

1 **The degradation potential of PET bottles in the marine environment: An ATR-**
2 **FTIR based approach.**

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16 **SUPPLEMENTARY INFORMATION**

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18 **1. Materials and methods**

19 On the basis of the assessment of marine litter on the seafloor of the Saronikos Gulf
20 (Aegean Sea – E. Mediterranean) from January 2013 to April 2014, plastic marine
21 litter items were collected from 70 hauls conducted by commercial bottom-trawl
22 fisheries in order to be examined in respect to environmental degradation. Plastic
23 bottles made of polyethylene terephthalate (PET) were collected on condition that the
24 expiration date was discernible. Eight colorless (1997(a-b), 1998, 1999, 2001, 2008,
25 2011, 2014) plastic bottles (PETs) were collected. The plastic bottles were sorted
26 according to their expiration date. The indicated on the plastic bottles expiration date
27 was used denotative to the time-period that the samples were present in the marine
28 environment.

29 In the laboratory, samples were rinsed with an electrolyte solution (NaNO₃ 0.1 M) to
30 remove all sediment compounds, in order to have a clear polymer surface for
31 investigation. All samples were only handled with laboratory gloves in order to avoid
32 external contamination.

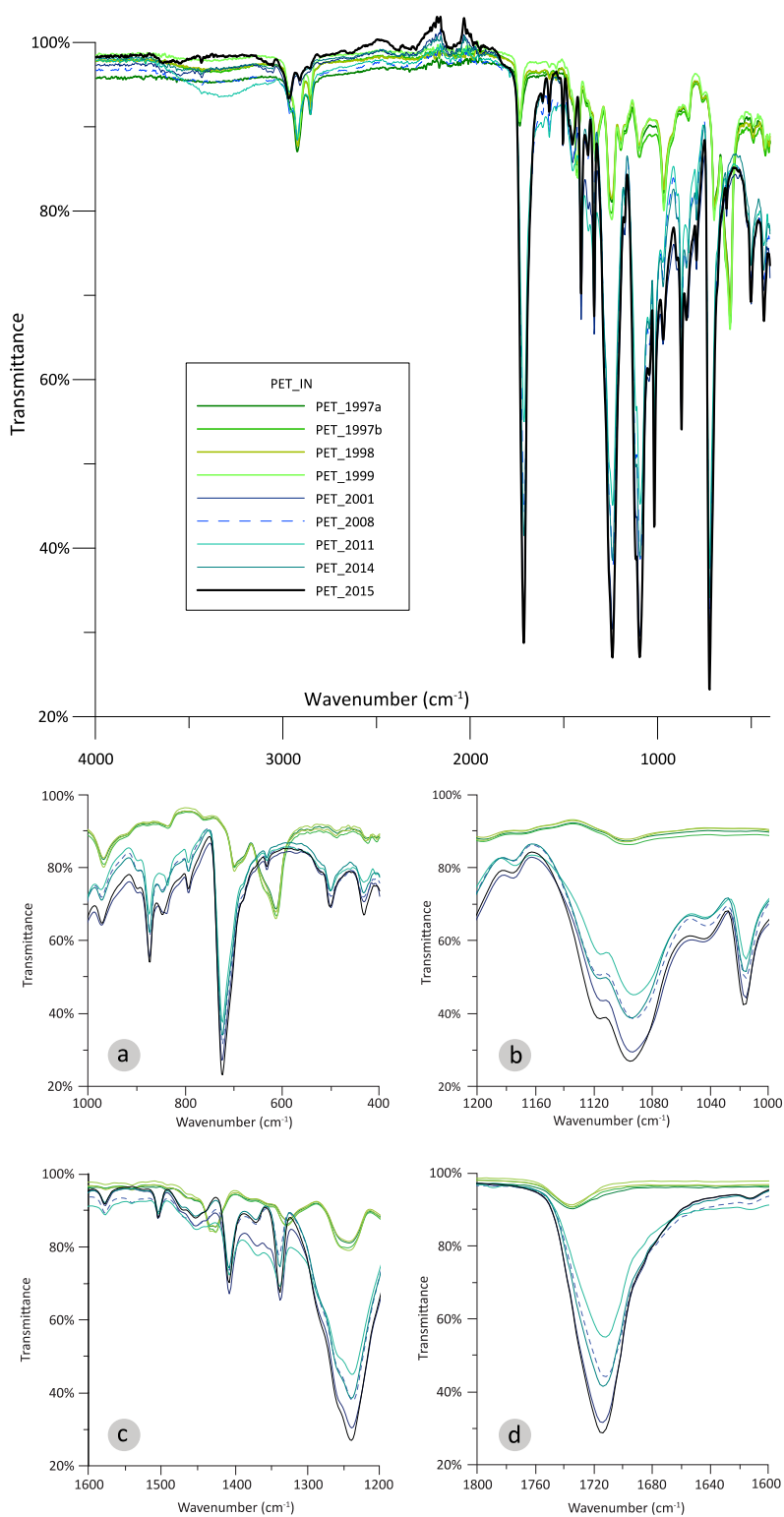
33 **Attenuated Total Reflection (ATR):** ATR-FTIR was used in order to determine
34 possible functional groups on the surface of PET, which could be further attributed to
35 environmental degradation. An ALPHA Platinum ATR-FTIR (Bruker Corporation)

