Pillot: Conceptualization, Methodology. Sébastien Rohais: Supervision.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Highlights

1. Quantification of plastics in the environment using a Rock-Eval® device
2. Specific Rock-Eval® parameters are defined to characterize each polymer family
3. Rock-Eval® parameters can be highly correlated together with plastic content
4. Sediments with polymers at different concentrations (0.2 - 4.2%) were investigated