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Chapter

Elemental Analyzer/Isotope Ratio Mass Spectrometry (EA/IRMS) as a Tool to Characterize Plastic Polymers in a Marine Environment

Daniela Berto, Federico Rampazzo, Claudia Gion, Seta Noventa, Malgorzata Formalewicz, Francesca Ronchi, Umberto Traldi and Giordano Giorgi

Abstract

In the last 60 years, plastic has become a widely used material due to its versatility and wide range of applications. This characteristic, together with its persistence, makes plastic waste a growing environmental problem, particularly in the marine ecosystems. The production of plant-derived biodegradable plastic polymers is assuming increasing importance. Here, we report the results of a first preliminary characterization of carbon stable isotopes ($\delta^{13}\text{C}$) of different plastic polymers (petroleum- and plant-derived) and a first experimental study aimed to determine carbon isotopic shift due to polymer degradation in an aquatic environment. The results showed that the $\delta^{13}\text{C}$ values determined in different packaging for food uses reflect the plant origin for “BIO” materials and the petroleum-derived source for plastic materials. Considering degradation, $\delta^{13}\text{C}$ values of both bio bags and HDPE bags showed a gradual decrease toward less negative values when kept immersed in seawater, recording a $\delta^{13}\text{C}$ variation ($\Delta\delta^{13}\text{C}$) of 1.15 and 1.78‰, respectively. With respect to other analytical methods, the characterization of the plastic polymer composition by isotope ratio mass spectrometry is advantageous due to low cost and rapidity of analysis, small amount of sample required, high sensitivity, and the possibility of analyzing colored samples.

Keywords: carbon isotopes, plastic polymers, EA/IRMS, plastic degradation, plastic pollution

1. Introduction

1.1 Plastic debris in the ocean: a global environmental issue of the twenty-first century

Since 1950, the production and use of plastics has been constantly increased reaching a global production of 280 million tons in 2016 (i.e., as thermoplastics and polyurethanes), with China as the major producer (29%) [1].

Plastics represent a group counting hundreds of different materials derived from fossil sources (e.g., oil and gas) among which the most produced are polypropylene (PP), high- and low-density polyethylene (HDPE, LDPE), polyvinyl chloride (PVC), polyurethane (PUR), polyethylene terephthalate (PET), and polystyrene (PS). Due to their high versatility, durability, low weight, and low cost, plastic materials find applications in almost any market sector, but primarily in packaging (39.9%) and building industries (19.7%) [1].

In recent years, the growing evidence about the massive presence of plastic litter in the ocean, its pressure on the marine environment and wildlife, and its impact on marine-related human activities (such as fishery, shipping, and tourism) has raised lot of attention in the scientific, regulatory, and civil communities (**Figure 1**).

Oceanographic surveys have recorded the presence of plastics in any geographical regions, including remote polar areas, and at any depth, from the sea surface to the seafloor of the oceans (**Figures 2–4**).

The amount of plastic debris in the sea is still unknown due to the large variability of its distribution as regards both spatial and temporal scale, which prevents accurate estimates. However, modeling studies have recently approximated that 5–13 million tons of plastics (i.e., equivalent to 1.5–4% of global plastic production) end up in the oceans every year [2].

The slow degradation rates of plastics under environmental conditions provide additional complexity to this global issue, by contributing to their accumulation in all terrestrial and aquatic environments. It has been estimated that, once in the ocean, the majority of manufactured polymers persist for decades and probably for centuries due to their low degradability (**Figure 5**) [3, 4].

In both terrestrial and marine environments, degradation of petroleum-derived plastics occurs through abiotic and biotic processes (i.e., UV degradation, hydrolysis, and decomposition by microorganisms), leading to their fragmentation into increasingly smaller pieces. Thus, plastic particles dispersed in the environment are commonly divided into three main classes based on their size: macro: >25 mm,

