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Carbonyl Index Variability and Trends in Marine Meso-Microplastics: Implications of Instrumental Effects and Spectral Preprocessing

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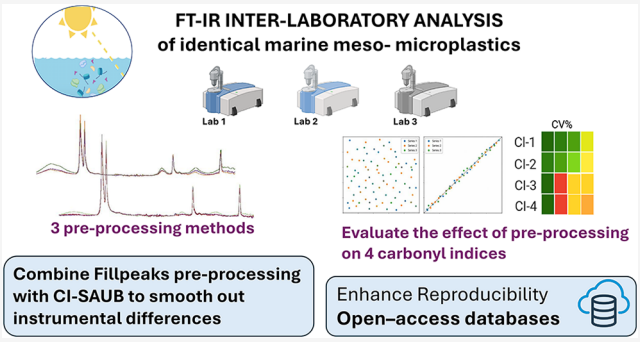
ABSTRACT: This study addresses the critical need to understand variability in the carbonyl index (CI) of marine plastics to effectively assess their environmental fate. Standardization is essential to ensure data interoperability and comparability across different research laboratories. We evaluated the effect of spectral preprocessing on the comparability of four carbonyl indices derived from analyses of marine meso- and microplastics across three ATR-FTIR instruments. The fillpeaks baseline spectral preprocessing correction yielded the highest consistency and interlaboratory correlation, thus supporting its adoption as a standard for environmental CI determination. Moreover, when used with the CI-SAUB index, defined as the ratio of the carbonyl peak area to the methylene peak area, instrumental differences are effectively smoothed out. We also demonstrated that index-specific CI values derived from spectra processed differently are not directly comparable, further underscoring the need for harmonized protocols. Our analysis supports the use of the CI as a reliable proxy for surface oxidation resulting from weathering mechanisms. To enhance reproducibility in future research, we provide a cross-validated, open-access spectral library of weathered plastics, along with a reference database for estimating the CI of weathered particles. Our results emphasize the importance of standardized approaches for improving the reliability and reproducibility of plastic pollution research and monitoring.



KEYWORDS: *environmentally weathered plastics, FT-IR spectral libraries, polyethylene, polypropylene, data harmonization, interlaboratory comparison, open access data*

INTRODUCTION

Marine plastic litter undergoes photo-oxidative, mechanical, chemical, and biological weathering, leading to polymer breakdown, fragmentation, and the formation of micro- and nanoplastics.[1,2] These particles pose ecological risks, making assessment of polymer degradation essential for evaluating plastic pollution exposure and impacts. To assess polymer composition, Fourier Transform Infrared (FT-IR) spectroscopy is among the most widely used methodologies for the chemical identification and classification of polymer types. By generating unique spectral fingerprints based on molecular structures and functional groups, FT-IR enables chemical identification by comparison with reference spectra.[3] Weathering, however, particularly photo-oxidative and thermal degradation, significantly alters the spectral signature of polymers.[4] Therefore, polymer identification can be challenging because the spectra of weathered plastics often differ from those of pristine plastics in standard software libraries. In polyolefins such as polyethylene (PE) and polypropylene (PP), photo-oxidation leads to the formation of carbonyl groups, which are depicted as "new" spectral bands.[5] A commonly used metric for estimating the oxidation and weathering of polyolefins is the carbonyl index (CI), defined as the ratio of the carbonyl peak (C═O) height or area to the height or area of a stable reference peak, usually the methylene peak (CH_2).[4] This index has been widely applied in plastic degradation studies to assess UV-induced changes in polyolefin properties,[7] thereby driving experimental research on plastic weathering under both natural and accelerated conditions to better understand microplastic formation and their interactions with chemicals and organisms.[8−13] However, only a limited number of studies have applied CI to field-collected microplastics to estimate weathering state and potential "age" based on CI values.[6,14−17] Moreover, existing CI-based studies do not follow a standardized calculation approach, resulting in limited

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comparability across the studies.[7] Although CI values generally increase under prolonged oxidation conditions,[18] their reliability across studies is compromised by multiple factors, including polymer chemistry, additives, exposure conditions, instrumentation, analytical methods, and data processing approaches.[19] Interoperability gaps highlight the need for harmonized spectral quality standards and uniform CI evaluation methods. Baseline correction is a critical preprocessing step that removes nonchemical spectral contributions arising from instrumental noise and ATR contact effects,[20] thereby isolating chemically meaningful signals and enabling more accurate and reproducible CI estimation.

Our objectives were: (1) to evaluate the impact of different spectral preprocessing methods on four different types of CIs obtained from FT-IR spectra of marine meso- and microplastics; (2) to assess the extent to which instrumental differences influence CI variability and comparability; and (3) to evaluate patterns in CI values among sea surface polyethylene (PE) and polypropylene (PP) meso- and microplastics (5−25 and 0.3−5 mm, respectively). To address these objectives, we conducted an interlaboratory comparison among three research institutions, using environmentally weathered PE and PP marine floating meso- and microplastics collected with a manta net. To inform future research, all processed spectra and corresponding estimated CI values from the laboratory intercomparison were uploaded to the online tool Open Specy,[21] providing a validated library of weathered spectra (https://www.openanalysis.org/openspecy/).

