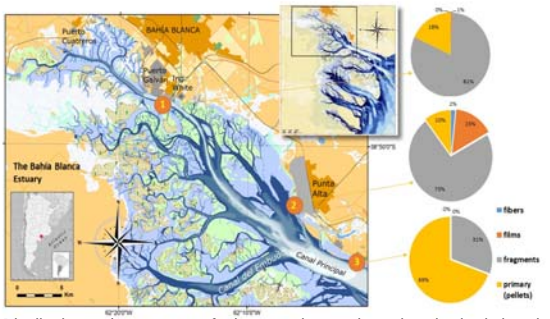
Distribution of beached microplastics carrying POPs at South Atlantic Estuary, Argentina

Andres H. Arias [1,2 (*)], Guadalupe Alvarez [3], Karla Pozo[6,7,8], Petra Pribylova[7], Jana Klanova[7], Lucas S. Rodríguez Pirani [5], A. Lorena Picone [5], Mónica Alvarez [2,4] Norma Tombesi [2,4]

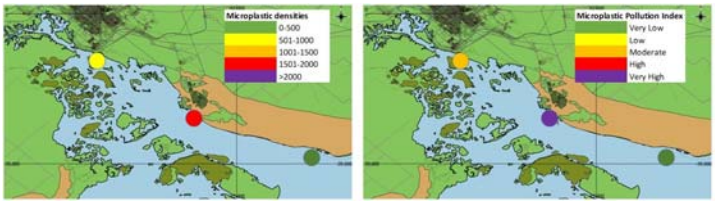
[1] IADO, Instituto Argentino de Oceanografía, CCT-CONICET, Bahía Blanca, Argentina.
[2] Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, Bahía Blanca, Argentina.
[3] HAPIC Humedal Arroyo Pareja Isla Cantarelli NGO, Punta Alta, Argentina
[4] INQUISUR-Departamento de Química, Universidad Nacional del Sur (UNS), Av. Alem 1253, Bahía Blanca, Argentina
[5] CEQUINOR (UNLP, CCT-CONICET La Plata, Associated with CIC), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Boulevard 120 N° 1465, La Plata (CP 1900), Argentina.
[6] Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Lientur, 1457 Concepción, Chile
[7] RECETOX (Research center for toxic compounds in the environment), Masaryk University, Brno, Czech Republic
[8] Fundación Bioera. Noruega 6427, of 4. Las condes, Santiago, Chile

Due to their water-sediment interface position, the coastal environments usually became a sink for many type of pollutants which includes microplastics; however, there is scarce available information for Argentinean beach sediments and microplastics. For instance; most of the study sites at the International Pellet Watch are located in the North Hemisphere, focusing on Europe, the United States of America (USA) and the Australasia region. This paper is focused at a highly anthropized South American coast which includes a relevant economic-industrial centre as well as an important transport node in association with its deep-sea natural port.

- One of the main aims of this work is to address sediment characteristics and pollution at highly anthropized beaches in regards to microplastics
- Secondly, to addresses the growing question regarding the role of plastic as a vector for organic pollutants in the marine environment as the highest produced and widespread plastic resins are commonly hydrophobic which joint to the high surface/volume ratio of microplastics turn them into an excellent non-polar phase for accumulation of POPs and other hydrophobic pollutants

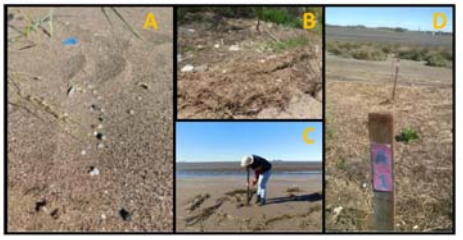


Distribution and occurrence of primary and secondary microplastics in beach sediments at the Bahía Blanca Estuary, Argentina. 1: Galvan Harbor 2: Arroyo Parejas 3: Baterías

