Sub-100 nm Nanoplastics: Potent Carriers of Tributyltin in Marine Water

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Figures

S1: DLS Size Distribution

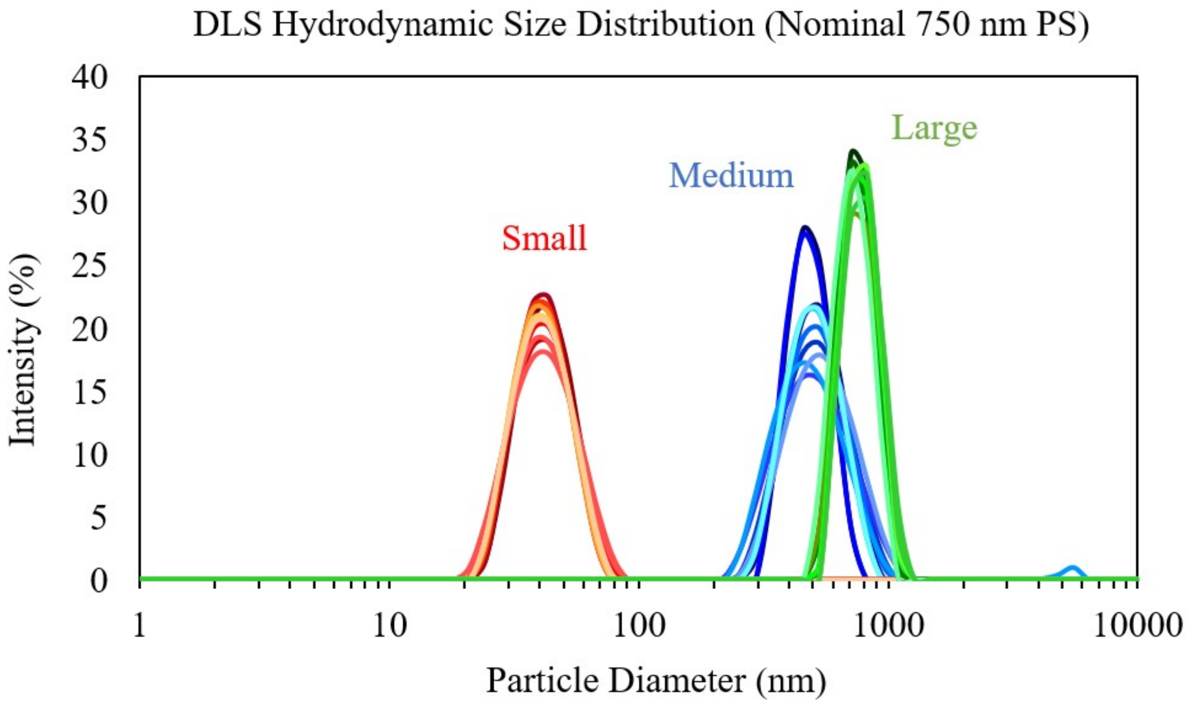

Fig. S1: Dynamic Light Scattering (DLS) measured hydrodynamic diameter distribution for 3 sizes of polystyrene nanoplastic (Large: 765 nm, Medium: 485 nm and Small: 40 nm). Each curve represents 10 instrument replicates, in addition to the 10 experimental replicates.

S2: Large PS SEM Image

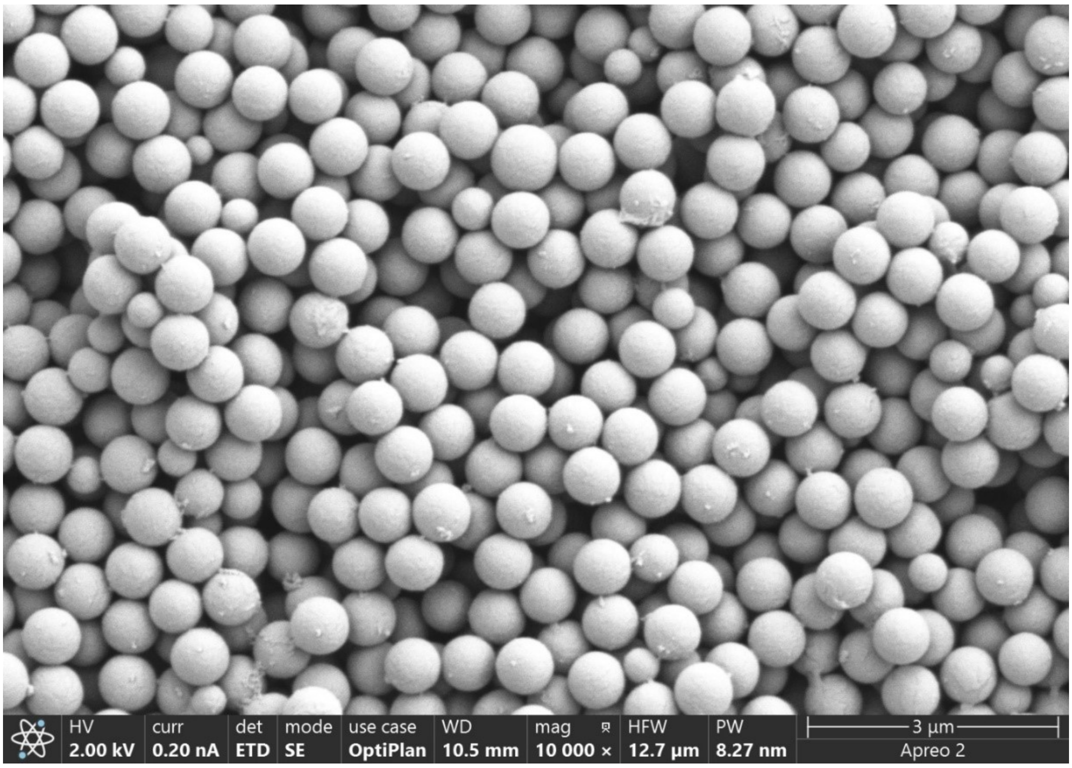

Fig. S2: Scanning Electron Microscopy (SEM, 0.2 nA, 2 KeV, 10000x mag.) image for Large polystyrene nanoparticles (dried via capillary action with filter paper, 6 nm gold sputter coated)

