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Environmental Chemistry

Supplementary Material

Influence of CNT loading and environmental stressors on leaching of polymer associated chemicals additives from epoxy and polycarbonate nanocomposites

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Table S1 Summary of optimized ESI-MS/MS conditions for the following analytes. Source conditions are spray voltage - 2.5 kV, vaporizer temperature 300 ◦C, capillary temperature 360 ◦C, sheath gas 40 psi and auxiliary gas 12 psi MW: Molecular weight; CE: Collision energy (V)

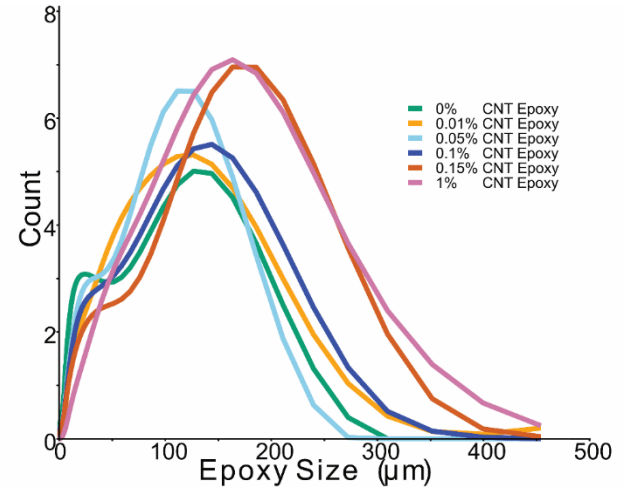
Compound	MW	Parent Ion	Product Ions*	Polarity (+/-)	CE (V)
BPA	228.29	227	212	-	18
			133		25
BPA-d8	236.34.	235	220	-	20
			137		27
Nonylphenol	220.35	219	133	-	31
			106		21
4-n-nonylphenol	220.35	219	133	-	31
			106		21
TBP	150.22	149	133	-	31
			114.9		21
BADGE	340.42	358.1	191	+	14
			135		28
BADGE-d6	346.2	364.2	197.2	+	14
			323		5

*First ion indicated for each compound was used for quantification while the second ion was used for confirmation.

Table S2

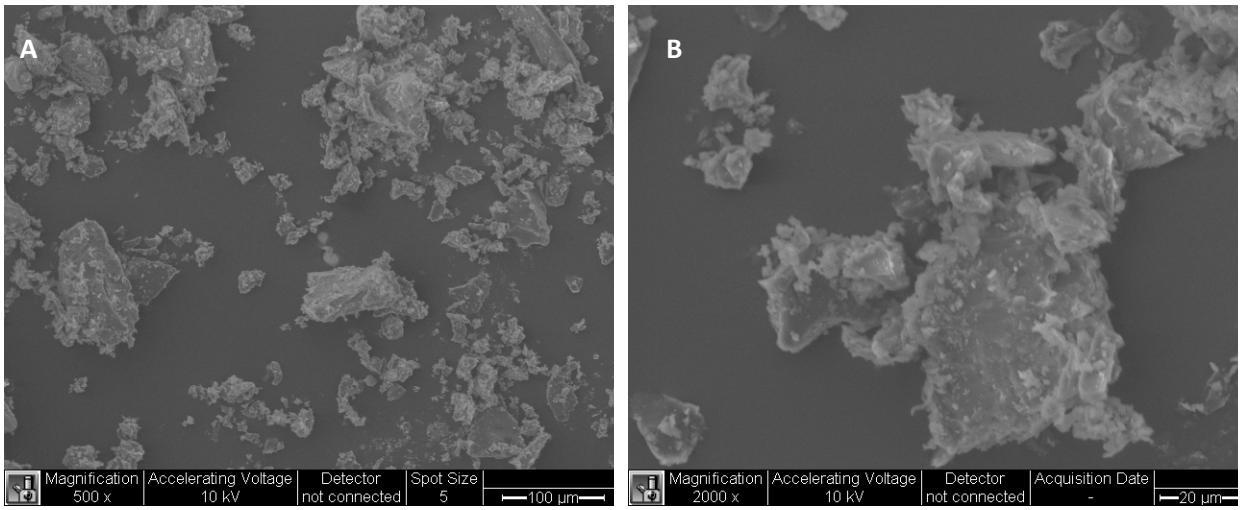
Compound	LOD (ng mL^{-1})	Reproducibility (% RSD)	Linearity R^2	Weighting
BPA	0.57	2.96	0.997	1/x
TBP	3.25	6.81	0.996	1/x
NP	1.84	7.97	0.993	1/x
BADGE	0.52	7.45	0.998	1/x

