

Anthropogenic microparticles in sea-surface microlayer at Osaka Bay, Japan

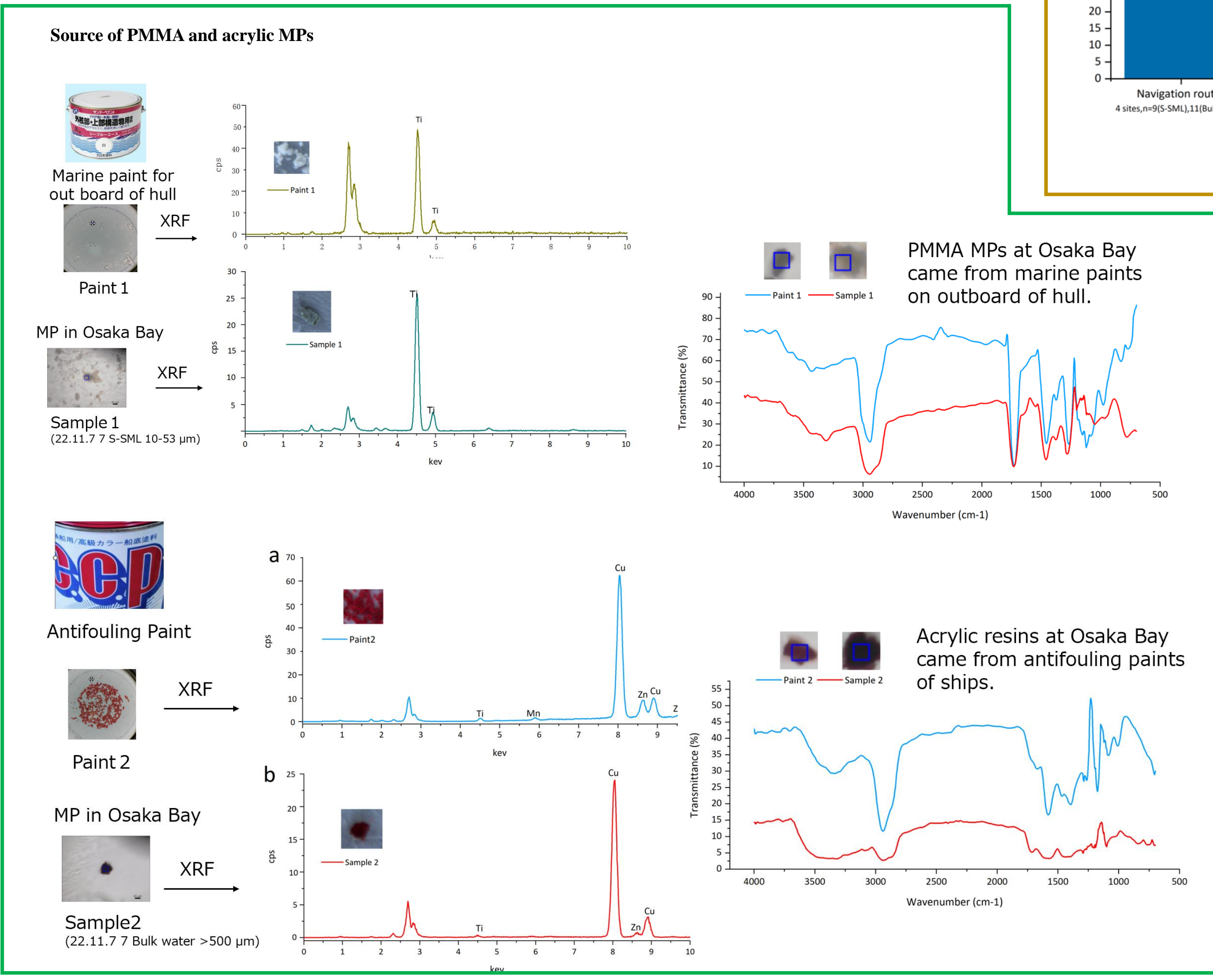
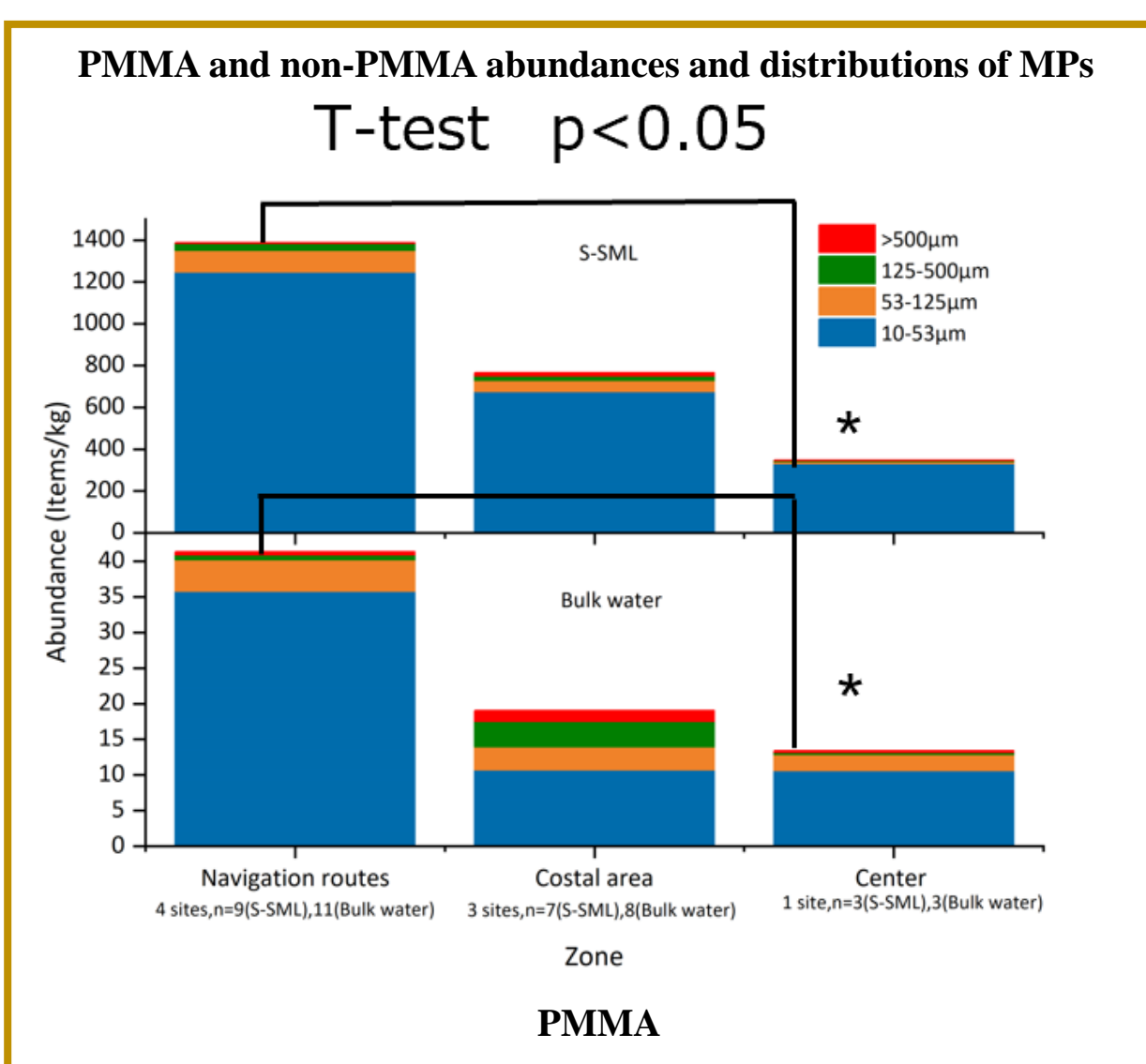
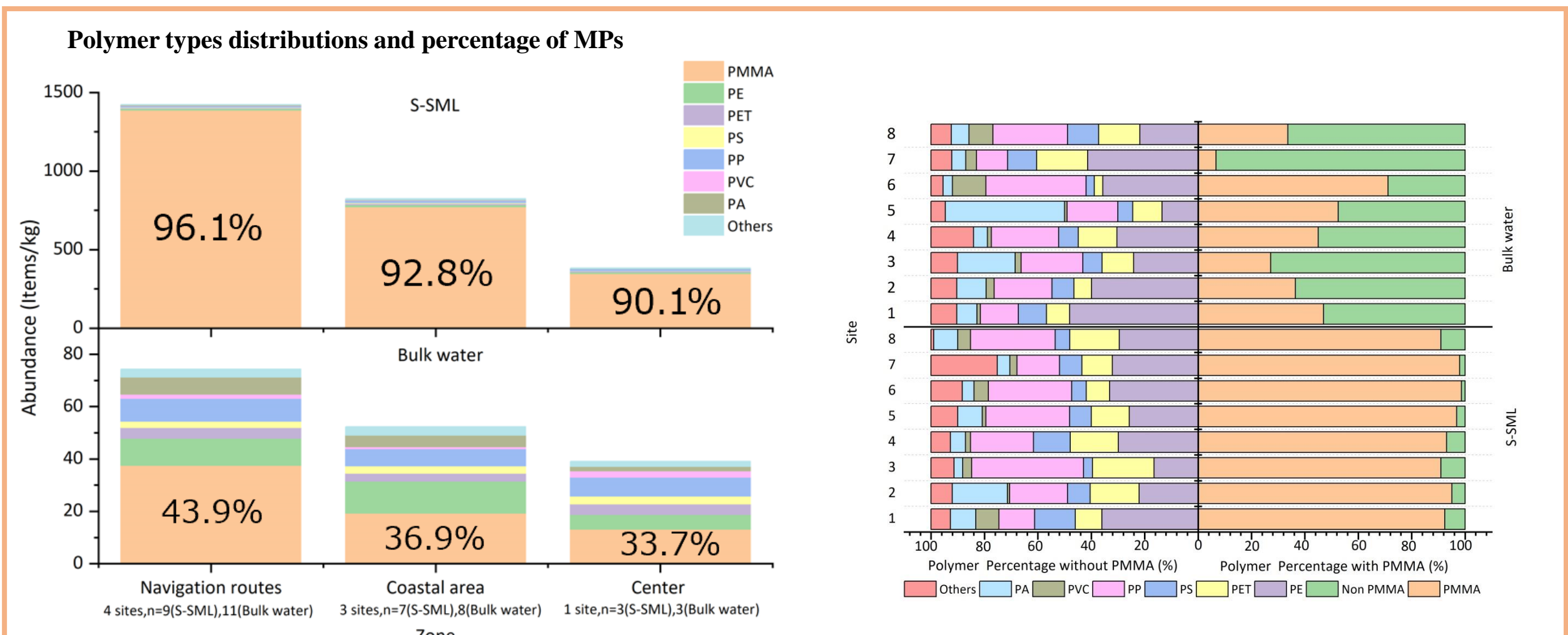
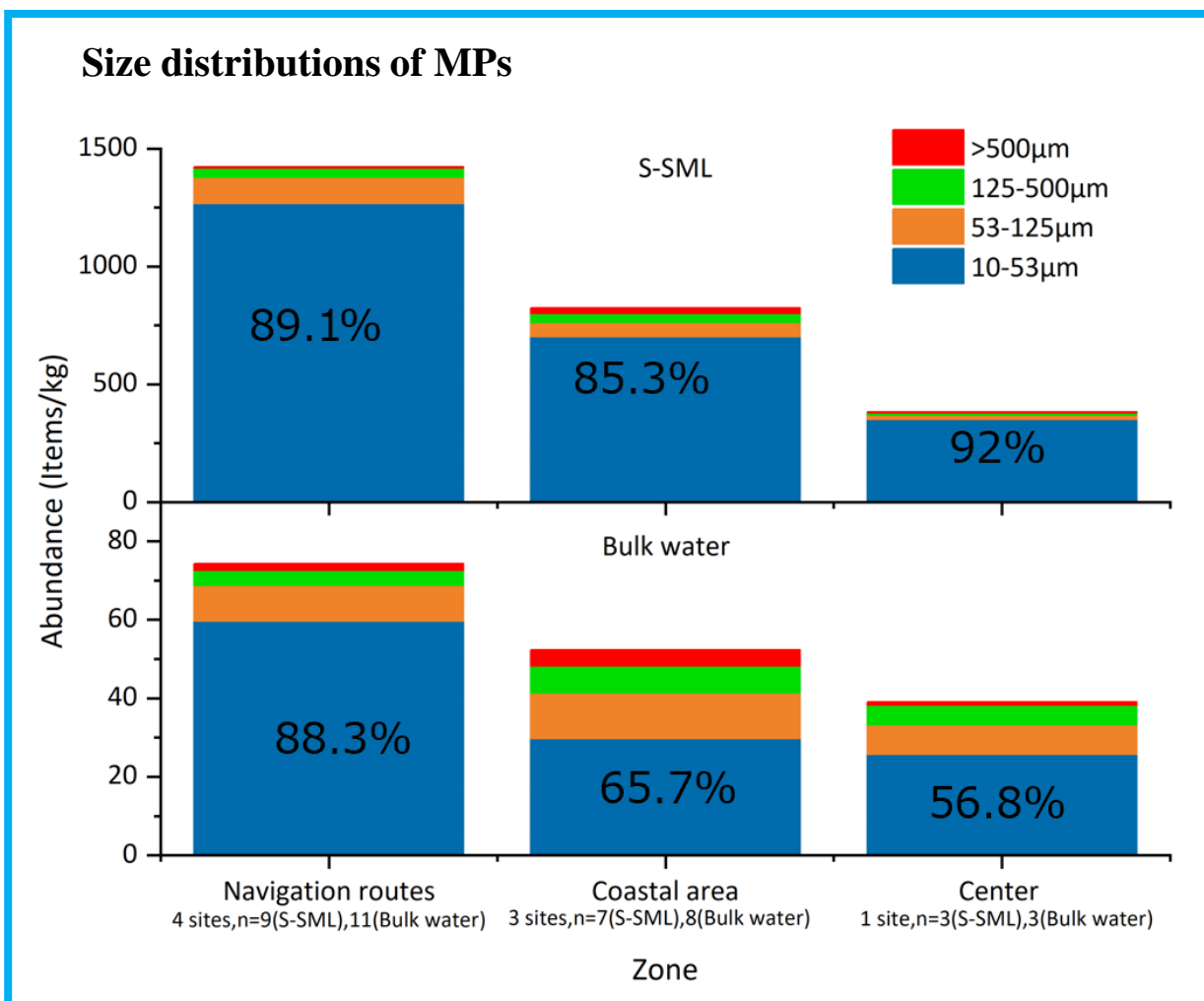
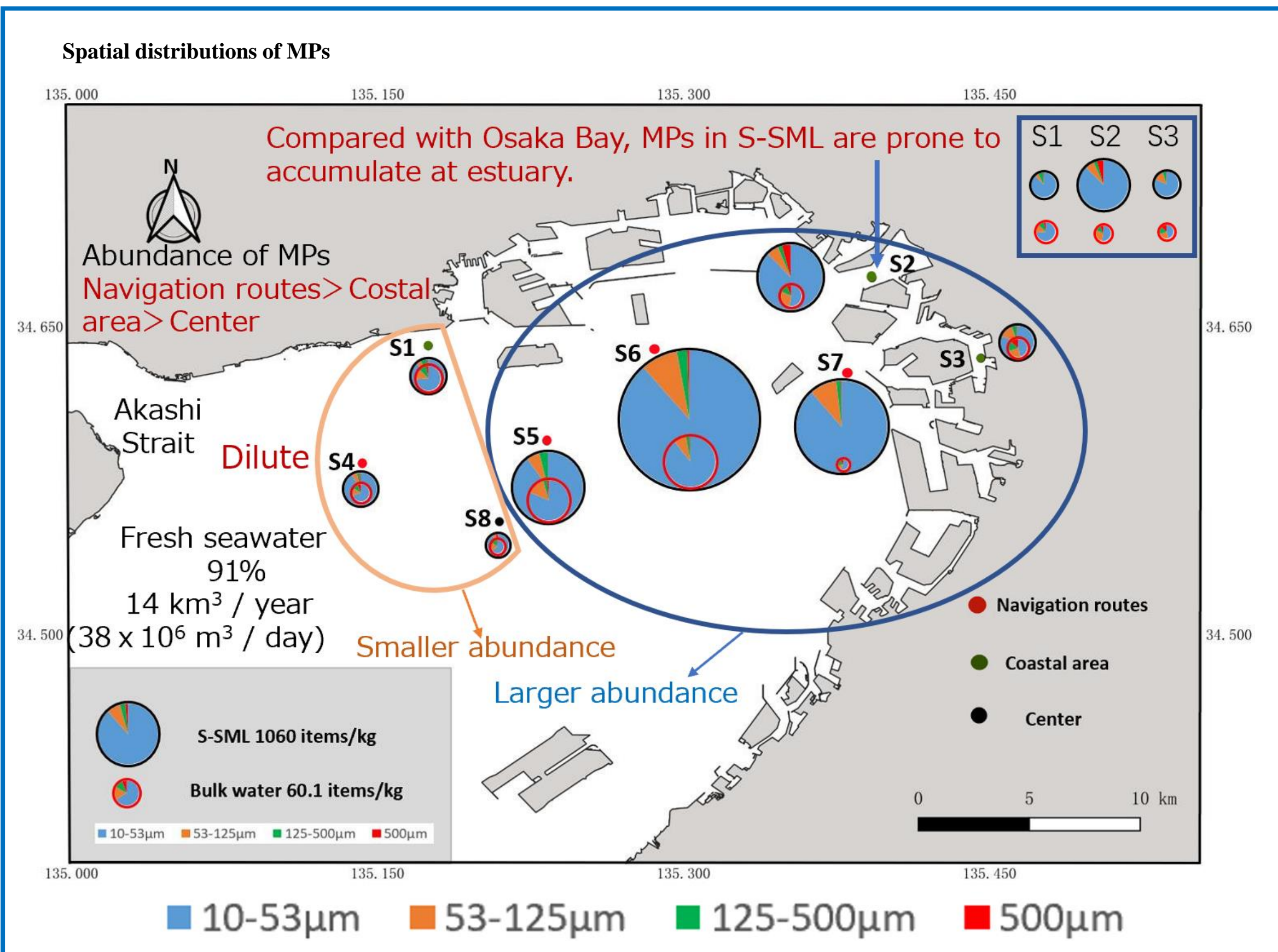
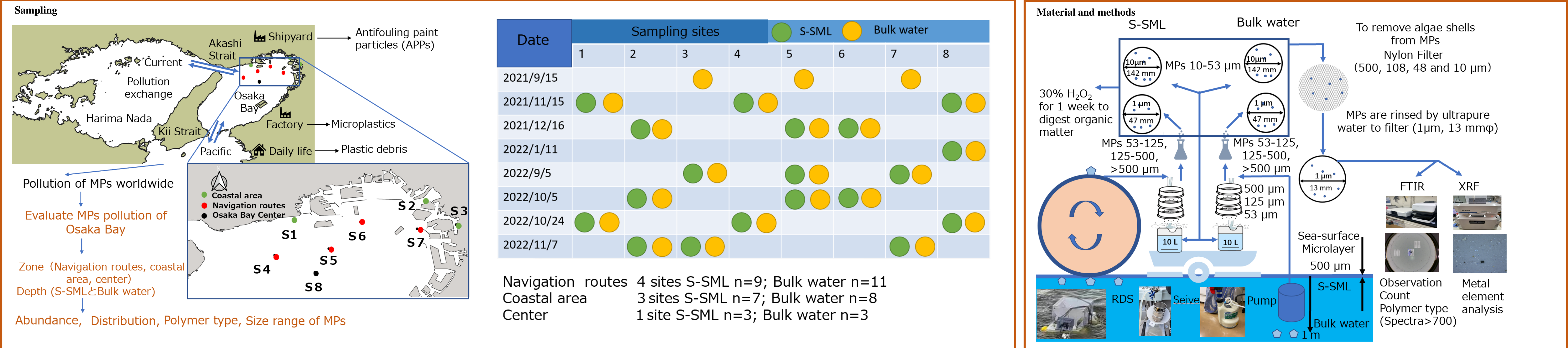
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Abstract

The abundance and composition of microparticles (MPs) in seawater surface microlayer (S-SML, 1mm of sea-surface) and bulk water (1 m under sea-surface) were investigated to evaluate pollution level of the MPs at Osaka Bay in Japan. Both seawaters were collected at eight sites including ship navigation routes, coastal