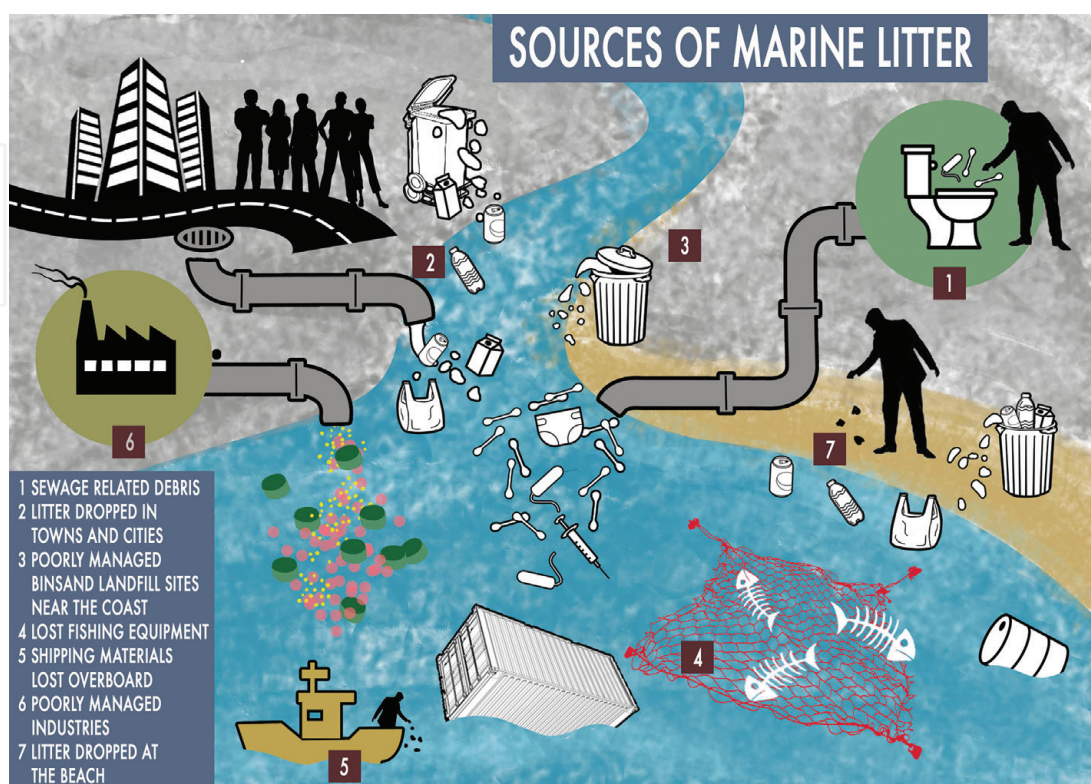


Figure 1. Pathways through which litter reaches the sea (illustration by Davide Zanella).

meso: 5–25 mm, and microplastics: <5 mm. The smaller-size class, which includes both primary microplastics (i.e., particles produced as such, e.g., plastic pellets, exfoliating cosmetics, or synthetic clothing fibers) and secondary particles (i.e., particles derived from the breakdown of larger plastic debris), is likely to be the most abundant in the ocean today [5].



Figure 2.
Marine litter on the beach (photo by Tomaso Fortibuoni).



Figure 3.
Seabird nesting on plastic nets (public domain).



Figure 4.
Tangle of fishing nets on a beach (photo by Francesca Ronchi).



Figure 5. Estimated decomposition times of different types of garbage dispersed in the marine environment (illustration by Davide Zanella).

The concern about the heavy contamination of the marine environment by plastics is related to the potential of plastic debris to cause harm to the inhabiting organisms via different mechanisms. Among the most alarming issues, there is an uptake and a bioaccumulation of plastic debris by marine organisms at almost all levels of the food web and the consequent trophic transfer. Recent studies have reported that micro and nanoplastics can easily be taken up and ingested by marine organisms (i.e., zooplankton, worms, bivalves, crustaceans, demersal and pelagic fishes, seabirds, reptiles, and mammals), resulting in a significant impact on the aquatic wildlife and possibly on human health via seafood consumption [6]. Furthermore, due to the large surface to volume ratio, microplastic fragments can potentially adsorb many kinds of common marine contaminants on their surface, in particular hydrophobic organic substances such as polychlorinated biphenyls, polyaromatic hydrocarbons, and organochlorine pesticides [7, 8]. This can promote their transport in the environment and induce toxic effects following ingestion and desorption (e.g., endocrine disruption, mutation, and cancer). Moreover, another source of concern is the possible release of additives commonly present in plastic formulations (i.e., bisphenol A, phthalates, and flame retardants) [8, 9], and although the leaching rates of these common additives in seawater are poorly known, their potential for toxicity is considered to be very high.

Several actions have currently been undertaken at national and international levels to tackle the contamination of marine environments by plastics. Their main aim is to achieve a general reduction of plastic use (in particular packaging and disposable items), recycling of plastic items at the end of their lifetime, and replacement of the use of plastics with more sustainable materials and biopolymers (e.g., plant-derived polymers [10]), which are more prone to degradation by microorganisms and show a shorter persistence once dispersed in the environment.

1.2 Experimental approaches to assess plastic debris in environmental samples

With the growing evidence of the severe impact caused by plastics on the wildlife, the assessment of the presence, behavior, and fate of plastics in the marine environments has become a fundamental research issue, highly advocated to the scope of putting in place more effective policies. However, especially for the smallest particles (i.e.,

microplastics), their efficient identification to the scope of assessing the plastic load in the environmental compartments (e.g., seawater, sediments, and biota) is a serious challenge for scientists. Many analytical techniques have been used to identify plastic debris in environmental samples, as largely reviewed in the literature [11, 12]. Among the most used approaches, there are electron scanning microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS, ESEM-EDS), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) [13], and thermal analysis (pyro-GC/MS). Other analytical methods used to identify plastic materials are near infrared spectroscopy (NIRS), differential scanning calorimetry [14], and UV-VIS spectroscopy [15, 16].

Stable isotope analysis, which is an analytical technique that measures the relative abundance of stable isotopes yielding an isotope ratio that can be used as a research tool, is finding application in a growing number of different research fields and practical case studies. For instance, it is widely used to trace the origin of organic matter in various environments [17, 18], to track fraud in the food industries [19] and to identify microtraces of drugs, flammable liquids, and explosives in forensic cases [20]. This technique has been only rarely applied to assess the presence of microplastics in environmental samples [21]. Its potential for detecting plastic debris in environmental samples relies on different isotopic signatures of carbon in (i) petroleum-derived materials, (ii) C4 plants used in the synthesis of bioplastics, and (iii) marine samples' matrices (e.g., particulate organic matter, plankton, tissues of marine organisms, algae, and marine plants).

1.3 Stable isotope analysis: principles of the method

The term isotopes (from the Greek *iso*, same and *topos*, place) identifies atoms of the same chemical element, that is, the same place in the periodic table of the elements, that has the same atomic number but different atomic mass number. In other words, isotopes are atoms having the same number of protons and electrons (equal chemical properties) and a different number of neutrons (different physical properties). Each element has known isotopic forms, and in total, there are 275 isotopes of the 81 stable elements, in addition to over 800 radioactive isotopes (Figure 6).

Isotopes of a single element possess almost identical properties. They are commonly classified as natural or artificial, stable, or unstable. The quantification of the ratio between two isotopes allows to determine if two chemically similar environmental samples have different origins, related to the difference of the original sources. The isotopic distribution characterizing the sources may be influenced by phenomena of a different nature, which in turn may cause significant variations in the final products.