Figure S1 Size distributions of cryomilled epoxy



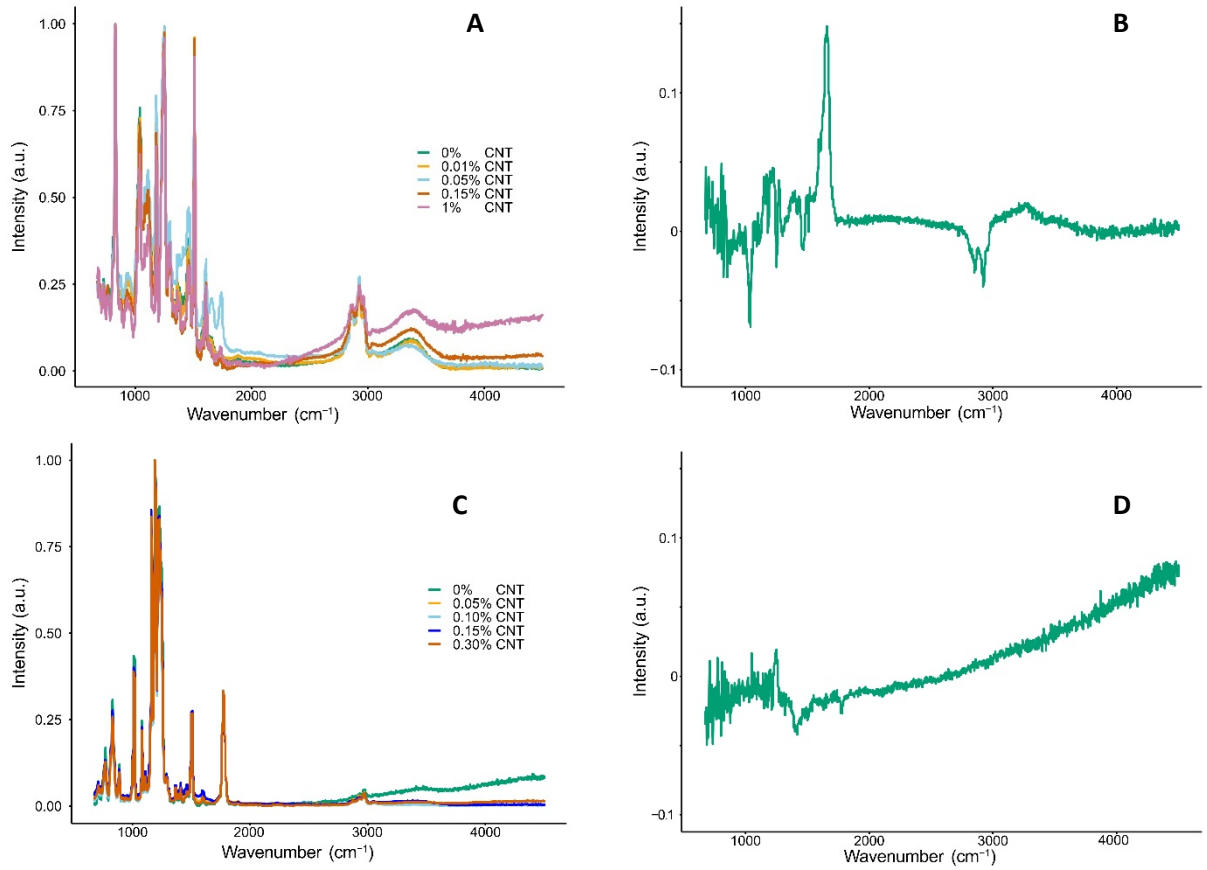
The particle size analyzer used a mastercizer 3000 with a small volume dispersion unit to determine the size distribution of each epoxy nanocomposite.