METHODS

Sampling and Description of the Analyzed Meso- and Microplastics

Meso- and microplastics, ranging from 5 to 25 and 0.3 to 5 mm in size, respectively, were collected, using a surface-towed manta net with a mesh size of 330 μm, in the Eastern Mediterranean Sea, including the Aegean, Ionian, and parts of the Levantine Seas. Our microplastics sampling did not include particles smaller than 300 μm, as the manta net's 330 μm mesh size did not retain them. We conducted one sampling campaign per year in 2015, 2017, and 2023, and two in 2020. Detailed sampling protocols and meso- and microplastic separation methods are described in Adamopoulou et al.,[22] and methodological details are provided in SI Part 1, Section 1.1. Briefly, samples were visually sorted using stereomicroscopes (OLYMPUS SZX10, SZX) equipped with a digital camera (Luminera; Nikon DLS3). After extraction, all plastic items were gently rinsed with deionized (D.I.) water and dried at 40 °C to remove sea salt and any excess of organic/inorganic matter. We avoided cleaning the samples with sonication or acid treatment, as these would remove the degraded surface layer of the polymer, thereby exposing unweathered material.[23] The longest dimension of each item (in mm) was measured using INFINITY ANALYZE software. A total of 1,493 polyethylene (PE) and 710 polypropylene (PP) meso- and microplastic fragments were analyzed to assess sea-surface weathering trends. A subset of these fragments collected in 2023, i.e., 284 PE and 89 PP fragments (including 65 PE and 17 PP mesoplastics, and 219 PE and 72 PP microplastics), was used for the interlaboratory comparison of CI values. The laboratories that participated in the interlaboratory comparison were: the Institute of Oceanography—Hellenic Centre for Marine Research (HCMR) in Greece, the Institute of Marine Sciences—National Research Center (ISMAR-CNR) in Italy, and the Flanders Marine Institute (VLIZ) in Belgium, which will be referred to as Lab1, Lab2, and Lab3, respectively.

Interlaboratory FT-IR Analysis

At Lab1, the MP's chemical characterization was performed with an Attenuated Total Reflectance Fourier transform infrared (ATR-FT-IR) spectroscope (Agilent Cary 630) with a diamond ATR crystal. The spectral range was 650−4000 cm^{-1} with a resolution of 4 cm^{-1}, using 32 coadded background scans and 32 coadded sample scans, Y−axis units measured in absorbance, and the search identification algorithm was "similarity". Polymer identification was performed by comparison with commercially available libraries and Open Specy. At Lab2, polymer characterization was performed using a LUMOS stand-alone FT-IR microscope (Bruker Optik GmbH), equipped with a motorized XY sample stage and an automated ATR probe (Ge crystal). Following background scans, ATR spectra were recorded by averaging 8 scans per particle at a spectral resolution of 4 cm^{-1} (range 650−4000 cm^{-1}). The CO_2 interference (adsorption at 2300−2400 cm^{-1}) was removed for clarity. The infrared spectra were processed and analyzed using the OPUS 7.5 software (Bruker). Polymer identification was performed by comparison with commercially available libraries and an additional custom library compiled within the framework of the JPI-Oceans project BASEMAN.[24] Lab3 used an FT-IR (PerkinElmer), equipped with a universal ATR accessory with a diamond/KRS-5 crystal. The spectral range was 650−4000 cm^{-1}, the resolution was 4 cm^{-1}, and 8 background and sample scans were used at 0.2 s^{-1}, and the Y−axis units were measured in absorbance. The polymer identification was performed by comparing the spectra of interest with commercially available libraries, across all laboratories. To ensure consistency, a minimum Hit Quality Index (HQI) threshold of 80% was applied across all laboratories for both PE and PP identifications. All items used in the interlaboratory study yielded consistent polymer identifications across the three laboratories.

Spectral Preprocessing

For spectra preprocessing, we used two types of baseline correction methods and min-max normalization as an alternative preprocessing method. Specifically, from the R package 'baseline' in the CRAN repository, we applied two baseline correction algorithms: fillpeaks and modpolyfit (https://cran.r-project.org/).[25−27] The fillpeaks algorithm is more rigorous, employing local spectral windows for baseline correction, whereas modpolyfit applies baseline correction across the entire spectrum. In particular, fillpeaks is an iterative baseline-suppression algorithm that uses local windows and is suited to nonlinear baselines with local variations and qualitative analyses, whereas modpolyfit uses modified polynomial fitting with baseline suppression relative to the whole spectrum. Additionally, we used min-max normalization, an alternative to baseline correction, which rescales the spectrum's intensity values to 0−1. We preprocessed the PE and PP spectra using R 4.4.1 (R Core Team, 2017) (SI Part 1, Section 1.2, Figures S1 and S2).

Carbonyl Indices

The carbonyl index (CI) is a widely used metric for quantifying polymer degradation in studies of plastic aging and polymer characterization. Usually, it refers to the ratio of the carbonyl (C═O) absorbance peak intensity or area (1650 to 1850 cm^{-1}) to the methylene (CH_2) bending peak intensity or area (1420 to 1500 cm^{-1}).[4,5] Pristine materials exhibit low CI values, while weathered or oxidized materials show higher CI values. However, the exact wavelengths selected by researchers can vary, thereby hindering reliable comparisons among laboratories.[7] To assess the appropriate application of the CIs, we first conducted a comprehensive systematic literature review of the various calculations used for polyethylene (PE), polypropylene (PP), and their composites and blends, following the methodology of Gomes et al. (2024).[7] Our methodology involved searching the Web of Science database for publications with "polyethylene" or "polypropylene" in their titles and the keyword "carbonyl index" for the period 2000 to 2023, adding "degradation" from 2024 to 2025. We reviewed a total of 181 publications on PE and 107 on PP. We excluded 23 articles on PE and 7 on PP due to issues such as inaccessibility, lack of CI data, or inclusion of irrelevant