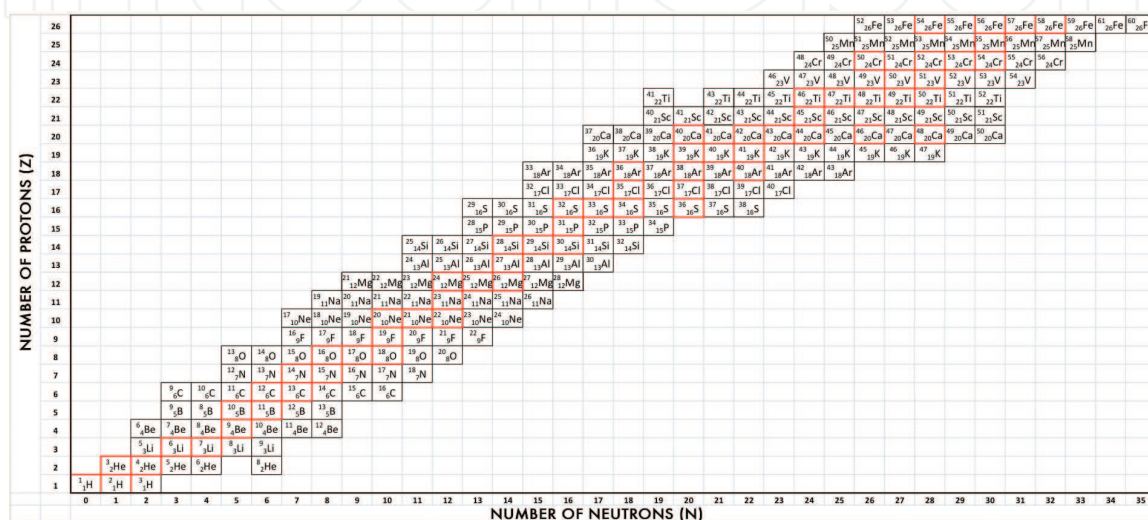


Figure 6.
 Stable isotopes have a proton/neutron ratio lower than 1.5.

Depending on the chemical element, variations in the relative mass abundance of its isotopes can be detected through the analysis of stable isotopes. Technological advances in isotope analysis have led to the development of scientific instruments able to measure very small variations in the abundance of stable isotopes with high precision and accuracy (mass spectrometry). Therefore, stable isotope analysis can be applied considering different elements, thus giving nowadays applications in different fields of science.

For a given chemically stable element, its isotopic composition in a sample (R) is equal to the ratio between the abundance of the heavy isotope with respect to the light one (e.g., $^{13}\text{C}/^{12}\text{C}$), and it is expressed as deviation, in parts per thousand, from an international reference standard material ($\delta\text{‰}$), according to the equation (Eq. (1)) given below:

$$\delta(\text{‰}) = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000 \quad (1)$$

where R_{sample} is the mass ratio of the heavy isotope to the light isotope measured in a sample and R_{standard} is the isotopic ratio defined for the standard. The standard reference material that is commonly used for carbon is Vienna Pee Dee Belemnite. Thus, positive δ values indicate that the heavy isotope is enriched in the sample compared to the standard, while negative δ values indicate that the heavy isotope is depleted in the sample.

The possibility of distinguishing two samples on the basis of their relative abundance of two isotopes bases on the phenomenon of isotopic fractionation, which can be enacted by a wide range of chemical (e.g., nitrification and ammonification), physical (e.g., evaporation and condensation), and biological (e.g., photosynthesis, assimilation, and excretion) processes. In fact, many natural (and anthropic) processes can alter the isotopic signature of a chemical element in a matrix by causing an imbalance of the isotope distribution that leads to a variation of its original isotopic signature [22]. Thus, as the extent of fractionation of many chemical elements have been proved to be sensitive to specific processes/variables, it can be used as a tool to investigate the involved process/variable itself. In general, two mechanisms of isotopic fractionation can be distinguished:

(1) Thermodynamic, that is, due to a difference in bonding energy of the isotopes in the compounds. This mechanism implies that:

- heavy isotopes accumulate in oxidized products;
- the isotopic fractionation is favored at low temperatures, since at high temperatures, the differences between the isotopes are attenuated;
- the process is not relevant in the case of chemical reactions of gaseous substances and biological reactions.

(2) Kinetic, that is, due to different reaction rates of the isotopes. In this type of mechanism, it is generally observed that fast, irreversible, and unidirectional processes are favored. This is the case of most of the biological processes, where lighter isotopes are preferentially used, as their employment requests less energy. It also occurs when the products are easily removed from the reagents, in processes such as evaporation, diffusion, etc. These processes are featured by:

- the preferential breaking of the bonds formed by light isotopes;
- the preferential distribution of light isotopes in products and of the heavy ones in the reagents.

Given a chemical substance AB characterized by the presence of a certain isotopic distribution of element X, we can calculate the fractionation factor by dividing the ratio of the number of isotopes X in product A with the ratio of the number of isotopes X in product B (Eqs. (2) and (3)).

$$\alpha_{AB} = \frac{R_A}{R_B} = 1 + \left[\frac{(\delta_A - \delta_B)}{1000} \right] \quad (2)$$

where

$$R = \frac{X_h [\text{atoms of the heavier isotope (rare)}]}{X_l [\text{atoms of the lighter isotope (abundant)}]} \quad (3)$$

However, the fractionation factor (α) is normally replaced by the isotopic enrichment factor (ϵ), which is defined as $(\alpha - 1) \times 1000$.