Figure S2 SEM Images



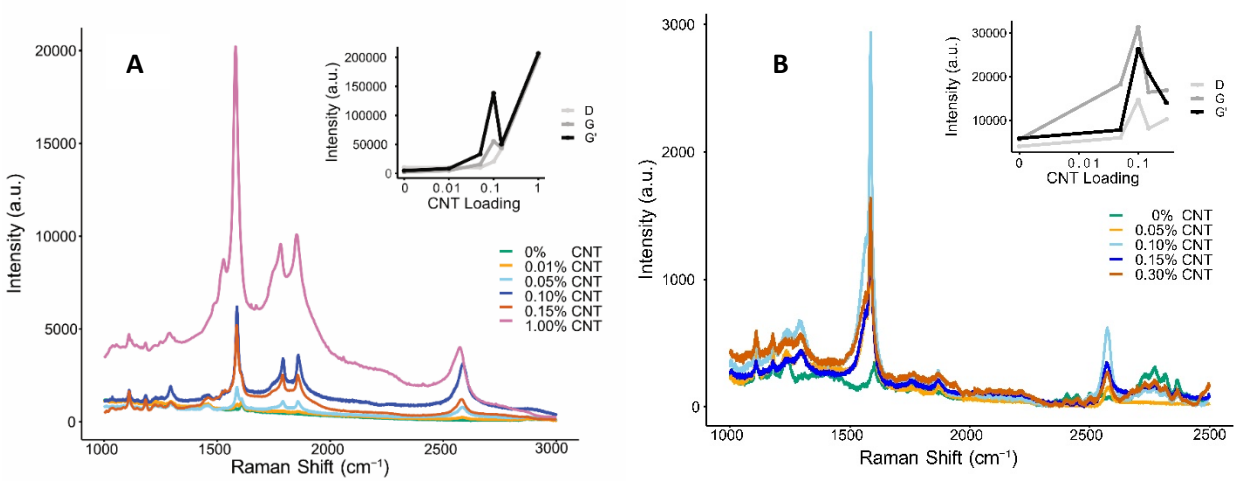
The FEI XL30 ESEM with Bruker XFlash 4010 EDS was used for SEM images to determine the typical shape of the microplastics used in the experiment. This image is 0.1% CNT epoxy at A) 500 and B) 2000 magnification.

Figure S3 Infrared Spectroscopy



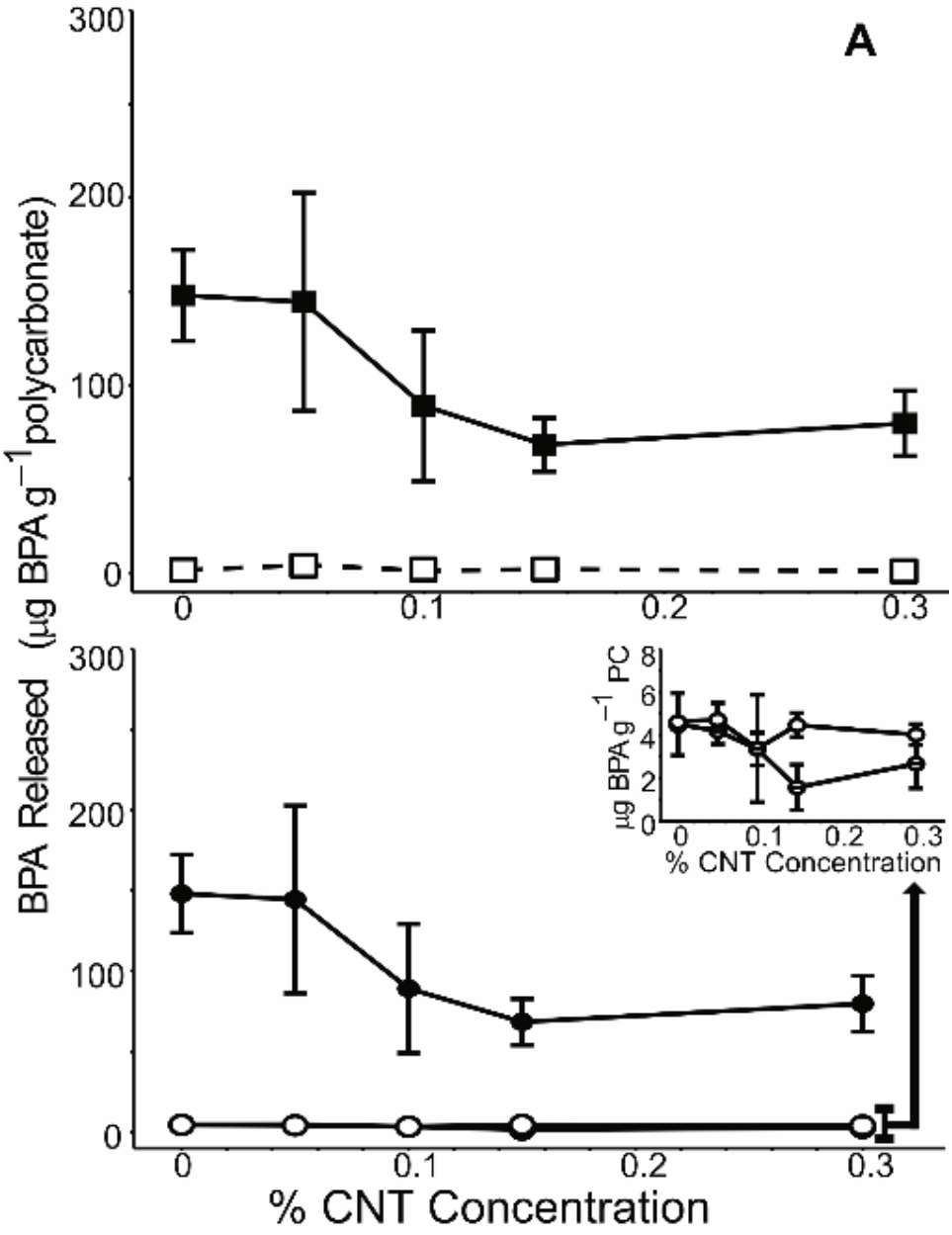
Thermo Electron Nicolet 8700 Fourier Transform - Infrared with Attenuated Total Reflection (FT-IR-ATR) spectrometer with OMNIC software was used for optical characterization of the polycarbonate and epoxy samples over Infra-Red wavelengths of 675 – 4500 cm^{-1}. The ATR attachment was a GE-1015 crystal to hold the samples. FTIR Spectra are plotted as such A) epoxy nanocomposites of CNT loading 0-1%, B) the difference between UV and not UV-exposed epoxy, C) polycarbonate nanocomposites of CNT loading 0-0.3%, D) the difference between UV and not UV-exposed polycarbonate. UV light exposure to the epoxy displayed a decrease in 1600 (C-C stretching vibration), increase in 1660 (OH stretching vibration), decreasing in 2870 and 2950 (CH_3 stretching vibration), and an increase in 3400 (phenolic OH stretching vibration).