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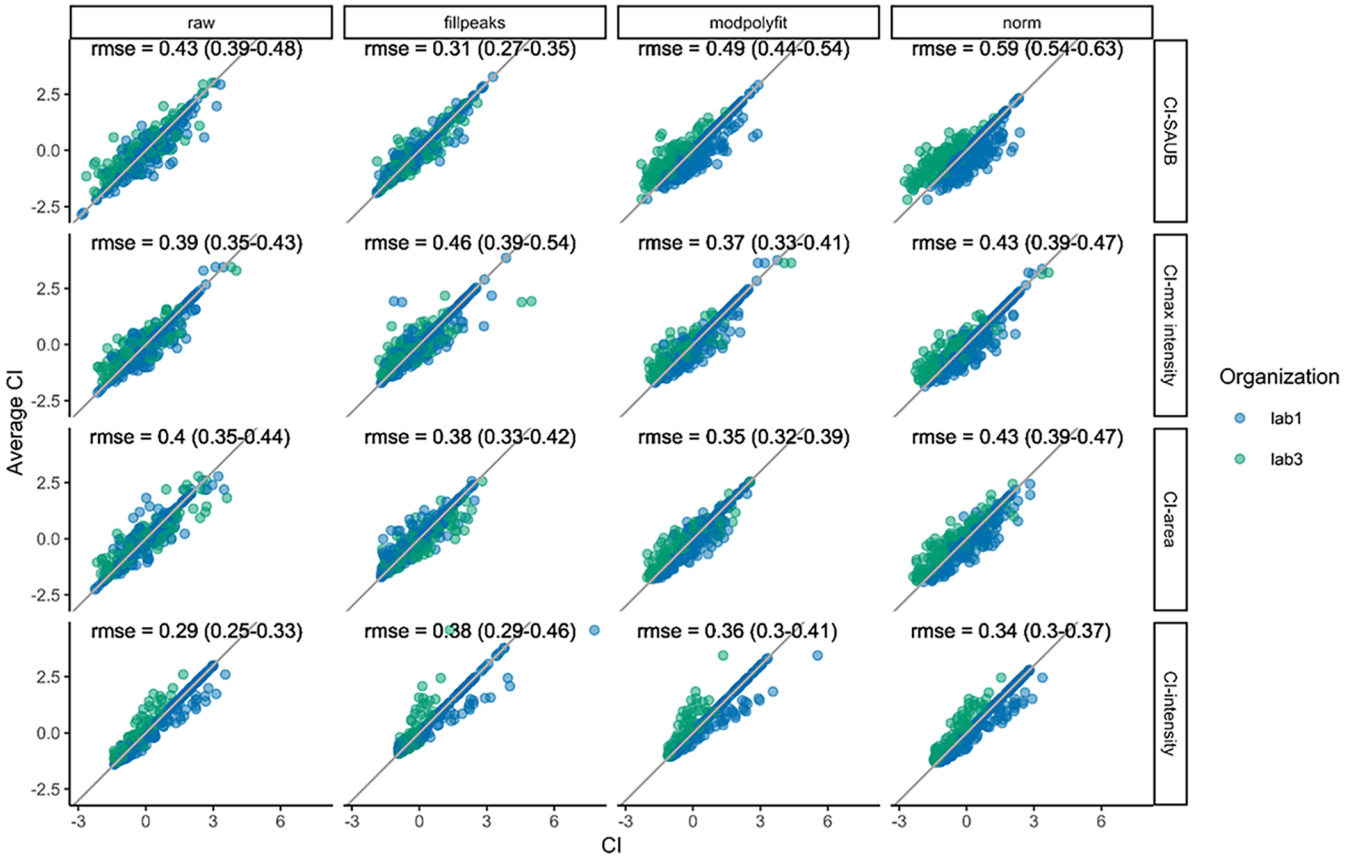

Figure 1. Root mean square error (RMSE) to 1:1 line between each laboratory's CI values and the mean CI across Lab1 and Lab3 are shown for all four CIs and preprocessing methods tested. Data from Lab1 and Lab3 are shown in blue and green, respectively. For each case, the RMSE across the two laboratories is reported, with the 95% bootstrap confidence intervals in parentheses.

polymer types (e.g., polyethylene terephthalate (PET) was mistakenly listed in the search results for PE). Ultimately, we analyzed 258 publications (SI Part 2, Tables S1 and S2). In our review, we identified inconsistencies in the calculations of CIs. Approximately 46%−49% of the reviewed papers either did not specify the carbonyl bands used as nominator and reference denominator, respectively, or relied on bands cited in fewer than three publications (SI Part 2 Figure S1). This means that nearly 50% of the reviewed publications refer to CIs calculations that are either mentioned only in their own articles, appear in fewer than three articles, or do not provide the calculations (SI Part 2, Figure S1, Table S1, S2).

In the remaining 50% of publications, we identified 13 (13) distinct carbonyl numerator wavelengths and 12 (12) distinct reference denominator wavelengths (SI Part 2, Figure S1). The most frequently reported carbonyl peak wavelength was 1715 cm^{-1} (ketones, carboxylic acids), observed in 15% of the studies. Following this, the integrated area from 1650 cm^{-1} to 1850 cm^{-1} (ketones, carboxylic acids, aldehydes, esters, lactones, amide-1) was used in 9% of studies, which accounted for the majority of research on environmentally weathered field plastics. Overall, the intensities chosen within the area 1700−1750 cm^{-1} (carboxylic acid, esters, aldehydes) account for 24% of the studies. The most commonly used reference wavelengths for the denominator are based on the integrated area between 1420 cm^{-1} and 1500 cm^{-1}, accounting for 11% of studies. Additionally, 22% of the studies selected specific peak wavelengths within this range. In 15% of the reviewed publications, reference wavelengths were selected from bands spanning 2020−2916 cm^{-1}, which the authors considered the most representative (SI Part 2, Figure 1b). The most commonly used index ratio for evaluating environmentally weathered polymers is the area ratio between the wavenumber ranges 1650−1850 cm^{-1} and 1420−1500 cm^{-1}. This index is referred to as the Specified Area Under Band (SAUB)[4] and is considered more representative of olefins' environmental degradation, as it includes carbonyl spectral signatures from a variety of oxidation processes (photo-, thermal, and microbial). Based on our literature review, we selected four CI indices for testing: two based on peak intensity and two on peak area (Table 1). All calculations of the FT-IR indices were conducted using R version 4.4.1 (RStudio Team, 2017).