36 with a singly reflection diamond accompanied by the OPUS software was used. For
37 the PET samples, pieces from both inner and outer part of the bottles were selected
38 for analysis.

39 **Scanning Electron Microscopy (SEM):** The surface topography, the roughness of
40 the polymers as well as any organisms inhabiting on the surface of the polymers were
41 visualized with a JEOL 6300, Scanning Electron Microscope (SEM). The SEM was
42 equipped with Spectrometers Energy Dispersion X-ray (EDS), Wavelength
43 Dispersion X-ray (WDS) and Cryotrans. The selected for examination surfaces of the
44 PET samples were coated with a layer of gold by sputtering using a JEOL, JFC-1100,
45 ions sputter. Before samples were coated with gold, were rinsed with ethanol solution
46 in order to avoid any kind of contamination. Since the degraded samples were
47 heterogeneous, the visualization was repeated at least three times for each sample, to
48 make sure that a similar image was observed for all degraded samples.
49 Photomicrographs were taken in various fold magnifications (x40, x270, x250, x1000,
50 x1600, x5000, x8000, x8500, x35000) depending on the samples.

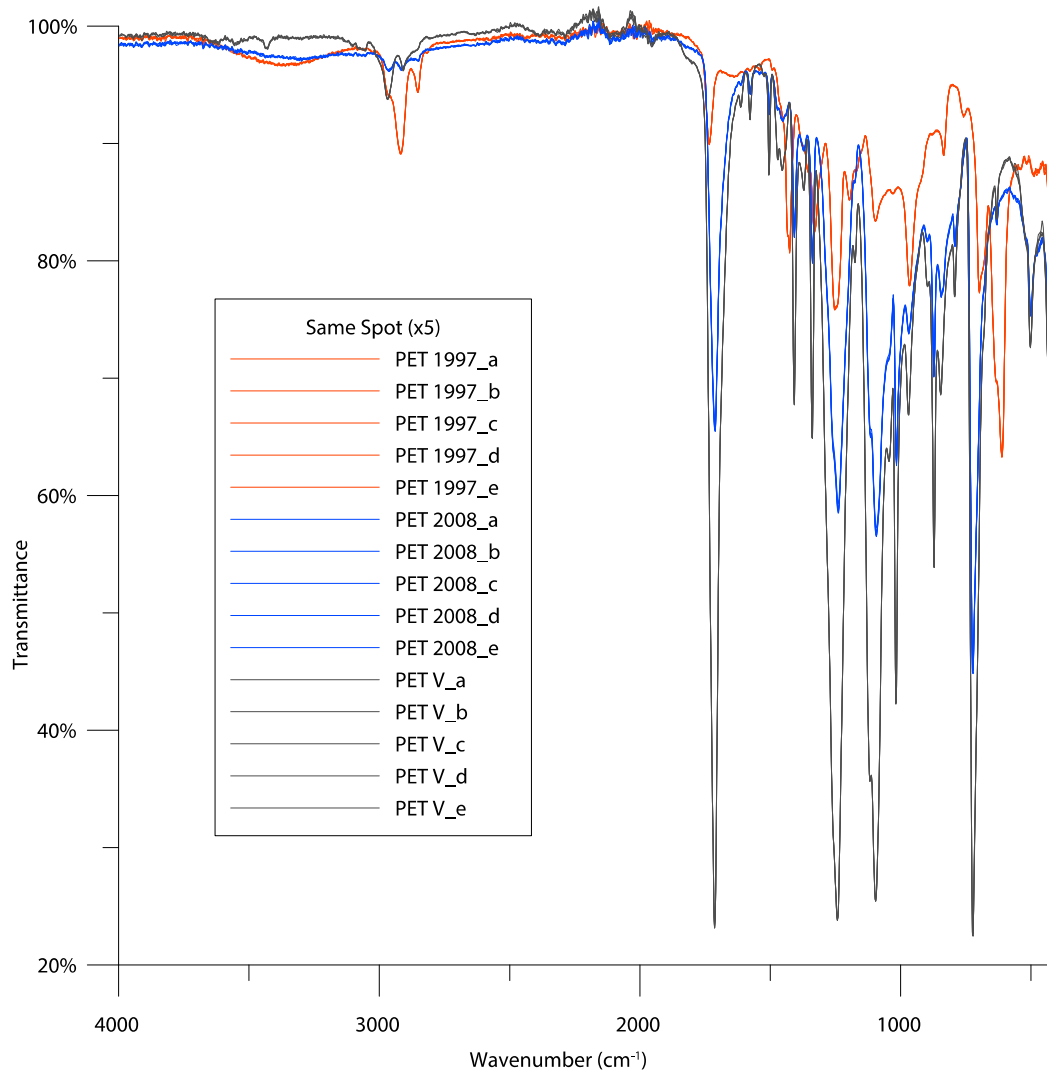
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52 2. Supplementary figures