S3: Medium PS SEM Image

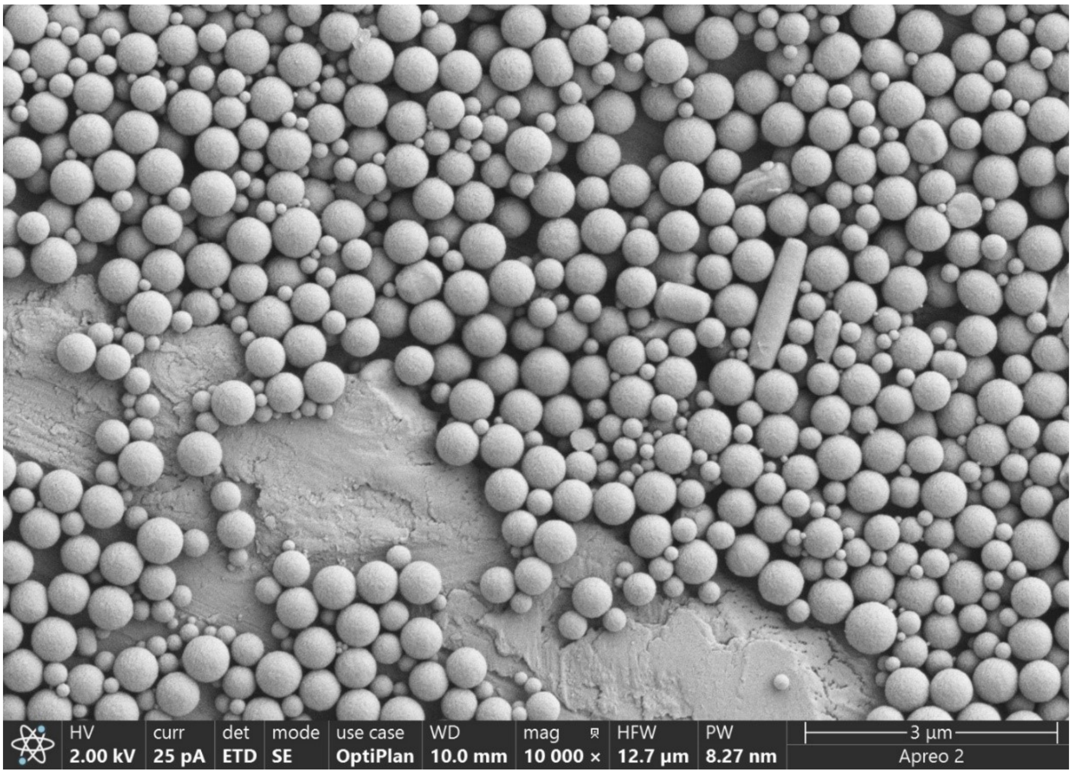

Fig. S3: Scanning Electron Microscopy (SEM, 0.025 nA, 2 KeV, 10000x mag.) image for Medium polystyrene nanoparticles (dried via capillary action with filter paper, 6 nm gold sputter coated)

S4: Small PS SEM Image

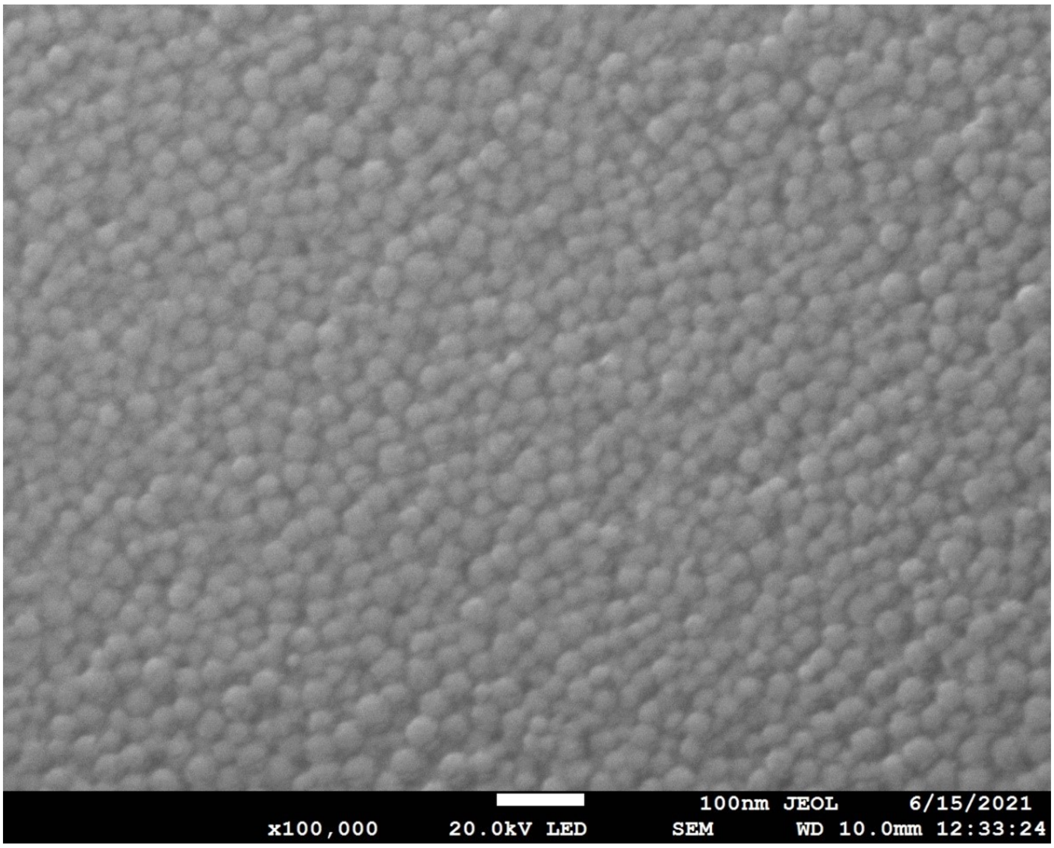

Fig. S4: Scanning Electron Microscopy (SEM, 0.2 nA, 20 KeV, 100000x mag.) image for Small polystyrene nanoparticles (dried via capillary action with filter paper, 6 nm gold sputter coated)

S5: Large PS BET Adsorption Isotherm

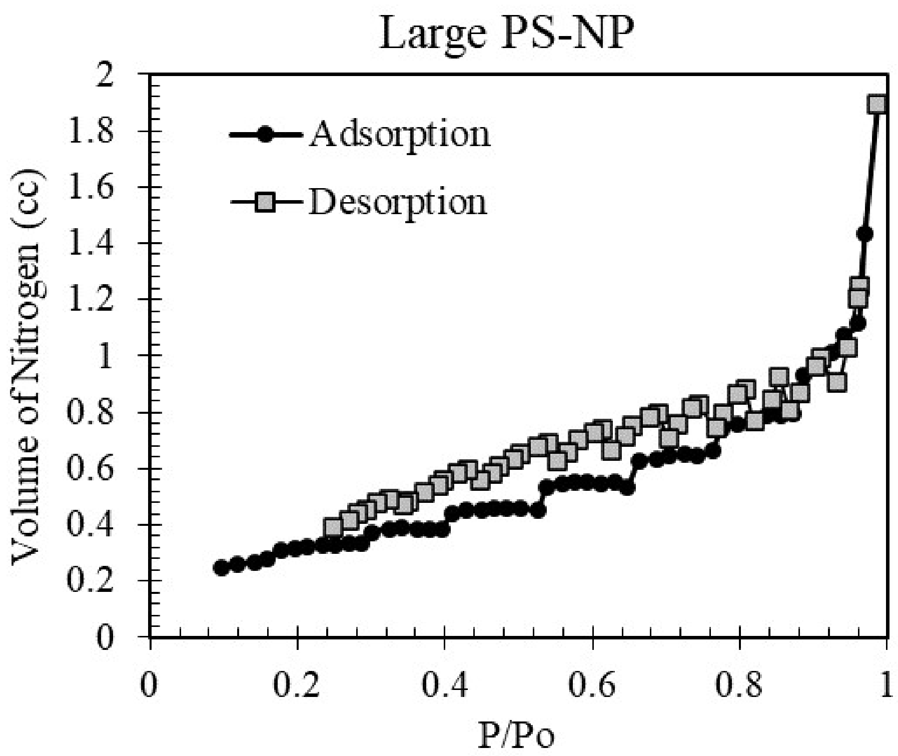

Fig. S5: BET adsorption and desorption isotherms for Large polystyrene nanoparticles under nitrogen pressure between 0.1 and 0.99 P/P_O, following outgassing at 70°C.