Table 1. Based on Our Literature Review, We Selected Four CI Indices: Two Based on Peak Intensity and Two on Peak Area

Index	Ratio Formula
CI-SAUB (Specified Area Under Band)	$\frac{1650-1850\ cm^{-1}}{1420-1500\ cm^{-1}}$
CI-max intensity	Maximum peak height within the SAUB wavelength range for the nominator and denominator
CI-area	$\frac{1700-1750\ cm^{-1}}{2800-2950\ cm^{-1}}$
CI-intensity	$\frac{1715\ cm^{-1}}{1472\ cm^{-1}}$

Based on our literature review, we observed that the presence of additives generally has a minor effect on variations in the CI index. Specific additives tend to produce more distinct and sharper peaks in the spectrum (see SI, Part 2, Table S1, Publications No. 18, 20, and 33). Notably, Celik et al. (2023) highlight that although commercial plastics are often mixed with various chemicals, such as antioxidants and plasticizers, these additives have minimal impact on the CI of microplastics.

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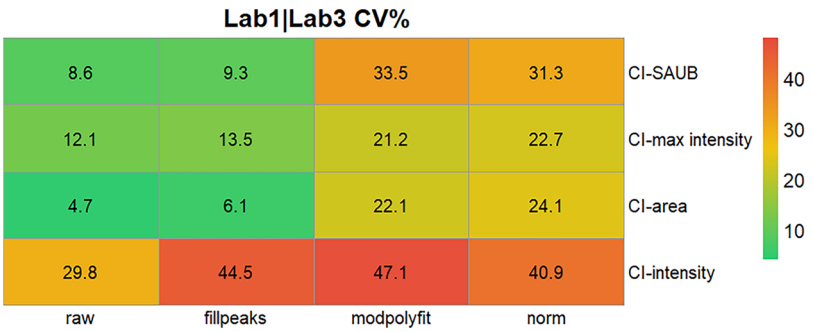

Figure 2. Heatmap plot of the coefficient of variation (%) for each of the CIs tested using pooled data from Lab1 and Lab3 for raw and preprocessed spectra.

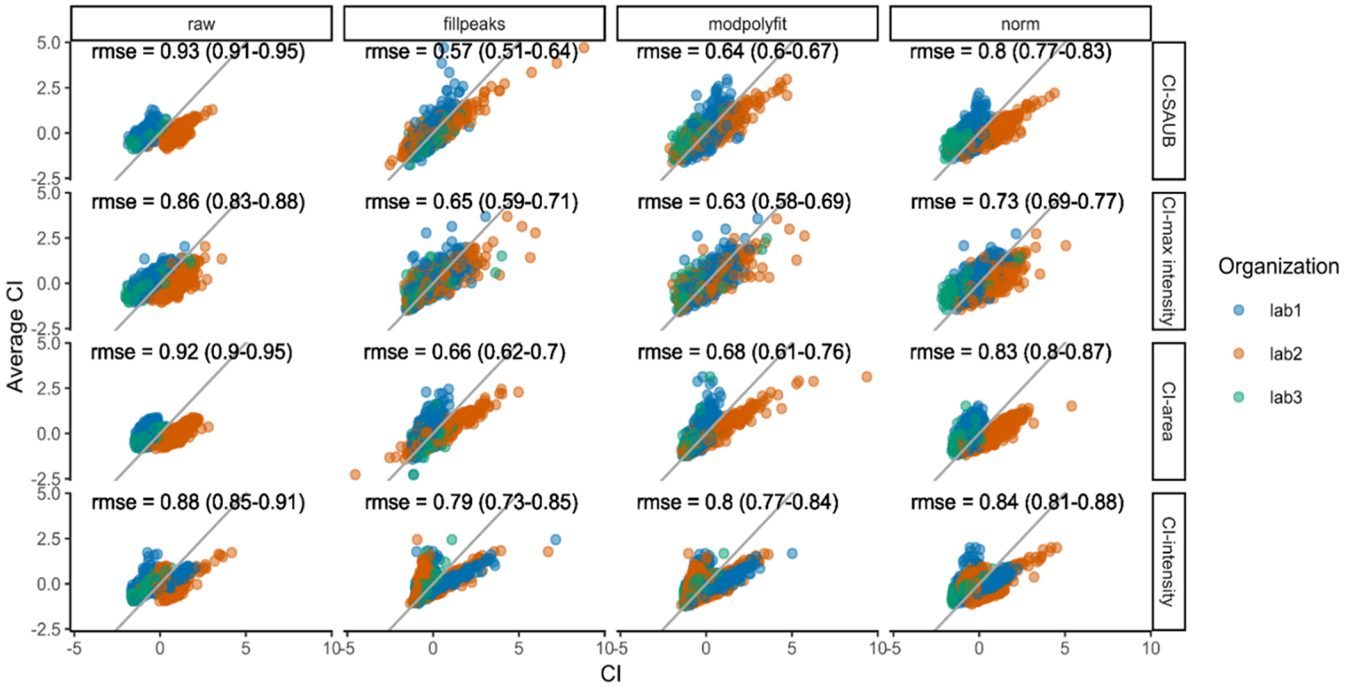

Figure 3. Root mean square error (RMSE) to 1:1 line between each laboratory's CI values and the average CI across Lab1, Lab2, and Lab3 are shown for all four CIs and preprocessing methods tested. Data from Lab1, Lab2, and Lab3 are shown in blue, red, and green, respectively. For each case, the RMSE across the three laboratories is reported, with 95% bootstrap confidence intervals in parentheses.