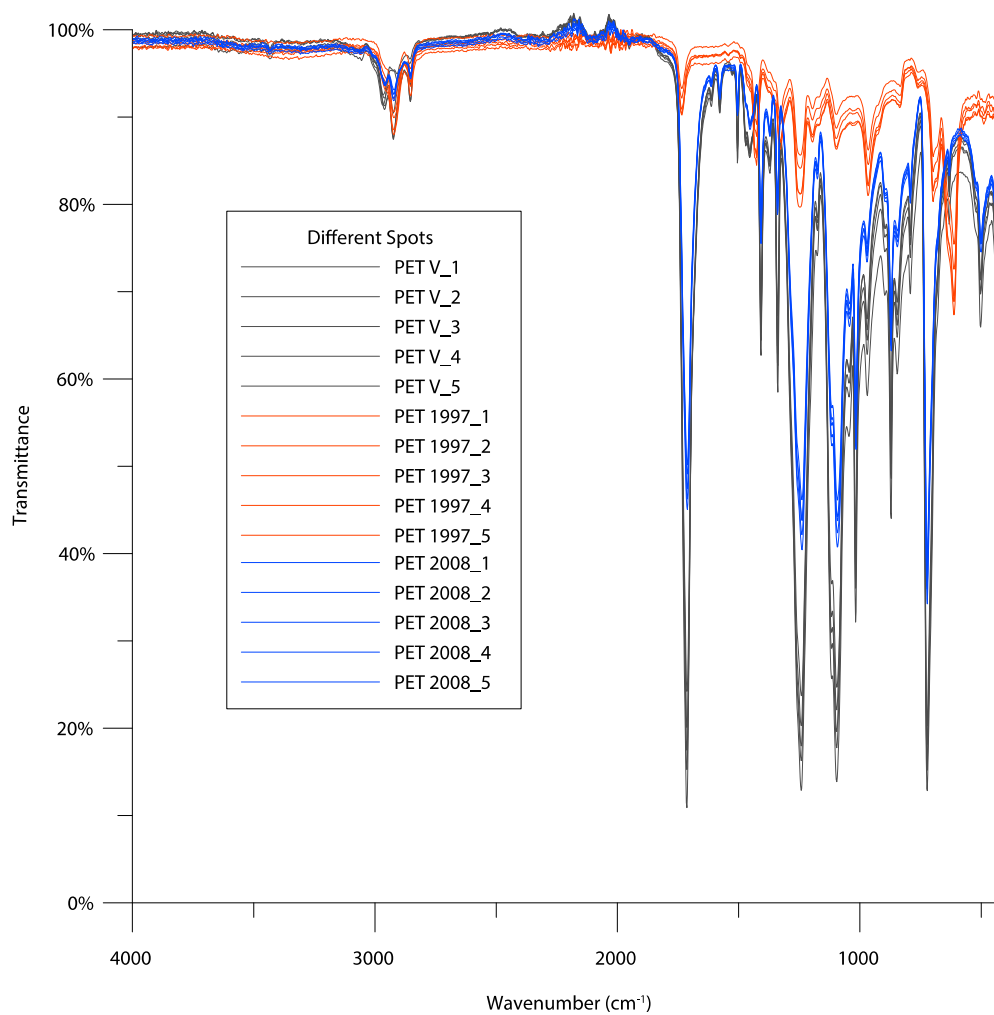


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54 **Figure S1:** ATR-FTIR comparative spectra of the inner (IN) surface of the degraded
 55 PETs (1997(a-b), 1998, 1999, 2001, 2008, 2011, 2014) compared with a virgin (V)
 56 sample. For better visualization, enlarged excerpts of the ATR-FTIR comparative
 57 spectra are given at wavenumbers (a) 400-1000, (b) 1000-1200, (c) 1200-1600, (d)
 58 1600-1800 cm^{-1} .