areas, and the centre of Osaka Bay in 2021-2022. The number and polymer types of the MPs, filtered for four size ranges (10-53, 53-125, 125-500, and >500 μm) and digested by H₂O₂, were analyzed by Microscope and Fourier Transform Infrared Spectrometer (FTIR). The average abundance of MPs collected in total 19 collections for 8 sites was 1060±685 items/kg in S-SML and 61.0±33.8 items/kg in bulk water, respectively. MPs in both S-SML and bulk water exhibited higher abundance at navigation route than other sites. The smallest MPs with 10-53 μm among 4 sizes accounted for 88% in S-SML and 66% in bulk water among all sites. Polymethyl methacrylate (PMMA) was the major MPs detected with minor one as Polyethylene, Polyesters, Polystyrene, Polypropylene, Polyvinyl chloride, Polyamide, etc. and was occupied 95 % of total MPs in S-SML and 40 % of total MPs in bulk water. In addition, PMMA accounted for 97.5 % in S-SML and 52.6 % in bulk water among all MPs with 10-53 μm, and its sources were suspected from marine paints (Primarily APPs: antifouling paint particles) and land-coatings.

Keywords: Microparticles (MPs), Seawater Surface Microlayer (S-SML), PMMA, Antifouling Paint Particles (APPs)



Size	Country	S-SML		Bulk water	
		Site	MPs abundance (Items/L)	Site	MPs abundance (Items/L)
>10 μm	Japan	Osaka Bay (This study)	1040	Osaka Bay (This study)	59.8