Statistical Analysis

For pairwise comparisons, the nonparametric Mann−Whitney U test was applied (R packages "stats" and "FSA") (10.32614/CRAN.package.FSA). Interlaboratory CI measurements were evaluated using Pearson correlation analysis; correlation coefficients (r) and corresponding p-values were calculated, with statistical significance defined at $p < 0.05$. Agreement between interlaboratory measurements was assessed using the root-mean-square error (RMSE), with 95% bootstrap confidence intervals; lower RMSE values indicate better agreement. This provided a quantitative measure of both systematic and random deviations in the measurements. Interlaboratory variability among the three laboratories was evaluated using the coefficient of variation (CV%). (R packages, ggplot2, tidyr[28] and dplyr) (R Studio Team).

RESULTS

Analytical Factors Affecting CI Indices: Interlaboratory Comparability and Preprocessing Methods

To evaluate instrument and laboratory variability, the same subset of 284 PE and 95 PP meso- (65 PE, 17 PP) and microplastics (251 PE, 72 PP) was independently analyzed by three laboratories (Lab1, Lab2, Lab3). Interlaboratory differences across indices and preprocessing methods were estimated. Specifically, pairwise comparisons (Mann−Whitney U test) between laboratories (Lab1, Lab2, and Lab3) revealed significant interlaboratory differences across all calculated carbonyl indices and preprocessing methods (SI Part 1, Table S3). Pearson correlations were strongest between Lab1 and Lab3; in contrast, correlations involving Lab2 (Lab1 - Lab2 and Lab2 - Lab3) were weak or nonsignificant, and in some cases negative. The lack of correlation for the Lab2 data is most likely due to instrumental differences among laboratories, as Lab2 used a Ge ATR crystal, which probes a shallower penetration depth than diamond crystals used in Lab1 and Lab3. Comparing the data from Lab 1 and Lab 3 revealed differences in RMSE across indices and preprocessing methods (Figure 1). For CI-SAUB, the lowest RMSE was achieved with the fillpeaks method (0.31). In the CI-area, modpolyfit and fillpeaks methods yielded the lowest RMSEs of 0.35 and 0.38, respectively. For the CI-max intensity, modpolyfit and raw methods presented the lowest RMSEs of

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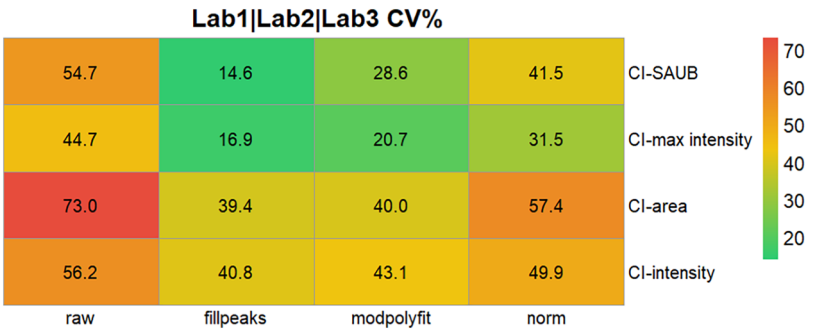

Figure 4. Heatmap plot of the coefficient of variation (%) for each of the CIs tested using pooled data from Lab1, Lab2, and Lab3 for raw and preprocessed spectra.

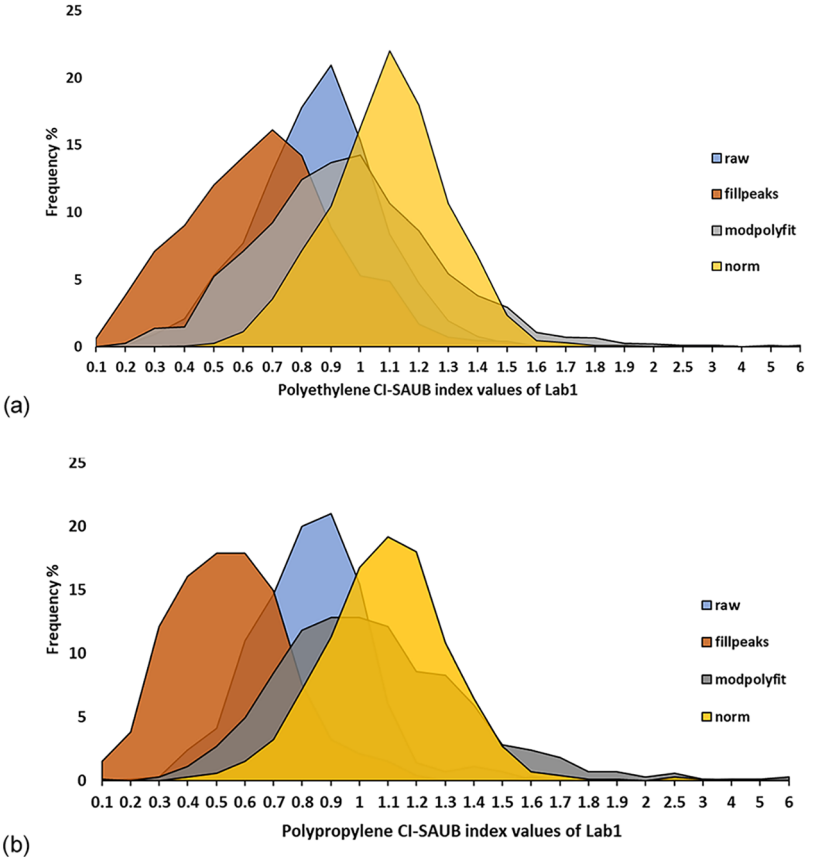

Figure 5. Effect of spectral preprocessing on CI-SAUB values for polyethylene (PE) and (b) polypropylene (PP). The figure presents the frequency distribution of raw and preprocessed carbonyl index values for floating meso- and microplastics composed of (a) PE (n = 1664 spectra) and (b) PP (n = 710 spectra) collected from surface waters and analyzed by Lab1. Raw CI-SAUB values are shown in blue, while results from different baseline correction methods are represented as follows: fillpeaks (brown), modpolyfit (gray), and min-max normalization (yellow). The CI-SAUB bin width is set to 0.1 for values up to CI-SAUB = 2 and to 1.0 for values from CI = 2.0 to 6.0.