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 60 **Figure S2:** Multiple (x5) FTIR-ATR readings for the same examined spot for the
 61 different PET bottles (*1997, 2008 and V*) corresponding in the different groupings
 62 (Old – New – V), have been plotted into a single graph in order to visually illustrate
 63 whether there is an alteration (i.e. decrease in band intensity) between the readings or
 64 not.
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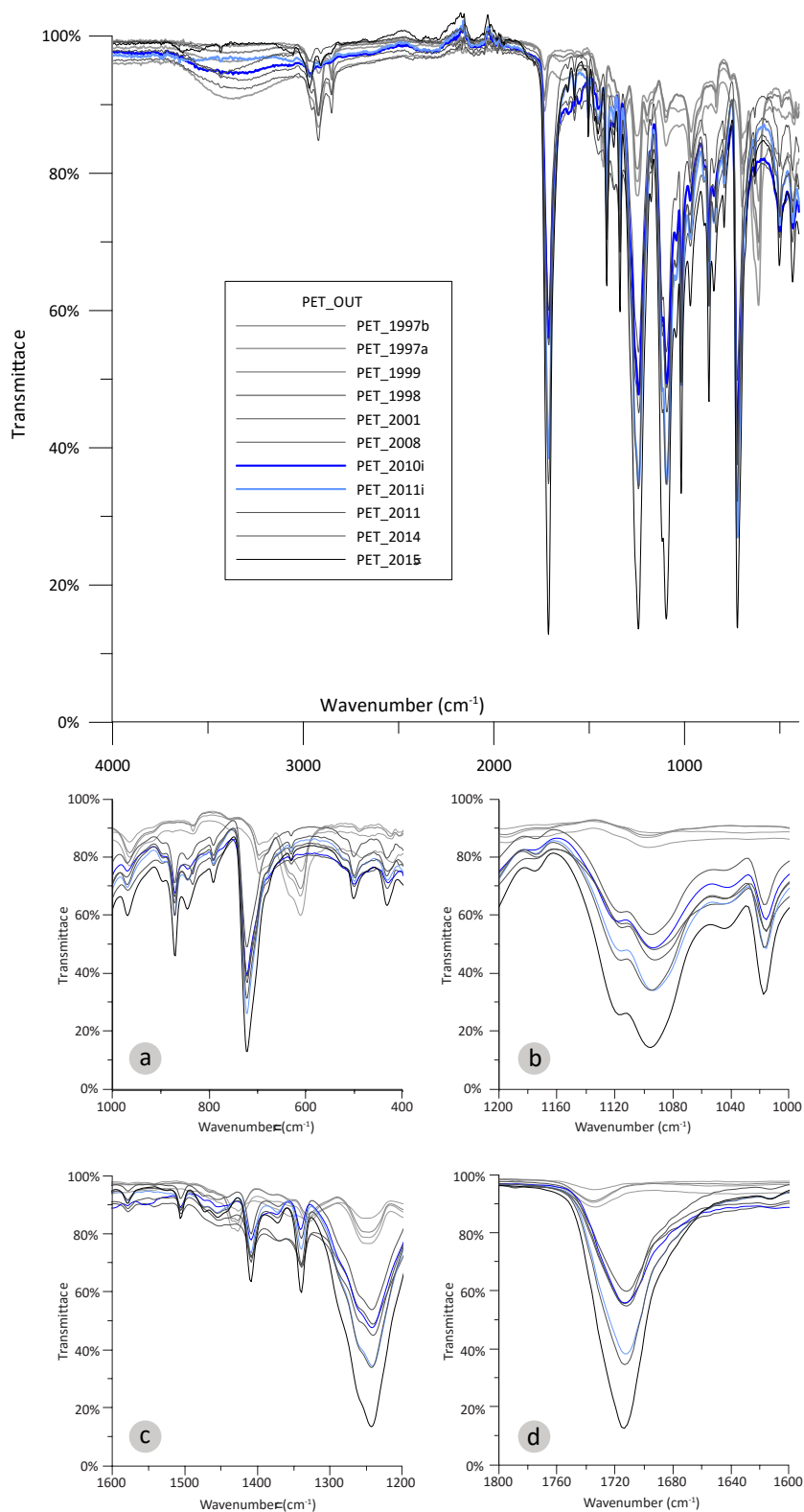


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 67 **Figure S3:** Different FTIR-ATR reading for different spots (#5) for the different PET
 68 bottles (1997, 2008 and V) corresponding in the different groupings (Old – New – V),
 69 have been plotted into a single graph in order to visually illustrate whether there is an
 70 alteration (i.e. decrease in band intensity) between the readings or not.



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72 **Figure S4:** The Ionian Sea (Western Greece) from where the PET samples were used
 73 for comparison to those sampled from the Saronikos Gulf (ArcMap, ArcGIS 9, V. 9.3;
 74 www.esri.com).



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76 **Figure S5:** ATR-FTIR comparative spectra of the outer (OUT) surface of the
 77 degraded PETs from the Saronikos Gulf (1997(a-b), 1998, 1999, 2001, 2008, 2011,
 78 2014) and the new samples from the Ionian Sea (2010i, 2011i) compared with a virgin
 79 (V) sample. For better visualization, enlarged excerpts of the ATR-FTIR comparative
 80 spectra are given at wavenumbers (a) 400-1000, (b) 1000-1200, (c) 1200-1600, (d)
 81 1600-1800 cm^{-1} .



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83 **Figure S6:** The degraded PETs with a clear indication of their expiration date (1997a,
84 1997b, 1998, 1999, 2001, 2008, 2013, 2014).