Figure S4 Raman Spectroscopy



A Horiba Jobin Yvon LabRam Aramis RAMAN/PL system with LabSpec 6.2 software was used for characterization of the carbon nanotubes in the polymer nanocomposite. The microscope was set to 100x objective, gratings at 1200 gr/min and filter at 100%. A diode laser using a wavelength of 785 nm was set to look for the D, G, and G' bands (at 1250, 1550, and 2600 cm^{-1} respectively) that characterize the presence of carbon nanotubes in a sample. There was an increase in intensity of these characteristic bands for A) epoxy and B) polycarbonate composites with single walled carbon nanotubes present.

Figure S5 Temperature and pH on release of BPA from PC

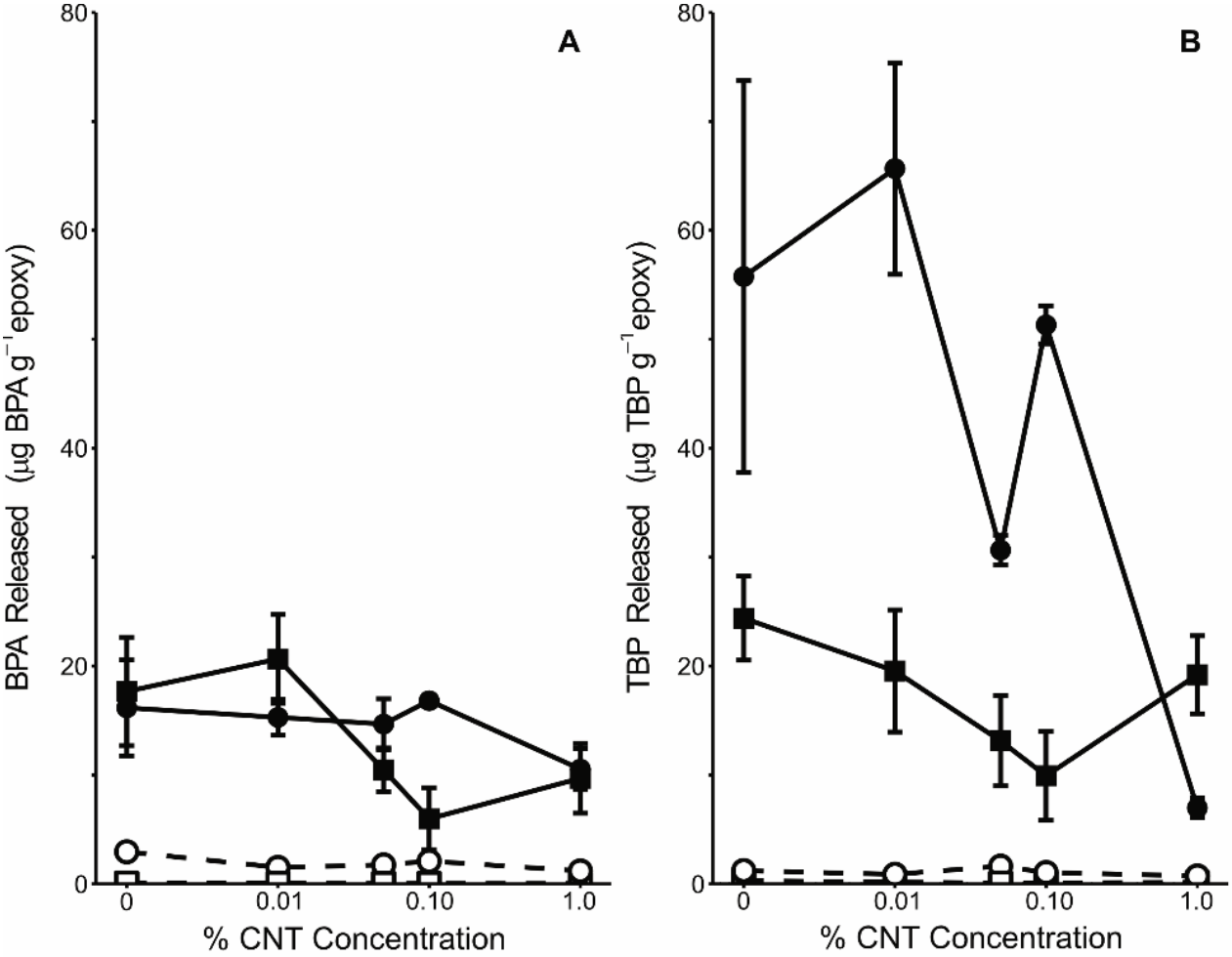


Experiments display the average concentration of BPA released from polycarbonate nanocomposites at day 5 when exposed to A) 65 (filled □) vs 25 ˚C (unfilled □) and B) pH ranges of 8.1 (filled black ○), 4.1 (unfilled crossed ○), and 2.8 (unfilled ○). The data for pH 4.1 and 2.8 are superimposed.

Table S6 BPA and TBP concentrations absorbed to glassware

Treatment	Temperature (˚C)	BPA (µg/g)	TBP (µg/g)
Disc	25	0.14 ± 0.05	0.07 ± 0.02
	45	0.08 ± 0.02	0.23 ± 0.15
	65	0.04 ± 0.01	0.05 ± 0.02
Cryomilled Epoxy	25	0.49 ± 0.26	0.22 ± 0.13
	45	1.61 ± 0.63	0.40 ± 0.18
	65	0.25 ± 0.19	0.07 ± 0.12
UV Disc	25	2.56 ± 1.27	2.86 ± 1.94
	45	0.21 ± 0.02	0.03 ± 0.01
	65	2.07 ± 0.30	1.79 ± 0.26
UV Cryomilled Epoxy	25	5.13 ± 1.05	1.83 ± 0.73
	45	10.9 ± 3.29	1.69 ± 0.88
	65	0.77 ± 0.25	1.05 ± 0.28

Figure S7 BPA and TBP concentrations released at 65 ˚C from Epoxy PNCs



Experiments were completed in EPAMHW at 65 ˚C. and display the average concentration released at 72 hours in µg of A) BPA and B) TBP per gram of epoxy over increased CNT concentrations. Each polymer treatment is represented by the following symbols: cryomilled epoxy (○) and epoxy disc (□). The filled symbols indicate those samples were previously exposed to UV light prior to leaching experiment.