S6: Medium PS BET Adsorption Isotherm

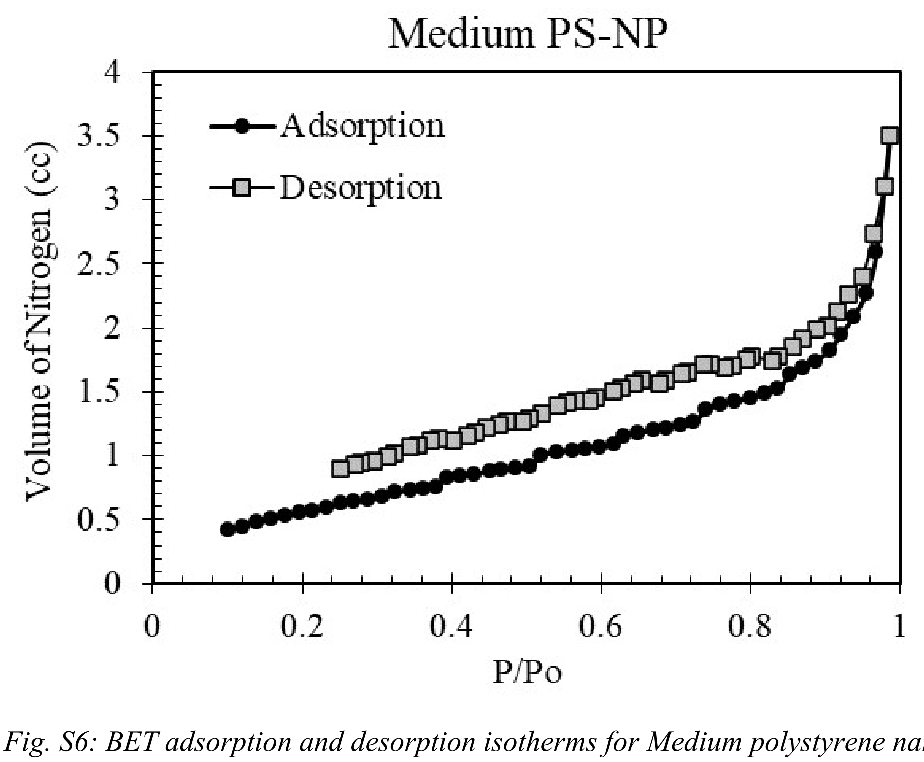

Fig. S6: BET adsorption and desorption isotherms for Medium polystyrene nanoparticles under nitrogen pressure between 0.1 and 0.99 P/P_O, following outgassing at 70°C.

S7: Small PS BET Adsorption Isotherm

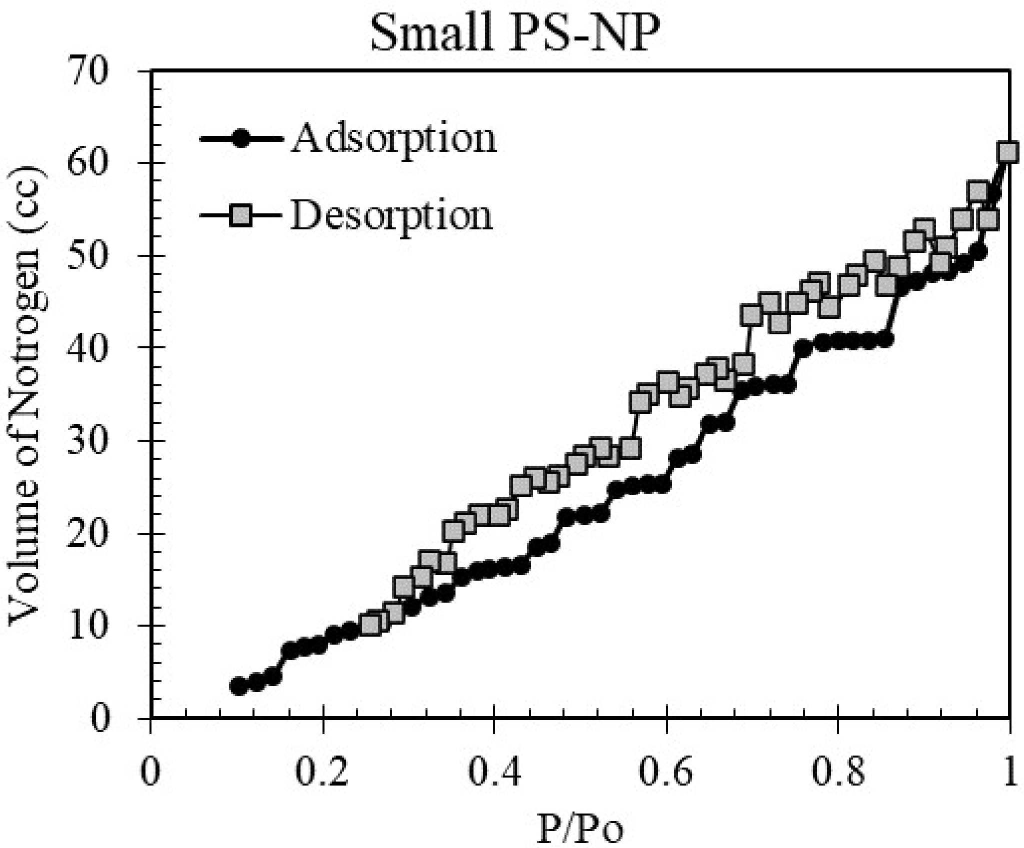

Fig. S7: BET adsorption and desorption isotherms for Small polystyrene nanoparticles under nitrogen pressure between 0.1 and 0.99 P/P_O, following outgassing at 70°C.