1.4 Carbon isotope ratio as a tool in environmental studies

Carbon and nitrogen isotope analysis is used to investigate the trophic web and the matter flows among the main components of an ecosystem (e.g., organic matter, producers, primary and secondary consumers); it can be used to understand chemical and biological processes occurring at both ecosystem and organism levels. Stable isotope analysis can also be a useful tool for assessing the origin of water, atmospheric, and soil pollution.

The two main carbon reserves in nature are represented by organic and inorganic carbon, which are characterized by different isotopic fingerprints due to the different processes in which they are involved (**Figure 7**). The inorganic carbon (carbonate) is involved in the exchange equilibrium among (i) atmospheric carbon dioxide, (ii) dissolved bicarbonate, and (iii) solid carbonate. The exchange reactions among these three forms lead to an enrichment of the heavy isotope in the

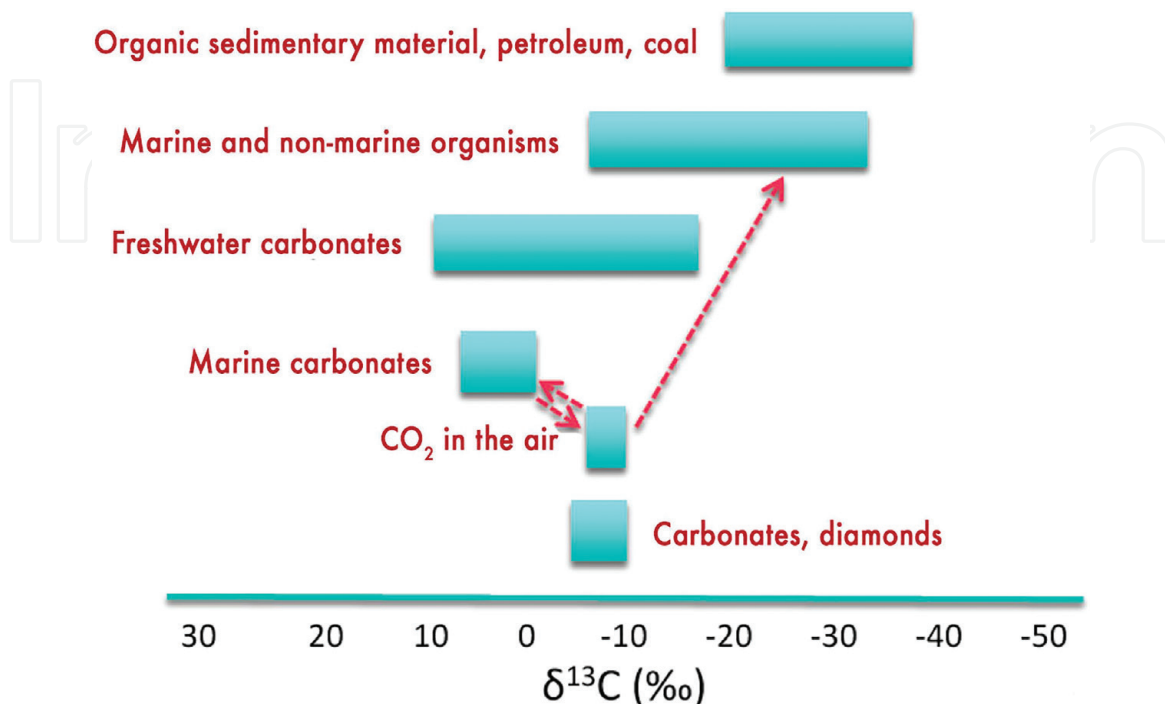


Figure 7.
 Isotopic fingerprint of naturally occurring carbon.

solid carbonate form ($\delta^{13}\text{C}$ equal to 0‰). In contrast, the kinetic reactions which mainly involve the organic carbon (i.e., photosynthetic process) determine a concentration of the lightest isotope in the synthesized organic material ($\delta^{13}\text{C}$ equal to about -25‰) [17].

The fractionation of organic carbon is mainly linked to the specific photosynthetic pathway featuring each plant. The terrestrial plants, classified as C3 and C4, can follow two different photosynthetic pathways. Both types synthesize organic matter characterized by $\delta^{13}\text{C}$ values more negative than that of carbon dioxide ($\sim -7\text{‰}$), because during the photosynthesis, the produced organic substance accumulates the light isotope compared to the heavy one. The C3 plants, typical of temperate climates, produce the 3-phosphoglyceric acid, a compound with three carbon atoms (Calvin cycle) with an average value of $\delta^{13}\text{C}$ of about -26.5‰ . The C4 plants generate oxaloacetate, a compound with four carbon atoms (Hatch-Slack cycle) characterized by a value of $\delta^{13}\text{C}$ around -12.5‰ .

The chemical composition of animal tissues is related to the food sources they assimilate, and therefore, it reflects the isotopic composition of the diet [23, 24]. The enrichment between primary producers and consumers (herbivores) has been estimated to be approximately $+5\text{‰}$, whereas at the successive trophic levels, the enrichment is less marked ($+1\text{‰}$) [25]. Thus, the isotopic value detected in the tissues of an organism can be potentially used as an indicator of its trophic position. However, since the variation of the $\delta^{13}\text{C}$ values due to trophic passages is relatively modest, $\delta^{13}\text{C}$ is mainly used to trace the primary carbon source used [26].

Through the analysis of the stable carbon isotopes, it is also possible to differentiate terrestrial and marine trophic webs. The “marine” carbon derives from the dissolved inorganic carbon (dissolved bicarbonate) characterized by an isotopic value equal to about 0‰, while the “terrestrial” carbon derives from the atmospheric carbon dioxide which has a lower $\delta^{13}\text{C}$ value (approximately -7‰). This difference is maintained at every trophic level both in the marine and terrestrial trophic chain (**Figure 8**).