0.35 and 0.4, respectively. Finally, the CI-intensity produced the lowest RMSE (0.29) on the raw data. Therefore, for CIs based on area calculations, as well as CI-max intensity indices when applying baseline preprocessing methods, the interlaboratory agreement was improved. Furthermore, the lowest CV% (<10%) was observed for the raw data and the fillpeaks method across the two area-based indices (CI-SAUB and CI-area) (Figure 2). However, the two intensity-based CIs exhibited the highest CVs (>10%) across all preprocessing methods (Figure 2). Combining RMSE and CV% results, it is shown that, among laboratories with similar instrumental configurations, CI comparisons are improved when using area-based indices (CI-SAUB, CI-area) after fillpeaks preprocessing.

To account for interlaboratory instrumental differences, we expanded the analysis to include all three laboratories (Figure 3). For CI-SAUB and CI-area, the lowest RMSEs were observed with the fillpeaks and modpolyfit methods (0.57, 0.64, and 0.66, 0.68, respectively), indicating the best agreement between laboratories. For CI-max intensity, modpolyfit and fillpeaks methods produced comparable RMSEs (0.63 and 0.65, respectively). The CI-intensity exhibited the highest values for all preprocessing methods, with RMSE exceeding 79%.

All calculated carbonyl indices showed that fillpeaks and modpolyfit preprocessing consistently reduced RMSE compared to raw data and min-max normalization, indicating better

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Table 2. Summary Statistics of Carbonyl Index Values (CI) for Polyethylene (PE) and Polypropylene (PP) of Meso- and Microplastics Fragments Based on Raw and Pre-Processed Fourier Transform Infrared Spectroscopy (FT-IR) Spectra Analysed by Lab1[a]

CI for PE meso- and microplastic fragments (n = 1664)				
	raw	fillpeaks	modpolyfit	norm
Maximum	2.91	4.07	5.79	2.90
90%	1.07	0.97	1.30	1.30
75%	0.94	0.79	1.09	1.18
Median	0.81	0.62	0.90	1.05
25%	0.67	0.44	0.70	0.92
10%	0.52	0.28	0.53	0.78
Minimum	0.19	0.05	0.17	0.37
Mean ± SD	**0.81 ± 0.23**	**0.63 ± 0.30**	**0.92 ± 0.35**	**1.05 ± 0.21**
CI for PP meso- and microplastic fragments (n = 710)				
	raw	fillpeaks	modpolyfit	norm
Maximum	5.98	4.03	5.62	3.82
90%	1.01	0.78	1.40	1.31
75%	0.91	0.64	1.19	1.18
Median	0.79	0.49	0.96	1.05
25%	0.65	0.35	0.76	0.90
10%	0.54	0.26	0.61	0.77
Minimum	0.19	0.07	0.06	0.30
Mean ± SD	**0.80 ± 0.32**	**0.51 ± 0.28**	**1.01 ± 0.42**	**1.05 ± 0.26**

[a]The table presents the mean, standard deviation, and range of CI values for PE and PP, reflecting the effects of spectra preprocessing on the quantification of polymer oxidation.

agreement among the three laboratories. The results demonstrate that both spectral preprocessing and carbonyl index selection play an important role in achieving reliable interlaboratory comparability. The CI-SAUB method achieved the lowest CV% (14.6%), followed by the CI-max intensity method (16.9%), both using the fillpeaks method (see Figure 4). Across the three laboratories, despite differences in instrumentation, the highest CV% for the four indices (CI-SAUB, CI-max intensity, CI-area, and CI-intensity) was observed for the raw data. The fillpeaks baseline correction consistently yielded the lowest RMSE and CV% across methods and indices, thereby minimizing interlaboratory variability and providing the most effective overall reduction in measurement variability, despite differences in ATR configurations. Among the evaluated indices, the area-based CI-SAUB, when applied to fillpeaks corrected spectra, showed comparatively high robustness, characterized by low RMSE values and limited data dispersion across laboratories (Figures 3 and 4). Taken together, these results suggest that combining fillpeaks preprocessing with the CI-SAUB index may provide a reproducible approach to improving consistency across instruments and laboratories.

Open-Access Validated Libraries of Weathered Polyethylene and Polypropylene with CI-SAUB Metadata

The interlaboratory comparison enabled the development of a validated, open-access library of weathered FT-IR spectra and CI-SAUB metadata specifically for marine meso- and microplastics, publicly available at Open Specy (https://www.openanalysis.org/openspecy/). The polymer type assigned to each spectrum was independently confirmed by the three participating laboratories, ensuring a high level of accuracy and reliability. All uploaded spectra underwent fillpeaks baseline correction, and the corresponding CI-SAUB metadata are provided. When users compare their spectra with the weathered reference library, higher Hit Quality Index (HQI) scores are obtained than with pristine libraries, indicating closer matches between the submitted and reference spectra. Consequently, users receive both polymer type identification and an estimated CI-SAUB value, providing insight into the weathering status of the analyzed meso-and microplastics.