S8: TGA Mass and Derivatized Plots

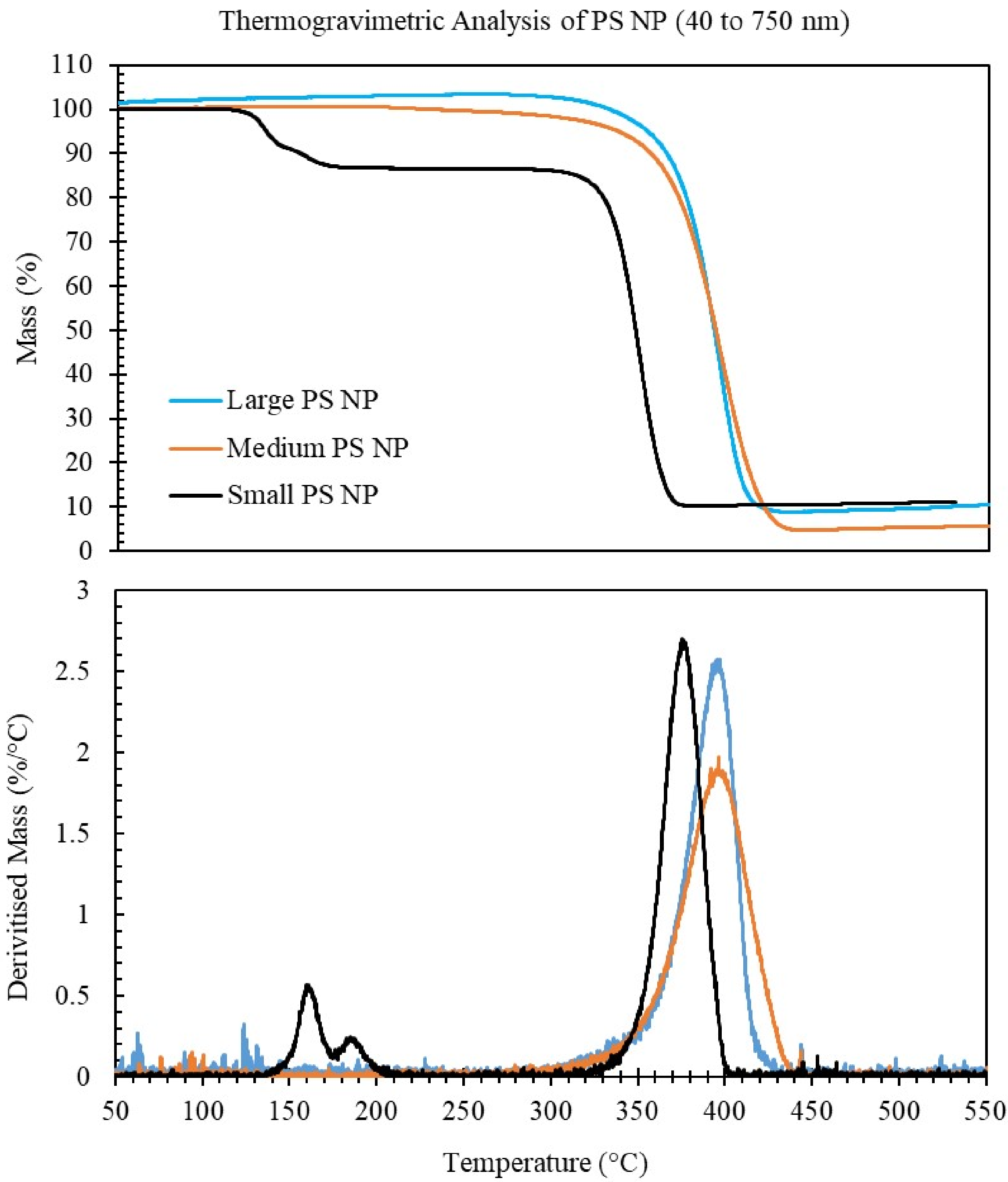

Fig. S8: Absolute and derivatised mass loss analysis by thermogravimetric analysis of Large, Medium and Small polystyrene nanoparticles between 50 and 550°C.

S9: Raman Spectra

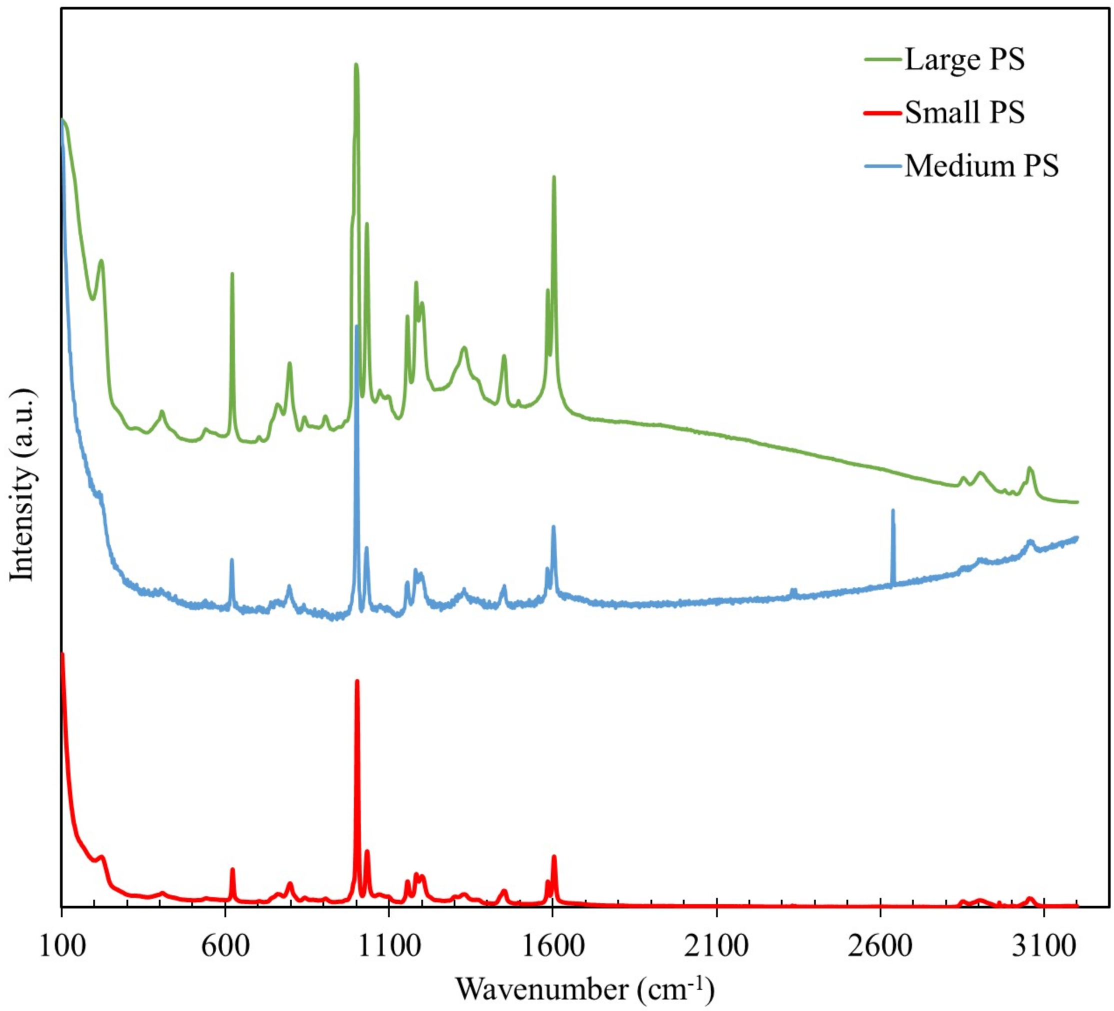

Fig. S9: Raman Spectra (785 nm laser, 100% laser power, 50XL objective) for Large, Medium, and Small polystyrene nanoparticles.