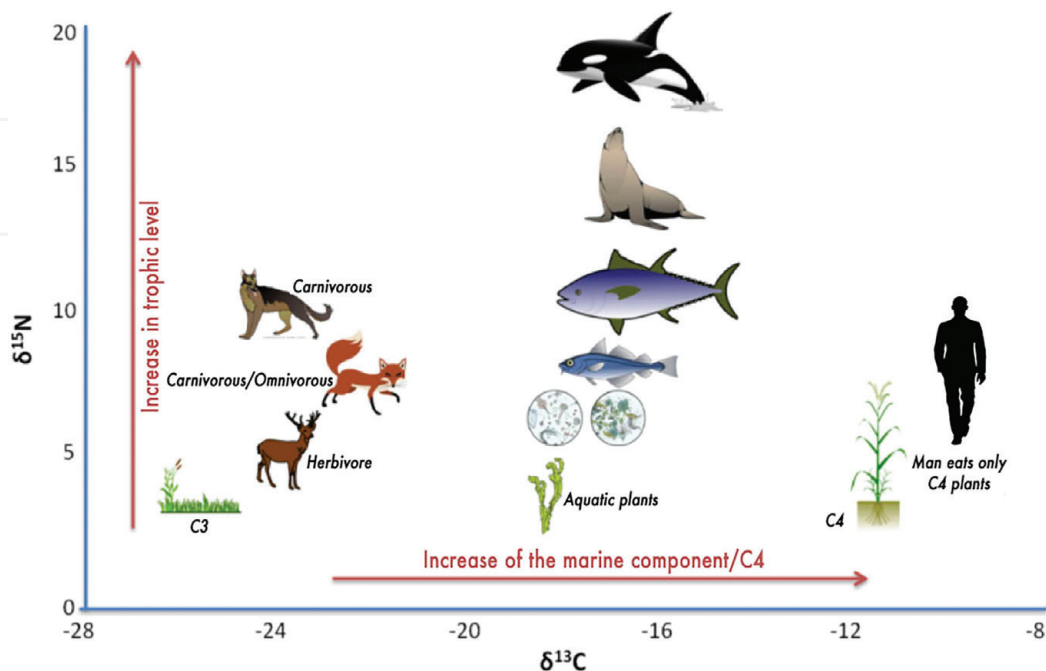


Figure 8. Variations of $\delta^{13}\text{C}$ carbon and $\delta^{15}\text{N}$ nitrogen (‰) isotopes in different organisms of the terrestrial and marine food chain.

2. Preliminary study to characterize plastic polymers using elemental analyzer/isotope ratio mass spectrometry (EA/IRMS)

In 2016, Berto and collaborators carried out a preliminary study aimed at evaluating the potentials of stable isotope analysis to discriminate a wider range of plastic and bioplastic materials (including those highly used in packaging, such as shopping bags and plastic bottles for drinking water) (**Table 1**) to the scope of using this analytical technique for the identification of plastic debris in marine samples in future field surveys [27].

Furthermore, considering the lack of knowledge on possible changes in the carbon isotopic signature of plastics due to degradation processes in the marine environment, this study also investigated the variation of $\delta^{13}\text{C}$ values of petroleum- and plant-derived polymers of packaging materials subjected to biotic and abiotic degradation. The study was carried out by using an isotope ratio mass spectrometer Delta V Advantage (Thermo Fisher Scientific, Bremen, Germany) coupled with an elemental analyzer Flash 2000 (Thermo Fisher Scientific, Bremen, Germany). The accuracy of the isotopic data was evaluated by the analysis of the certified polyethylene foil ($-31.8 \pm 0.2\text{‰}$, IAEA-CH-7, International Atomic Energy Agency, Austria). The analytical precision of measurements was 0.2‰ for C.

Sample type	Use
Acrylonitrile butadiene styrene (ABS)	Thermoplastic polymer; used for pipes, musical instruments, sport equipment, automobile industry, toys, and electronic component assemblies
Fluorocarbon	Polymers characterized by high melting temperature, resistance to sunlight degradation and chemical inertness; used for industrial coatings (electronics, automotive, and food industry)
High density polyethylene (HD PE)	Thermoplastic polymer; used for beverage bottles, food storage containers, plastic bags, fuel tanks, piping systems, electrical boxes, folding furniture, sport equipment, storage sheds, and wood-plastic composites; packaging material for food use
Low density polyethylene (LD PE)	Utilized as thin films used for coatings or plastic bag production, recipients made in injection molding (bottles, bags, and laboratory equipment), pipings, food containers, corrosion resistant surfaces, and computer components; packaging material for food use
Low density polyethylene (LD PE) recycled	As above
Chlorosulfonated polyethylene (HYPALON)	Is a synthetic rubber; used in folding kayaks and inflatable boats, sport equipment (snowshoes), and roof coatings
Polychloroprene (NEOPRENE)	This synthetic rubber is more degradation resistant than the natural one and is used for corrosion-resistant coatings and hoses, clothing and equipment for water sports, car seats or covers, computer or tablet holders, mouse pads, and gloves
Polyamide (PA)	Polymers used in carpets, textiles, sportswear, due to their strength and durability
Polyethylene terephthalate glycol-modified (PETG)	This strong and glass-like thermopolymer is employed in production of electronic devices, covers, food and medical applications, and credit cards; it is fully recyclable