>0.75 μm	Korea	Geoje Island (Song et al., 2014)	210	Geoje Island (Song et al., 2014)	0.946
>0.75 μm	Korea	Jinhae Bay (Song et al., 2015)	182	Hudson River (Miller et al., 2017)	0.98
>0.45 μm	UK	Southampton (Stead et al., 2020)	75.4	Saigon River (Lahens et al., 2018)	172-591
>53 μm	Japan	Osaka Bay (This study)	114	Osaka Bay (This study)	16.6
>50 μm	Korea	Incheon/Kyeonggi Coastal (Chate et al., 2015)	153	Incheon/Kyeonggi Coastal (Chate et al., 2015)	1.6
>63 μm	US	Wiyah Bay (Gray et al., 2018)	30.8	South China Sea (Cai et al., 2018)	2.57
>63 μm	US	Charleston Harbor (Gray et al., 2018)	6.6	Shore of Rayong (Prarat et al., 2021)	1.78

CONCLUSIONS

Abundant MPs dominated by PMMA polymer types (95% in S-SML and 40% in bulk water) were discovered both in S-SML and bulk water at Osaka Bay with a higher pollution level worldwide, and their concentrations exhibited a distribution trend of higher abundances at navigation routes than that at coastal area and center. MPs abundance in S-SML was significantly higher than that in bulk water. MPs with 10-53 μm occupied overwhelming proportion of abundances and their abundance in S-SML was nearly 40 times larger than that in bulk water. Abnormally high abundance of MPs especially PMMA and acrylic resins MPs at navigation routes suggested a pollution source from marine paints that always with Ti as pigment used on outdoor of hulls and antifouling paints that always with Cu and Zn as biocides used on bottom surface of ships. PMMA MPs and acrylic resin MPs samples at Osaka Bay were detected to contain Ti and Cu respectively, and their FTIR spectra was consistent with that of the polymer of marine paints and antifouling paints respectively, which suggested that PMMA MPs originated from marine paints used on outdoor of hulls and acrylic resins came from antifouling paints. The abundance of non-PMMA MPs retained similar between S-SML and bulk water, which implied that PMMA MPs not only determined the huge discrepancy on abundance distribution among navigation routes, coastal area and center between, but also led the significant differences of MPs concentration between S-SML and bulk water.