S10: FTIR Spectra

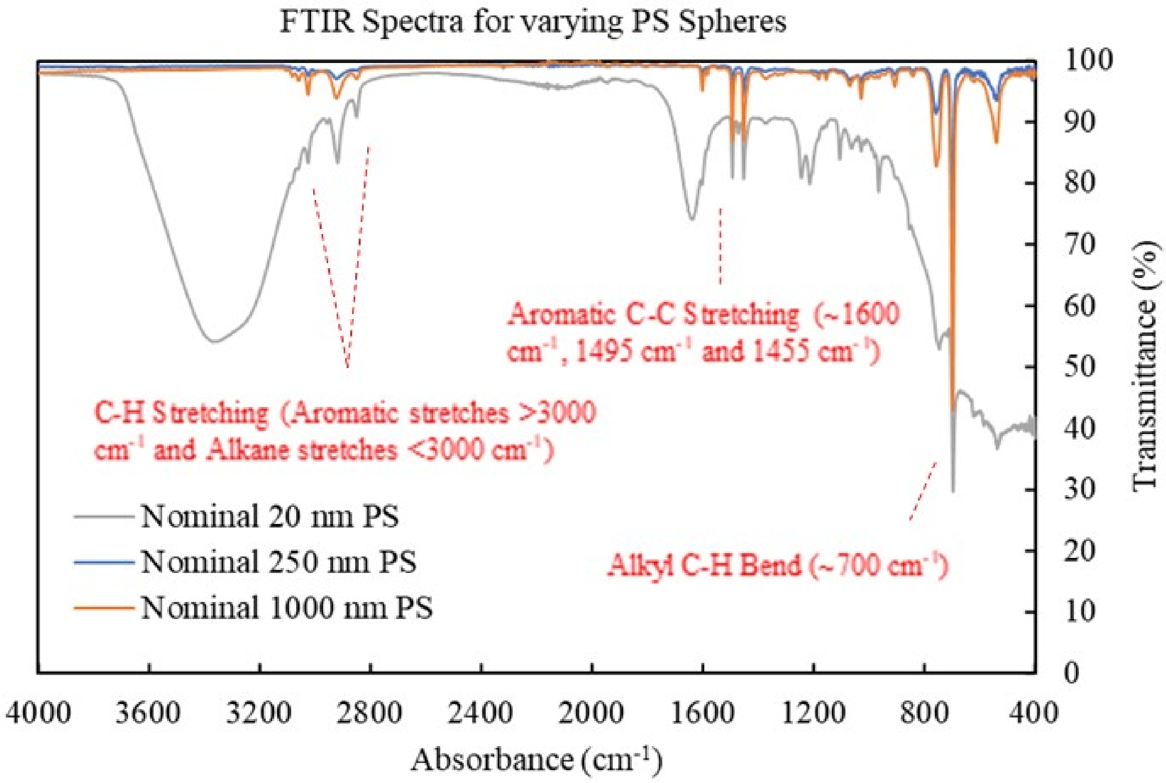

Fig. S10: FTIR Spectra for Large, Medium, and Small polystyrene nanoparticles.

S11: Q_{SAT} and K_D values of adsorption

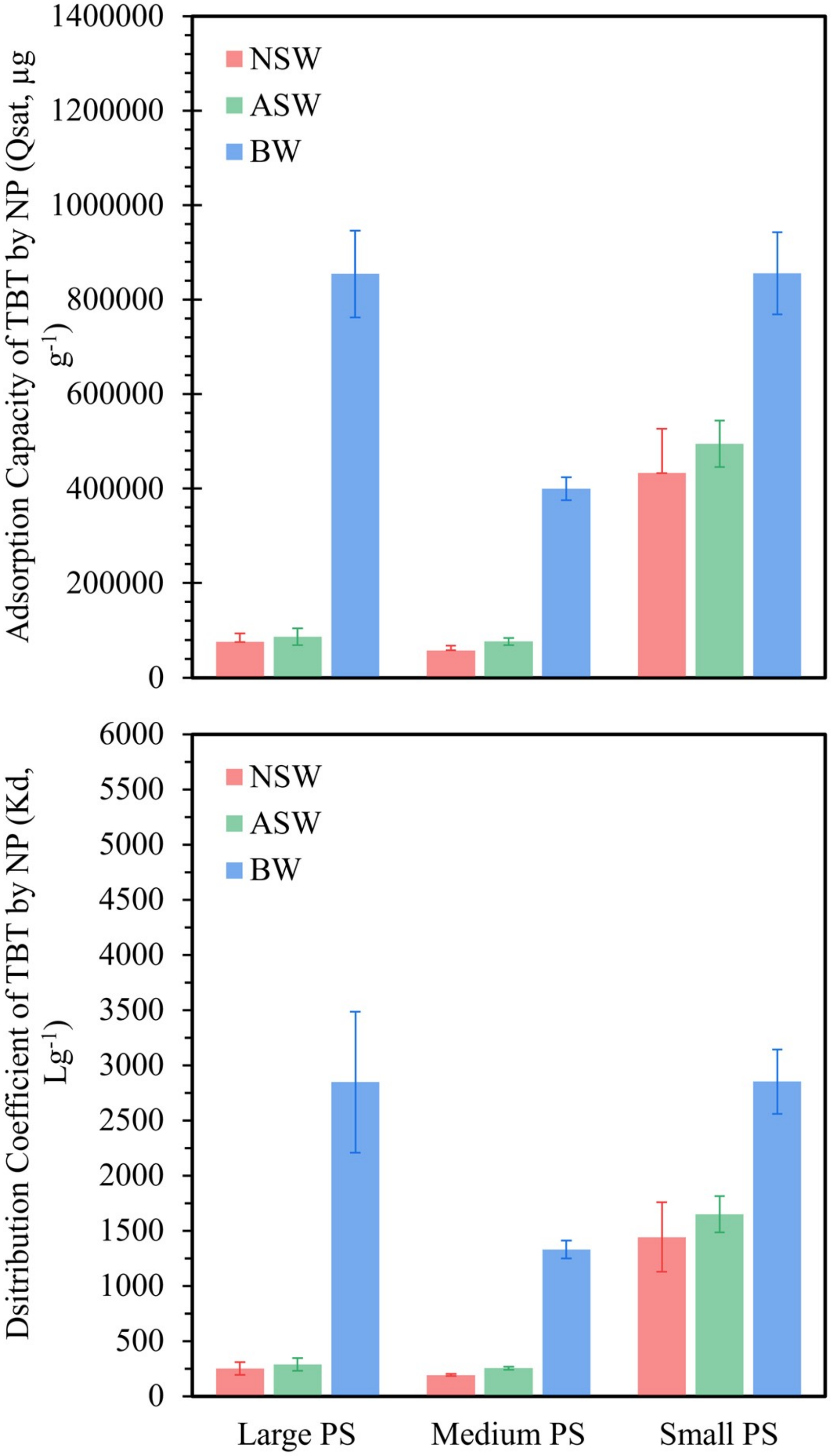

Fig. S11: Adsorption capacity (µgg^{-1}) and distribution coefficient (Lg^{-1}) for Large, Medium, and Small polystyrene nanoparticles within natural seawater (NSW), brackish water (BW) and artificial seawater (ASW).