Sample type	Use
Polypropylene (PP)	As it is chemically resistant to many acids, bases, and solvents, it is used for laboratory equipment, medical devices and textiles, but also for piping systems, plastic furniture, carpets, ropes, roofing waterproof membranes, insulation for electrical cables, bottles and storage boxes, and concrete additives
Polystyrene (PS)	In its solid form, it is employed for packaging, containers, bottles, disposable cutlery, dishes, and razors. Also widely used in foamed form in protective packaging
Polytetrafluoroethylene (PTFE)	This fluoropolymer is hydrophobic and nonreactive and displays an extremely low friction coefficient. It is used in industrial applications, wire production as insulators, carbon fiber and fiberglass composites production, a nonstick coating in cookware, and textiles (like Gore-Tex)
Polyurethane (PU)	Thermoplastic and thermosetting polymers are available; used for the production of cushions, mattresses (flexible foams), construction industry, wheels, tires, furniture, synthetic fibers, hard-plastic parts, shoes, and surface coatings
Polyvinyl chloride (PVC)	Production of door and window frames, siding, pipes, bottles, and credit cards (rigid form); also used in electrical cable insulation, inflatable products, leather imitation, and shower curtains (flexible form)
Polyvinylidene difluoride (PVDF)	Chemically, electrically and flame resistant resin, used for containers in chemical industry, pipes, and food containers. Also applied in electronics (transducers and insulators) and in medical and defense industries
Styrene acetonitrile (SAN)	Polymer similar to polystyrene; used in plastic optical fibers, packaging material, bottles, and food container, as well as in computer products and battery cases
Polysiloxanes (SILICONE)	Used in electrical and thermal insulation, sealants, medical applications, and cooking utensils
Polyethylene terephthalate (PET)	Used for packaging of food and beverages, textiles (known as polyester), and thermoforming applications
PET recycled	As above
LATEX/RUBBER	Plant-derived plastic polymer. The natural latex rubber is employed in the production of gloves, mattresses, balloons, and swim caps
Poly lactide (PLA)	Is a thermoplastic, plant-derived polyester. Used as a packaging material, compost bags, disposable tableware, gardening (mulch film), and medicine (implants)
“BIO” bag	Biodegradable bags are used in food packaging and composting of food waste and to collect dog waste
Cellulose	C3 plant used in bioplastic production
Cotton	C3 plant used in bioplastic production.
Potato	C3 plant used in bioplastic production.
Rice	C3 plant used in bioplastic production
Tomato	C3 plant used in bioplastic production
Corn	C4 plant used in bioplastic production
Sugarcane	C4 plant used in bioplastic production

Table 1. Plastic (petroleum and plant-derived polymers) and natural matrices analyzed in this study.

This chapter gives a review of the main insights obtained and critically discusses the potentials of the carbon isotope ratio analysis to study the behavior and fate of plastics in the aquatic environment.

2.1 $\delta^{13}\text{C}$ as a possible tool to investigate plastic polymers

$\delta^{13}\text{C}$ values recorded in this study for the most used petroleum-derived plastic polymers, plant-derived polymers, some commercial items made by petroleum- and natural-derived polymers, which are largely found in the marine litter worldwide (i.e., food packaging items), and natural matrices are reported in **Figure 9**.

Due to their high stability and durability [28], in the last decades, petroleum-derived plastic materials have largely replaced paper and other cellulose-based products with a continuously increasing trend. At the moment, a wide variety of petroleum-based synthetic polymers are produced worldwide (approximately a total of 335 million tons in 2016), and significant quantities of these polymers end up into natural ecosystems as waste products [1].

The $\delta^{13}\text{C}$ values of the majority of the analyzed petroleum-derived plastic polymers ranged over a wide interval, that is, between -33.97 and -25.41‰ . Only a few polymers, such as PTFE, silicon, and ABS showed more negative $\delta^{13}\text{C}$ values (-40.70 ± 1.17 , -39.37 ± 0.27 , and $-35.17 \pm 0.98\text{‰}$, respectively), possibly due to fractionation processes during their synthesis.

With the exclusion of PTFE, ABS, and silicon, the recorded $\delta^{13}\text{C}$ range results are comparable to that reported for crude petroleum [29]. Petroleum is constituted by a complex mixture of organic substances, with a predominance of hydrocarbons, whose exact composition depends on the site of extraction. Petroleum usually shows negative values of $\delta^{13}\text{C}$, ranging between -34 and -18‰ depending on the specific extraction field. In fact, as reported by Stahl [29], petroleum could be originated from the lipid fraction of organic matter. In particular, the carbon