Carbonyl Index Trends in the Sea Surface Floating Meso- and Microplastics

Building on our previous analysis, we examined the trends in CI-SAUB values for a larger cohort of sea surface-floating meso- and microplastics. This included 1,664 samples of polyethylene (PE) and 710 samples of polypropylene (PP), using both raw and preprocessed FT-IR spectra as analyzed by Lab1. For PE raw spectra, 83% of the particles had CI-SAUB values in the range of $0.6 < CI \leq 1.1$. In contrast, those with $CI \leq 0.5$ and $CI > 1.1$ represented 8.2% and 8.6%, respectively. (Figure 5a). For PE, the average CI-SAUB value from the raw data was 0.81 ± 0.23 (mean ± standard deviation), with CI distribution peaking at 0.9. The fillpeaks baseline correction yielded a mean CI-SAUB of 0.63 ± 0.30, peaking at 0.65, while the modpolyfit baseline correction had a mean of 0.92 ± 0.35, peaking at 1. The min-max normalization yielded the highest mean CI value (1.05 ± 0.21), with a distribution peak at 1.1 (Table 2, Figure 5a). The fillpeaks method for PE suppresses CI values, resulting in a leftward shift of the CI frequency distribution relative to the raw data (Figure 5a). In contrast, the other two preprocessing methods yield higher CI values than the raw data, shifting the distribution to the right, with the min-max normalization method having the most pronounced effect. Similarly, 88% of PP fragments had CIs in the range $0.6 < CI \leq 1.1$, peaking at 0.9 (Figure 5b), with preprocessing methods exhibiting similar patterns for PP spectra as for PE (Table 2; Figure 5b). The effect of preprocessing raw spectra was statistically significant (Mann−Whitney U test, $p < 0.05$), with each distribution differing significantly from the raw data distribution, underscoring that CI-SAUB values derived from

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different preprocessing methods are not directly comparable. The shift highlights the CI's sensitivity to the choice of baseline or normalization method. These findings underline that CI values derived using different preprocessing approaches should not be compared indiscriminately. It is important to note that the majority of CI-SAUB values (approximately 80−90%) fall within a narrow range, even though the meso- and microplastics examined in this study originated from various parent materials with unknown exposure durations and environmental weathering histories. Low CI-SAUB values (less than 0.5) were found in about 4.4%, 7.4%, and 6.5% of particles collected from the sea surface in the size classes of 5−25 mm, 1−5 mm, and 0.3−1 mm, respectively (SI Part 1, Figure S3). There was also significant overlap in CI ranges across both meso- and microplastics. Although some of the highest CI values were observed with decreasing particle size, this trend was nonlinear.

DISCUSSION

Our findings emphasize the significant impact of both instrumental configuration and spectral preprocessing on the reliability and robustness of FT-IR-derived carbonyl indices across diverse analytical conditions. Baseline correction methods such as fillpeaks and modpolyfit substantially improved interlaboratory agreement by removing nonchemical spectral contributions, i.e., instrumental noise and ATR contact effects.[20] However, systematic differences arising from ATR crystal type can introduce significant bias, reducing comparability of FT-IR measurements across laboratories. Factors such as crystal material, beam contact angle, and internal reflection geometry directly determine ATR penetration depth. Restricting measurements to laboratories with comparable ATR configurations (diamond crystal) markedly reduced interlaboratory variability, with area-based indices (CI-SAUB and CI-area) showing the highest reproducibility and lowest dispersion (Figures 1 and 2). For a universal methodology applicable across laboratories using different ATR crystals (diamond and Ge), the best performance was achieved by combining the CI-SAUB index with fillpeaks baseline correction (Figures 3 and 4). Remarkably, our systematic literature review revealed that only 6% of studies applied baseline corrections or other postprocessing prior to CI calculation.[29−45] Furthermore, most existing studies (91%) have relied on well-characterized, laboratory-sourced polymers (SI Part 2, Tables S1 and S2). The expanding application of FT-IR to naturally weathered microplastics underscores the need for unified methodological guidelines to support robust interlaboratory comparisons. Likewise, Yang et al.,[16] have argued that preprocessing methods should be employed when calculating the CI, as they remove the spectral noise, thereby enhancing the carbonyl group peak. In the current literature, the use of the Carbonyl Index (CI) to estimate the weathering of marine floating microplastics is an emerging approach, with most studies published in 2023 and 2024.[6,15−17,46] A study conducted off the Japanese coast[17] using microplastics collected with manta nets, and the CI-SAUB, reported average CI values for PE and PP, 0.69 ± 0.34 and 0.70 ± 0.34, respectively. These results are comparable to our findings in terms of CI ranges and the similarity observed between the polymers (mean CI-SAUB for raw spectra PE: 0.81 ± 0.23; PP: 0.80 ± 0.32; Table 2). However, caution is warranted when comparing raw CI values across studies due to variations in instrumentation, sample handling, and data processing, as demonstrated by our intercalibration exercise.