S12: Raman Adsorption Mechanism for Large Nanopolystyrene Particles

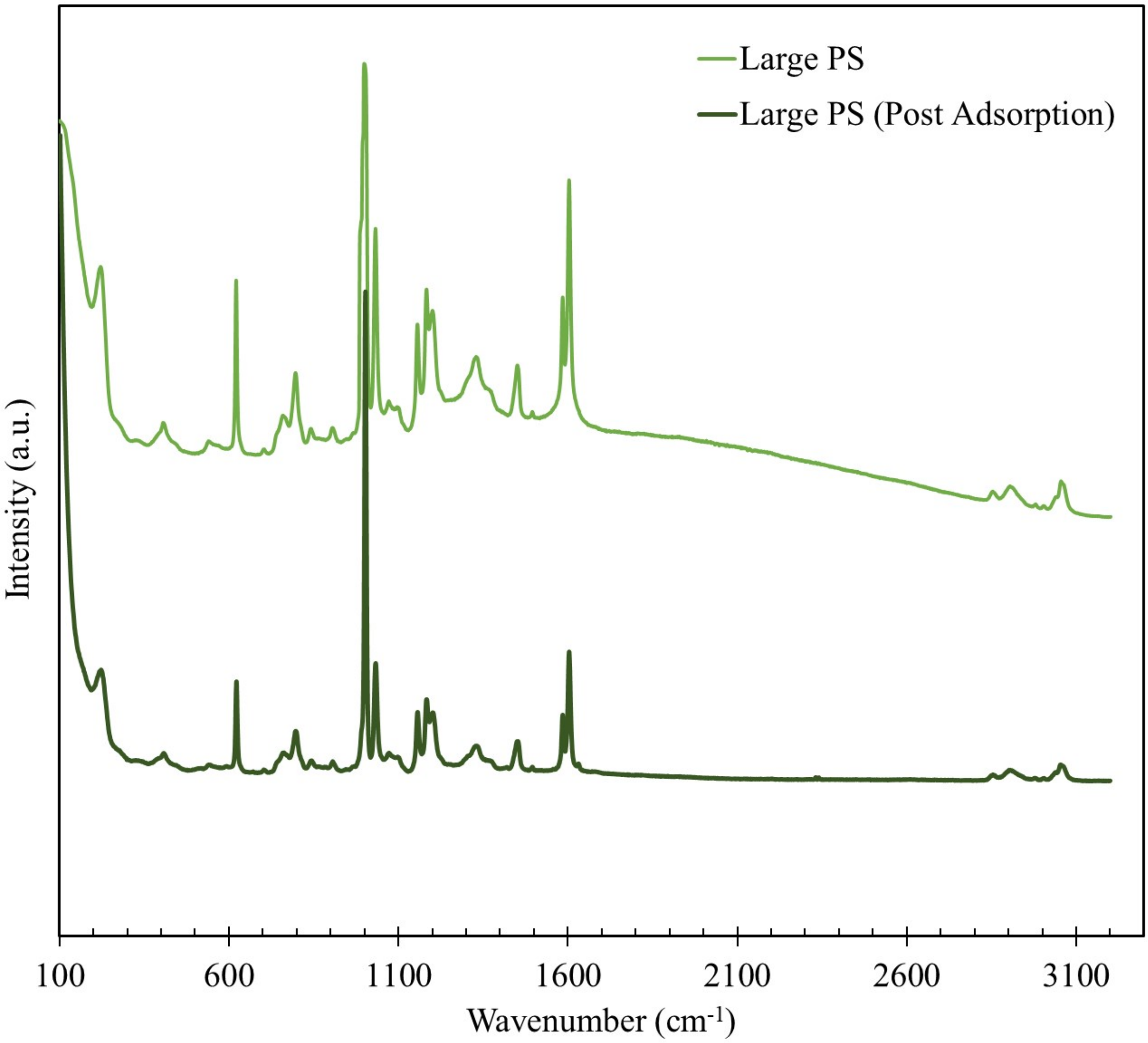

Fig. S12: Raman Spectra (785 nm laser, 100% laser power, 50XL objective) for Large polystyrene nanoparticles, before and after combined agitation with tributyltin (24 hours).