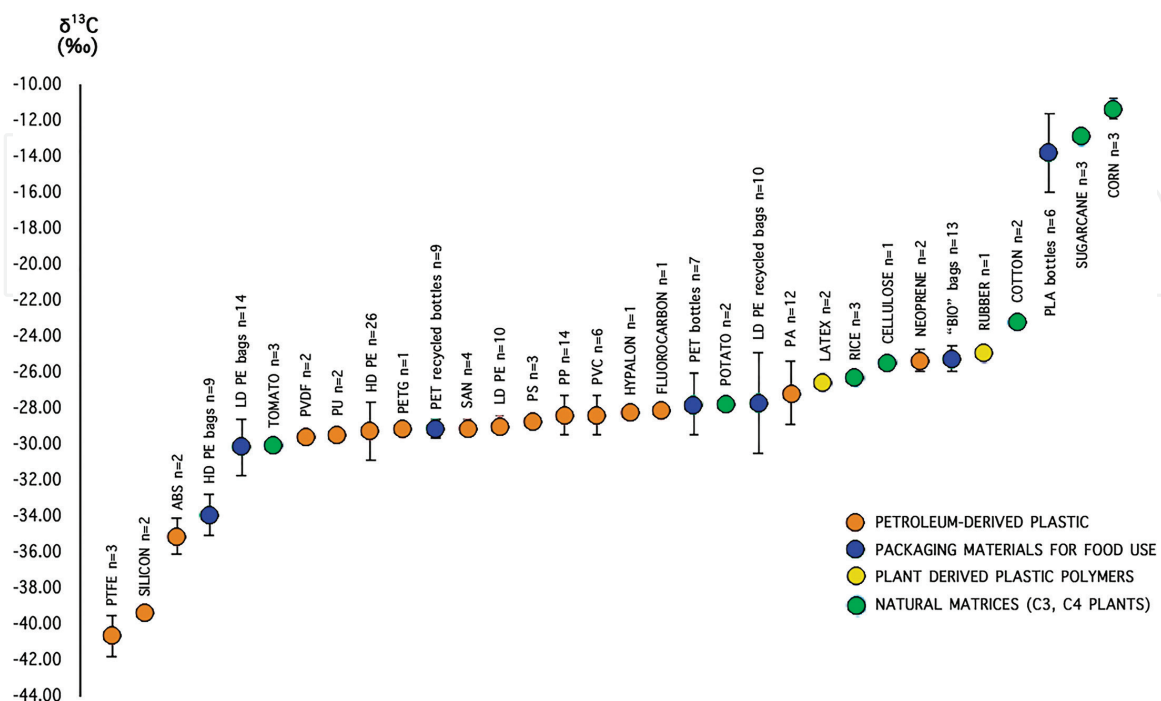


Figure 9. $\delta^{13}\text{C}$ values determined in various petroleum- and plant-derived polymers, as well as in natural matrices analyzed in this study.

isotopic value of petroleum can vary in relation to the marine vs. terrestrial origin of the source, with an enrichment of ^{12}C with respect to ^{13}C in the marine environment compared to the terrestrial one [30].

Interestingly, different $\delta^{13}\text{C}$ values were recorded for some polymers as pure material and once in packaging commercial items. For instance, a significant ($p < 0.05$) more negative $\delta^{13}\text{C}$ value was determined in the HDPE shopping bag for food use with respect to the original HDPE polymer. This could be related to the addition of some organic additives (i.e., stabilizers) in the final materials used for food packaging. In fact, depending on the commercial use, plastic formulations can be enriched with monomeric ingredients to improve their processing, end-use performance, and appearance (e.g., colorants, photostabilizers, etc.). Among these possible additives, our preliminary data excluded colorants as the main cause of isotopic variation in the investigated samples. These results were confirmed by the lack of significant difference among polymers of different colors ($p > 0.001$). The independence of the $\delta^{13}\text{C}$ value from the plastic color could provide an important analytical advantage to the isotopic approach over some of the other analytical methods used for plastic characterization. In particular, the spectroscopic methods have been proved to be limited by the color of the plastic samples, because of the occurrence of interferences due to a decrease of the diffuse reflection intensity in dark color samples [31]. Further investigation and larger analytical data set are required in order to strength these results.

2.2 $\delta^{13}\text{C}$ as a possible tool to distinguish petroleum-derived plastics from plant-derived plastics

To reduce the impact of plastic debris in the environment, recyclable and more biodegradable polymers (i.e., plant-derived polymers) have been introduced increasingly into the market [10]. Plant-derived plastic polymers used for food packaging, such as bags and bottles for drinking water, showed a significant difference in isotopic values with respect to the petroleum-derived plastic products. In fact, petroleum-derived packaging materials for food use, such as shopping bags for fruits and vegetables (HD PE) and plastic bottles for drinking water (PET), were characterized by the $\delta^{13}\text{C}$ mean values of -33.97 ± 1.15 and $-27.84 \pm 1.71\text{‰}$, respectively, whereas plant-derived supermarket envelopes (“BIO” bags) and bottles (PLA, a biodegradable polyester derived from the fermentation of starch and condensation of lactic acid) recorded the $\delta^{13}\text{C}$ mean values of -25.30 ± 0.70 and $-13.87 \pm 2.18\text{‰}$, respectively. As regards to the results obtained for “BIO” bags, values reflected those of C3 plants, while for PLA, the analyses highlighted $\delta^{13}\text{C}$ values similar to those of C4 plants, suggesting their specific origin.

This difference suggests that stable isotope analysis could be a useful method to discriminate between petroleum- and plant-derived plastic debris [21, 27]. The most used biopolymers are in fact produced starting from C3 (rice, potatoes, cotton, and cellulose) and C4 (corn and sugarcane) plants, species which differ for photosynthetic pathways and, consequently, for the carbon fingerprint. C3 plants recorded more negative $\delta^{13}\text{C}$ values (ranging from -30 to -25‰) than C4 plants (ranging from -13 to -11‰), in agreement with Suzuki et al. and authors therein [21]. Considering the isotopic signature of the “BIO” bags, a common and widespread biodegradable product used for many commercial purposes, $\delta^{13}\text{C}$ values are generally comparable with those reported for C3 plants. Regarding “recycled” polymers, LD PE recycled envelopes showed a $\delta^{13}\text{C}$ mean value of -27.75‰ . The presence of a low quantity of other polymers as impurities or different recycle processes could explain the less negative average value with respect to the row LD PE (-30.19‰) given by an ^{13}C enrichment or depletion (fractionation).

2.3 $\delta^{13}\text{C}$ as a possible tool to study degradation processes in the marine environment

The influence of natural degradation processes on the fractionation of carbon in plastic materials under marine conditions, according to a preliminary field study carried out by Berto et al. [27] in Venice lagoon, is showed in **Figure 10**. Over a 60-day period and under variable conditions of temperature and salinity (i.e., 24–35°C and 7.8–8.1, respectively), the $\delta^{13}\text{C}$ values of both “BIO” bags and HD PE bags showed a gradual decrease toward less negative values, recording a $\delta^{13}\text{C}$ variation ($\Delta\delta^{13}\text{C}$) of 1.15 and 1.78‰, respectively. This shift could be reasonable due to physical, chemical, and/or biological degradation, even if the latter is a controversial matter.