Soxhlet Extraction

Epoxy with and without prior UV exposure were subjected to a soxhlet extraction to determine total available TBP and BPA. A mass of 250 mg Epoxy was placed in a paper extraction thimble and extracted with 250 mL of methanol for 24 hours. All solvent was evaporated to 10 mLs and an aliquot of 100 µl was added to 100 µl of acetonitrile. Additions of 10 µL of internal standard and 800 µls of water were made prior to analysis by HPLC-MS/MS as described.

Statistical Analysis Tables

Table S8. Comparisons of BPA concentration leached from PC-PNCs in each environmental treatment on day 5 at 65 ˚C, using One-way ANOVA test with Tukey HSD post-hoc. Statistically significant differences ($p < 0.05$) are indicated in bold font.

% CNT loading comparison	EPAMHW 25 ˚C NO UV NO NOM	EPAMHW 65 ˚C NOUV NO NOM	TCLP1 65 ˚C NO UV NO NOM	TCLP2 65 ˚C NO UV NO NOM	EPAMHW 65 ˚C UV NO NOM	EPAMHW 65 ˚C NOUV NOM
0.00 ≠ 0.05	0.248	0.761	0.999	0.995	0.926	0.761
0.00 ≠ 0.1	0.999	0.997	0.705	0.663	0.713	0.997
0.00 ≠ 0.15	0.993	0.269	0.999	**0.038**	0.587	0.269

Table S9. Comparisons of BPA concentration leached from PC-PNCs in each environmental treatment on day 5, using One-way ANOVA test. Statistically significant differences ($p < 0.05$) are indicated in bold font.

Treatment	P value
UV ≠ NOUV	0.073
TCLP1 ≠ TCLP2	0.994
TCLP 2 ≠ EPAMHW	**1.35e-14**
EPAHWM ≠ TCLP 1	**1.35e-14**
25˚C ≠ 65 ˚C	**1.43e-09**
NOM ≠ NO NOM	0.339

Table S10. Comparisons of BPA and TBP concentration leached from EP-PNCs in each environmental treatment on day 5, using One-way ANOVA test. Statistically significant differences ($p < 0.05$) are indicated in bold font.

Treatment	BPA, P value	TBP, P value
25 ˚C ≠ 65 ˚C	**1e-07**	**4e-07**
UV ≠ NOUV	**3e-16**	**5.07e-09**
Disc ≠ Micro	**0.011**	**0.005**

Table S11. Comparisons of BPA and TBP concentration leached from EP-PNCs in each environmental treatment on day 5 at 25 ˚C, using One-way ANOVA test with Tukey HSD post-hoc. Statistically significant differences ($p < 0.05$) are indicated in bold font.

% CNT loading comparison	Disc		UV Disc		Micro		UV Micro	
	BPA	TBP	BPA	TBP	BPA	TBP	BPA	TBP
0.00 ≠ 0.01	0.998	0.999	0.985	0.948	0.991	0.593	0.643	**0.002**
0.00 ≠ 0.05	0.636	**0.0002**	0.995	0.978	0.201	0.633	1	**0.0004**
0.00 ≠ 0.1	0.786	**2E-05**	0.961	0.444	0.844	0.999	0.992	**0.005**
0.00 ≠ 0.15	0.995	**4E-06**	0.104	0.283	0.85	0.392	0.976	**4E-05**
0.00 ≠ 1	0.539	**2E-05**	0.999	0.9	0.996	**0.002**	0.854	**8E-06**

Table S12. Comparisons of BPA and TBP concentration leached from EP-PNCs in each environmental treatment on day 5 at 65 ˚C, using One-way ANOVA test with Tukey HSD post-hoc. Statistically significant differences ($p < 0.05$) are indicated in bold font.

% CNT loading comparison	**Disc**		**UV Disc**		**Micro**		**UV Micro**	
	BPA	**TBP**	**BPA**	**TBP**	**BPA**	**TBP**	**BPA**	**TBP**
0.00 ≠ 0.01	0.946	0.459	0.839	0.653	**0.002**	**0.022**	0.992	0.686
0.00 ≠ 0.05	0.745	0.097	0.174	0.057	**0.007**	**0.006**	0.945	0.046
0.00 ≠ 0.1	0.823	0.142	**0.016**	**0.014**	0.263	0.359	0.997	0.973
0.00 ≠ 1	0.473	0.257	0.118	0.598	**0.0004**	**0.002**	0.116	**0.0005**