S13: Raman Adsorption Mechanism for Medium Nanopolystyrene Particles

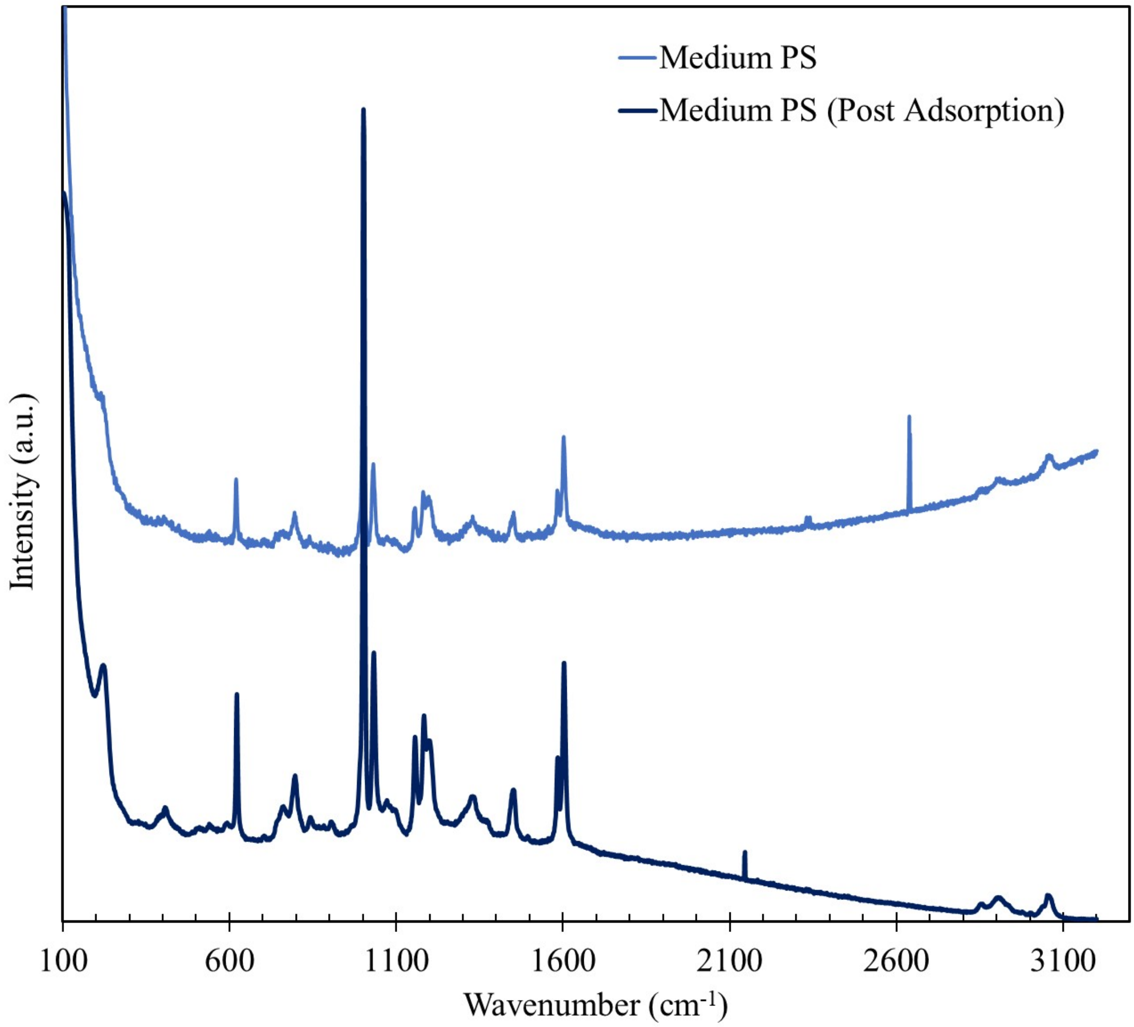

Fig. S13: Raman Spectra (785 nm laser, 100% laser power, 50XL objective) for Medium polystyrene nanoparticles, before and after combined agitation with tributyltin (24 hours).

S14: Raman Adsorption Mechanism for Small Nanopolystyrene Particles765

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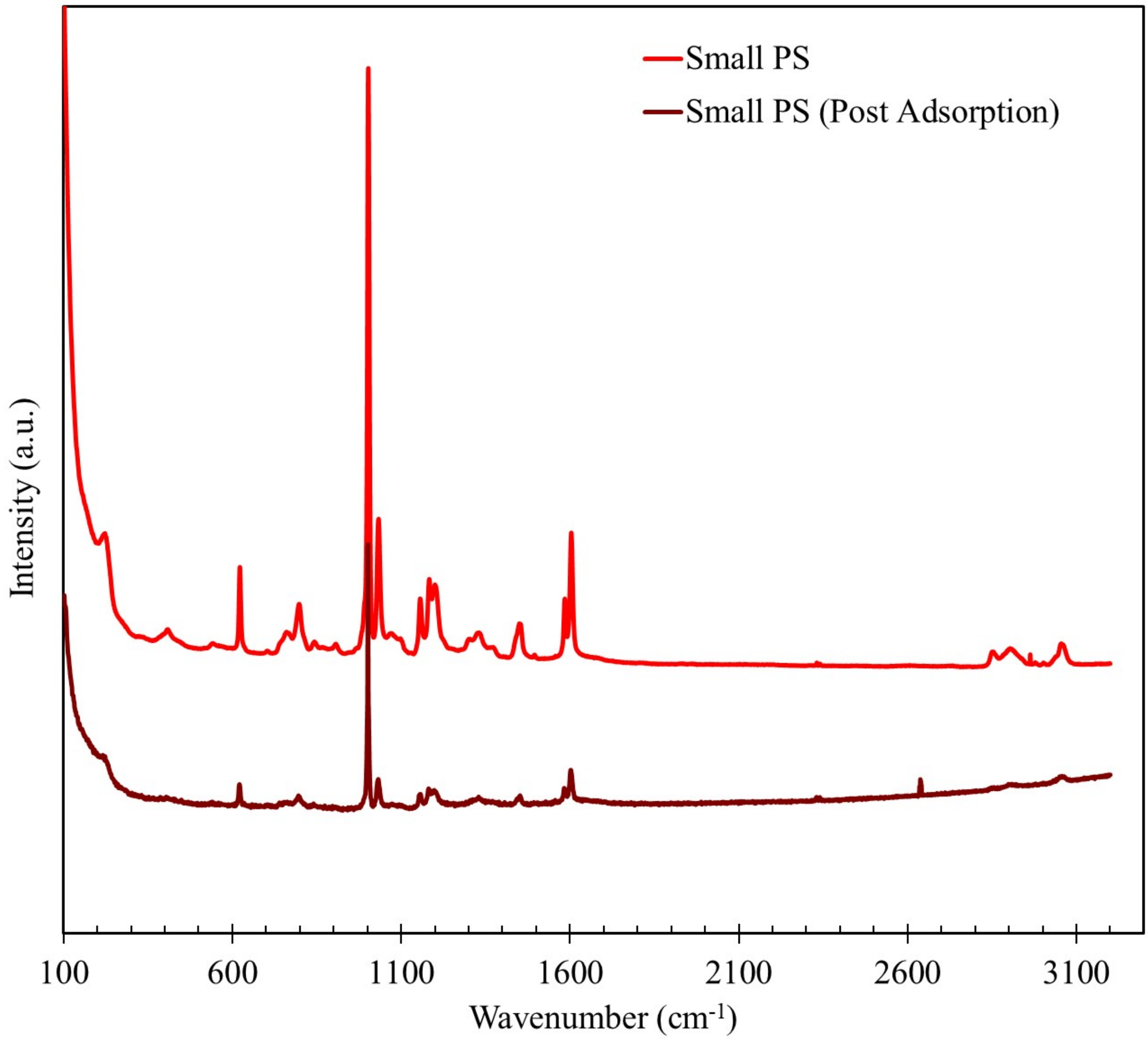

Fig. S14: Raman Spectra (785 nm laser, 100% laser power, 50XL objective) for Small polystyrene nanoparticles, before and after combined agitation with tributyltin (24 hours).

Tables

S1: Filtration Recovery

Table S1: TBT (100 ng mL^{-1}) filtration spike recoveries during ultrafiltration (30 kDa) and syringe filtration (0.22 and 0.45 µm) methods.

	Recovery (% TBT Recovered)		
Rep.	Ultrafiltration (30 kDa)	0.22 µm Syringe Filtration	0.45 µm Syringe Filtration
1	97.6	100.2	99.4
2	98.1	101.3	96.8
3	99.0	99.6	94.8
4	95.4	97.3	101.6
5	93.9	100.9	104.3
6	96.6	98.6	97.5
7	97.2	97.1	94.9
8	92.8	97.8	98.0
9	95.6	102.7	99.9
10	94.3	101.6	100.6
Average	96.1	99.7	98.8
StDev	2.0	1.9	3.0

S2: Freundlich Parameters

Table S2: Freundlich parameters calculated following adsorption experiments between tributyltin and 3 sizes of polystyrene nanoparticles.