The degradation of plastic polymers in the environment involves many factors (photodegradation, thermooxidation, hydrolysis, and biodegradation by microorganisms) [32], and it proceeds according to the rates highly dependent on the environmental conditions. For instance, several authors have reported that degradation processes and the rate of hydrolysis of most plastic polymers become insignificant in the ocean when the temperature and the concentration of oxygen are reduced [32, 33].

However, the physical/mechanical degradation occurring in the marine environment can alter the plastic polymers at the surface layer and favor the starting of microbial deterioration processes. By considering that, in many biochemical reactions, such as autotrophic fixation of CO_2 by plants [34] and microbial degradation processes, the lightest isotope (^{12}C) are preferentially used as a substrate over the heaviest isotopes, and the different isotopic values recorded by Berto et al. [27] for “pristine” and “aged” plastic materials sampled from the marine environment suggested the occurrence of degradation processes. Further studies are needed to evaluate the pathway and the time featuring this process.

In fact, some researchers are confident in thinking that biopolymer (such as cellulose in plants) plastics are not generally biodegradable. Bacteria and fungi coevolved with natural materials, while plastics have only been around for about 70 years. So microorganisms simply have not had much time to evolve the necessary biochemical tool kit to latch onto the plastic fibers, break them up into the constituent parts, and then use the resulting chemicals as a source of energy and carbon that they need to grow [35]. However, in 2016 a team of researchers from Kyoto Institute of Technology and Keio University, after collecting environmental samples

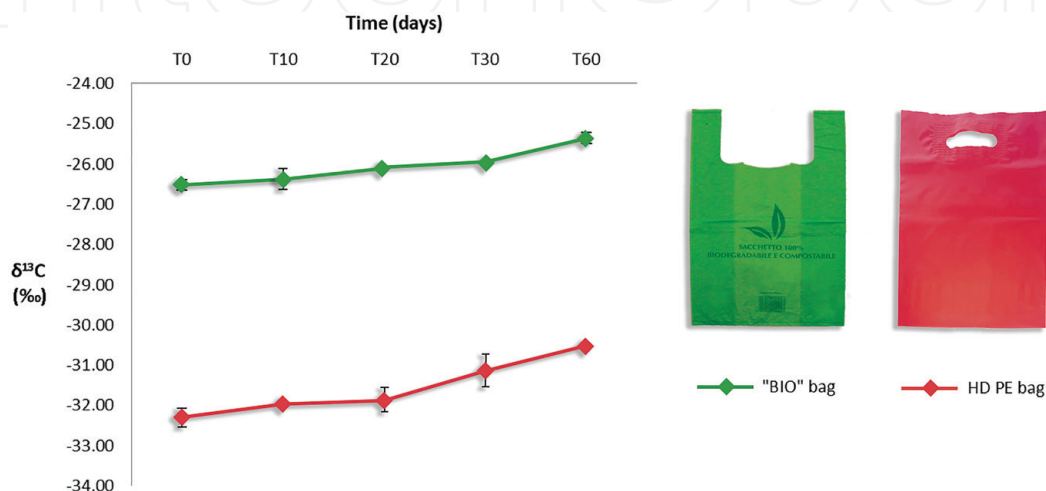


Figure 10. Degradation of “BIO” bag and HD PE bag in lagoon environment, reflected by $\delta^{13}\text{C}$ variation in time.

containing PET debris, observed a novel bacterium (*Ideonella sakaiensis* 201-F6) which is able to use PET plastic for carbon growth. This bacterium produces two distinct enzymes hydrolyzing PET plastics into terephthalic acid and ethylene glycol. This discovery has potential importance for the recycling process of PET [36].

A large number of tests (respirometric, loss of weight, tensile strength, spectroscopic) have been conducted to evaluate the extent of degradation of polymers, either alone or in blended forms, mainly under terrestrial environmental conditions.

It is worth noting that most recalcitrant polymers can be degraded to some extent in the appropriate environment at the right concentration. A screening program to study the ability of organisms and enzymes in degrading plastic polymers in a marine environment is required, considering the increasing importance of biodegradable plastics in the last few years.

Considering the new data presented in this study, it is possible to hypothesize the new paths for stable isotope research applied to the plastic polymers in the environment.

3. Conclusive remarks

In this chapter, we focused on plastic polymers, both petroleum- and plant-derived, commonly used in commercial packaging products for food use, giving preliminary overview of their $\delta^{13}\text{C}$ values. The low difference of $\delta^{13}\text{C}$ values among polymers suggested that the different chemical pathways used for their synthesis did not induce fractionation of carbon stable isotopes, yielding to $\delta^{13}\text{C}$ values meaningful of the raw material (i.e., petroleum and terrestrial plants). Thus, this technique showed interesting perspective for its application in discriminating petroleum- and plant-derived polymers in marine samples.

Furthermore, the method showed to be unaffected by additional variables, such as color, and thus, it seems a valuable alternative to the spectroscopy methods for the characterization of plastic polymers in marine samples, which in contrast found the analytical limitation especially with dark colored plastic samples.

Finally, an important potential of the isotope mass spectrometry is its application to the study of the degradation processes (abiotic and biotic) of plastic waste released in the marine environment and the assessment of the degradation rates. In particular, this technique could be applied for analysis of suspended plastic debris, after filtration of both marine and fresh water samples collected along the water column. In this regard, however, further studies are needed to discriminate the isotopic values of suspended organic matter from those of plastic polymers, with major concern for micro and nanoplastics. Such possible application is of particular interest for the estimation of the fate of plastics in the marine environment and the evaluation of the effectiveness of the policies developed to reduce the environmental impact of marine litter.

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Conflict of interest

No potential conflict of interest was reported by the authors.

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