Several processes may explain the variability in CI values observed among marine plastics of different sizes (meso- and microplastics) (SI Part 1 Figure S3). Environmental factors such as sunlight exposure, temperature, and the degree and type of biofilm formation are expected to exert variable effects on the surface properties of plastics and subsequent fragmentation.[12,13,47] Biofilms themselves contain functional groups that can be identified by FT-IR spectroscopy, and microorganisms may use plastic carbon as an energy source, leading to further plastic degradation.[11,48−50] Previous studies investigating the relationship between CI values and the size of sea-floating microplastics have not reached consistent conclusions.[6,17] Conversely, researchers examining large macroplastics in the marine environment have demonstrated clear degradation signatures in FT-IR spectra.[51−53] During outdoor photodegradation of polyolefins in beach environments, Syranidou et al.[11] have demonstrated that the onset of fragmentation of HDPE and PP films to microplastics starts at a CI value of 0.7, and the process follows 3 stages after exposure (initial stage: < 0.1, rapid growth: 0.1−0.7, stationary >0.7). Our CI values are not directly comparable because these authors calculated CIs from peak intensity. Nevertheless, their findings can assist in interpreting our results, since the majority of microplastics exhibit CIs fluctuating between 0.5 and 1.1, with a peak around 0.8−0.9. We may hypothesize that microplastics in surface waters have undergone degradation and have reached a stationary phase, making further increases in CI unlikely. Polymer degradation studies highlight that CI reaches a limit despite prolonged exposure to weathering conditions.[54,55] Several factors are responsible for this observation, including saturation of reactive sites, cross-linking of small polymer chains, depletion of reactive radicals, and analytical measurement limitations with FT-IR due to extensive carbonyl formation. During this phase, the CI initially increases as oxidative processes act on the particle surface but may subsequently decrease due to surface material loss through fragmentation and carbon loss through its dissolution, often not involving complete disintegration, but rather the progressive shedding of oxidized outer layers. The degraded, brittle surface of plastics detaches small fragments or crumbs, exposing the underlying unweathered layer, and this pattern is repeated as successive fragmentation occurs. Even when minimal fragmentation occurs, sunlight exposure has been observed to convert plastic carbon to dissolved organic carbon, thereby removing the submillimeter plastic surface.[56] The low CI values (<0.5) observed in this work across all sizes of marine meso- and microplastics likely reflect surface erosion, exposing less-degraded material.

Our results show that the majority of raw calculations for meso-and macroplastics exceed 80% and exhibit CI-SAUB values between 0.5 and 1.1. This may be due to a cyclical pattern of CI increases and decreases, reflecting a nonlinear degradation process in which CI values fluctuate while the particles' overall volume and molecular weight gradually decline. Moreover, biofilm may contribute to CI variation. It is understood that CIs of marine PE and PP do not reflect their size classes but rather the total effect of weathering, including photodegradation, biofilm formation, and the cyclic pattern characterized as reverse weathering. This dynamic could explain the predominance of midrange CI values across all particle-size classes in the marine environment. Each marine

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plastic, whether a microplastic or a larger item, has its own weathering history, as reflected in the variability of spectral alterations and CIs. The small yet significant proportion of low CI values (<0.5) across all plastic sizes analyzed corroborates layer-by-layer oxidation continuously removing weathered material, revealing unweathered polymer beneath. The nonlinear increase in CIs as plastic item sizes decrease aligns with the nonlinear process of plastic fragmentation. During this process, larger plastic items break apart, producing smaller fragments of varying sizes. This fragmentation generates crumbs along surface cracks, exposing areas of unweathered plastic. Degradation precedes fragmentation of plastics; the latter being facilitated by mechanical stress in the marine environment.[57].

The distribution of CI values in the analyzed marine meso- and microplastics reflects the diverse weathering pathways plastics may undergo in the marine environment, processes that do not result in a linear or uniform increase in carbonyl groups. Under an optimistic scenario in which the input of large plastics into the environment is eliminated and the generation of secondary microplastics is halted, our analysis suggests that CI values would not necessarily continue to increase over time. In contrast, microplastic particle size would be expected to decrease due to ongoing fragmentation and carbon loss. These findings indicate that CI is not a reliable indicator of a particle's "age." Instead, it shows the presence of oxygen-containing functional groups formed by oxidation of the polymer surface. However, it does not provide information about the duration of the particle's exposure to the environment.

Taken together, our findings demonstrate that spectral preprocessing, particularly baseline correction, is crucial for generating reproducible and comparable CI values when analyzing marine meso- and microplastics. Among the methods evaluated, the fillpeaks baseline correction achieved the highest consistency across laboratories. Furthermore, by testing four CI options (CI-SAUB, CI-maximum intensity, CI-area, and CI-intensity), we found that the CI-SAUB index, combined with the fillpeaks baseline correction, performs best for data interoperability, as this approach effectively smooths instrumental differences among laboratories. Therefore, we recommend using the CI-SAUB index with fillpeaks corrected spectra as a standard method for determining CI in environmental data. Furthermore, our results emphasize that CI values derived from spectra processed differently should not be compared indiscriminately, and that a consistent baseline correction should be adopted in future CI calculations. To that end, our work in providing validated spectra and respective CI -SAUB values of weathered microplastics to the Open Specy libraries supports Open Specy as both a polymer identification and CI estimation tool, serving the broader scientific community as a reference database for weathered plastics. Additionally, our results support that CI is not a reliable proxy for estimating the environmental 'age' of meso- and micro plastics. Instead, it reflects the extent of surface oxidation, which results from a complex interplay between degradation and fragmentation. Our work further underscores the need for harmonized analytical protocols in research on environmental plastic degradation. Establishing common standards and accessible reference libraries for polymer identification and CI estimation will yield more robust, consistent data on plastic degradation, ultimately informing the development of more effective monitoring and mitigation strategies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.6c02609.

Spectra from the intercalibration exercise among the three laboratories are available as weathered libraries, together with their CI values, and are free to use at Open Specy (PDF)

CI measurements for PE in the literature; CI measurements for PP in the literature; box plot of CI-SAUB distribution for different-sized meso-microplastics, based on raw spectra measured by Lab1. mesoplastics (113 items), Microplastics above 1mm (775 items), microplastics below 1mm (980 items) (PDF)

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Author Contributions

A.A. and C.Z. conceived the study. A.A. designed the intercalibration methods. A.A. and E.P. processed the spectra and the data. A.A., W.C., and C.Z. produced the figures. A.A. and G.B. produced tables and the literature review. A.A. and G.B did the stereoscopic analysis. A.A., G.B., M.N.M., and A.P. analyzed the samples at the FT-IR. W.C uploaded weathered libraries and CI metadata in Open Specy. A.A., A.C., M.N.M., W.C., G.S., and C.Z. provided resources and drafted and revised the manuscript.

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Notes

The authors declare no competing financial interest.

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