Matrix	c (LogKf)	Kf	Kf Error	x (1/n)	1/n Error
pH8 (L)	-0.112	0.772681	0.220766	0.9441	0.06
NSW A (L)	0.2214	1.664945	0.721157	0.5633	0.139
NSW B (L)	0.1197	1.317346	0.670346	0.6962	0.091
BW (L)	-0.4285	0.372821	0.048378	1.3237	0.37369
ASW (L)	-0.1027	0.789405	0.207382	1.0826	0.0947

Matrix	c (LogKf)	Kf (ug/g)	Kf Error	x (1/n)	1/n Error
pH8 (M)	1.4187	26.22406	1.602792	0.2391	0.0231
NSW A (M)	0.3712	2.350715	1.069811	0.5255	0.02268
NSW B (M)	-1.1705	0.067531	0.031826	1.1846	0.07002
BW (M)	-0.2029	0.626758	0.335321	1.1322	0.186
ASW (M)	-0.2462	0.567283	0.483183	1.2411	0.371

Matrix	c (LogKf)	Kf (ug/g)	Kf Error	x (1/n)	1/n Error
pH8 (S)	-0.8569	0.139027	0.021676	1.9493	0.2238
NSW A (S)	-0.6457	0.2261	0.018313	1.4451	0.06755
NSW B (S)	-	-	-	-	-
BW (S)	1.1954	15.68195	0.857955	0.5832	0.1376
ASW (S)	0.9875	9.71628	0.843717	0.7012	0.1621

S3: Surface Area Normalised Adsorption Capacity

Table S3: The adsorption capacity of TBT by PS-NP particles (Q_{sat}) in artificial seawater (ASW), natural seawater (NSW) and brackish water (BW), calculated in terms of particle surface area.

	Q_{sat}, Surface Area Normalised (ug cm^{-2})		
	Large PS	Medium PS	Small PS
NSW	6.30 ± 1.23	2.51 ± 0.18	0.40 ± 0.08
BW	71.18 ± 6.34	17.38 ± 0.46	0.79 ± 0.07
ASW	7.22 ± 1.21	3.32 ± 0.14	0.45 ± 0.04

S4: QC Recovery

Table S4: Internal QC recoveries for Sn analysis in MilliQ water, artificial seawater (ASW), natural seawater (NSW) and brackish water (BW) by ICP-MS and MP-AES. True Conc. (ppb) refers to the concentration of Sn as prepared by dilution of 1000 ppm Sn CRM (Sigma Aldrich, Germany).

		ICP-MS	
QC ID	True Conc. (ppb)	Measured Conc. (ppb)	Recovery (%)
MilliQ QC1	2.48	2.1	84.7
MilliQ QC1	2.48	2.03	81.9
MilliQ QC1	2.48	2.34	94.4
ASW QC1	2.42	2.31	95.5
ASW QC1	2.42	2.33	96.3
ASW QC1	2.42	2.68	110.7
ASW QC1	2.42	2.31	95.5
ASW QC1	2.42	2.1	86.8
ASW QC1	2.42	2.63	108.7
NSW QC1	2.45	2.09	85.3
NSW QC1	2.45	2.43	99.2
NSW QC1	2.45	2.48	101.2
NSW QC1	2.45	2.71	110.6
NSW QC1	2.45	2.26	92.2
NSW QC1	2.45	2.07	84.5
BW QC1	2.52	2.52	100.0
BW QC1	2.52	2.12	84.1
BW QC1	2.52	2.5	99.2
	Average	2.33	95.04
	Min	2.03	81.9
	Max	2.71	110.7
MilliQ QC2	0.25	0.21	84.0
MilliQ QC2	0.25	0.26	104.0
MilliQ QC2	0.25	0.21	84.0
ASW QC2	0.24	0.25	104.2
ASW QC2	0.24	0.22	91.7
ASW QC2	0.24	0.23	95.8
ASW QC2	0.24	0.22	91.7
ASW QC2	0.24	0.2	83.3
ASW QC2	0.24	0.2	83.3
NSW QC2	0.25	0.24	96.0
NSW QC2	0.25	0.22	88.0
NSW QC2	0.25	0.26	104.0
NSW QC2	0.25	0.28	112.0
NSW QC2	0.25	0.24	96.0
NSW QC2	0.25	0.22	88.0
BW QC2	0.26	0.27	103.8
BW QC2	0.26	0.28	107.7
BW QC2	0.26	0.24	92.3

Average	0.24	94.99
Min	0.2	83.3
Max	0.28	112.0

QC ID	True Conc. (ppm)	MP-AES Measured Conc. (ppm)	Recovery (%)
MilliQ QC1	25.02	26.35	105.3
MilliQ QC1	25.02	24.61	98.4
MilliQ QC1	25.02	24.22	96.8
MilliQ QC1	25.02	26.08	104.2
MilliQ QC1	25.02	25.03	100.0
ASW QC1	24.89	24.52	98.5
ASW QC1	24.89	25.97	104.3
ASW QC1	24.89	25.63	103.0
ASW QC1	24.89	26.9	108.1
ASW QC1	24.89	26.12	104.9
ASW QC1	24.89	25.07	100.7
NSW QC1	25.33	25.8	101.9
NSW QC1	25.33	27.03	106.7
NSW QC1	25.33	25.77	101.7
NSW QC1	25.33	25.03	98.8
NSW QC1	25.33	26.05	102.8
NSW QC1	25.33	24.23	95.7
BW QC1	24.61	24.82	100.9
BW QC1	24.61	24.69	100.3
BW QC1	24.61	26.4	107.3
BW QC1	24.61	26.67	108.4
	Average	25.57	102.32
	Min	24.22	95.7
	Max	27.03	108.4
MilliQ QC2	2.62	3.24	123.7
MilliQ QC2	2.62	2.8	106.9
MilliQ QC2	2.62	2.24	85.5
MilliQ QC2	2.62	2.7	103.1
MilliQ QC2	2.62	2.06	78.6
ASW QC2	2.54	2.26	86.3
ASW QC2	2.54	3.29	125.6
ASW QC2	2.54	3.24	123.7
ASW QC2	2.54	2.72	103.8
ASW QC2	2.54	2.15	82.1
ASW QC2	2.54	3.41	130.2
NSW QC2	2.43	2.6	99.2
NSW QC2	2.43	2.97	113.4
NSW QC2	2.43	2.95	112.6
NSW QC2	2.43	3.44	131.3

NSW QC2	2.43	3.06	116.8
NSW QC2	2.43	2.48	94.7
BW QC2	2.51	3.32	126.7
BW QC2	2.51	2.12	80.9
BW QC2	2.51	2.81	107.3
BW QC2	2.51	3.33	127.1
	Average	2.82	107.58
	Min	2.06	78.6
	Max	3.44	131.3