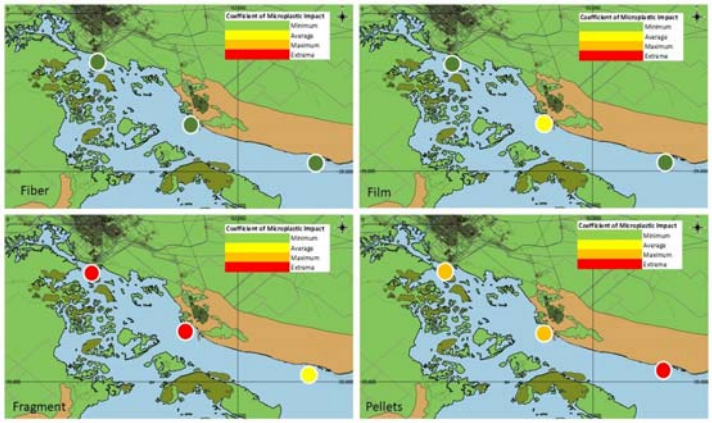


Geographical distribution of Microplastic densities and **Microplastic Pollution Index (MPPI):** the Microplastic Pollution Index MPPI which reports the presence of MPs in an environment (Rangel-Buitrago et al., 2021) and calculates the existing relationship between the number of MPs and sampled surface, defining five different classes which vary from "Very low presence" to "Very high presence" of MPs.

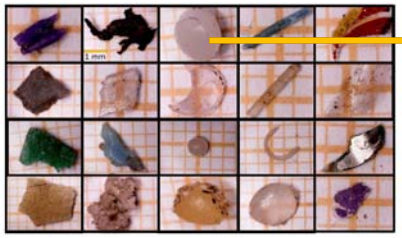
Along each sampling point, three transects (A, B and C) were sampled. The maximum distance between transects were of 20 meters with a minimum of 5 meters, depending on the beach morphology, obstacles, etc. Sediment samples were collected in duplicate up to 10 cm depth which is commonly the range with maximum microplastics occurrence (Ballent et al., 2016). We used metallic sampling cores of 10 x 10 cm which resulted in ~ 1 dm^3 of sediment sampled (10 cm depth) at each quadrant which were collected in muffled (450 °C) glass jars with aluminum caps and then samples were kept at 4 °C for further analysis.



A: Storm Berm line at Site 3. B: Storm Berm line at site 1. C: Sampling at Site 3. D: Beach transect at Site 2.



Geographical distribution of Coefficient of **Microplastic Impact (CMPI)** by shape: the Microplastic Impact Coefficient (CMPI - Rangel-Buitrago et al., 2021) balances the relationship between a specific shape of MPs and the total amount of plastics



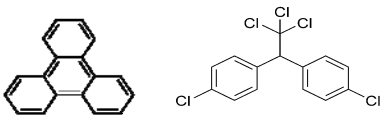
Fibers, Pellets, Fragments and Films recovered from the BBE Estuary sediments

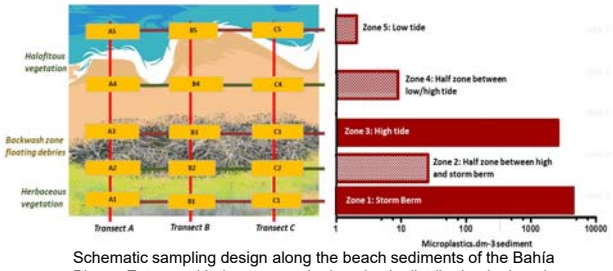
PAHs

DDXs

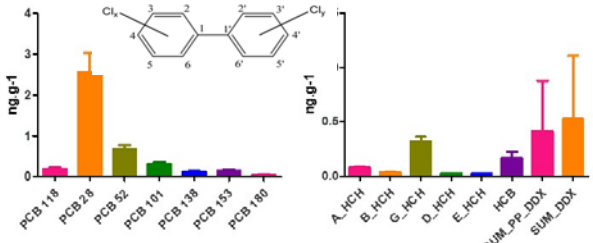
PCBs

Analyses of pollutants
They were performed at RECETOX laboratory (Czech Republic). The samples were enriched with recovery standards of isotopically labeled PAHs (D8-Naphtalene, D10-Phenanthrene, D12-Perylene: 333 ng/sample, Supelco, PA, USA) and PCBs+OCPs ($_{13}C^{12}$PCB19, $_{13}C^{12}$PCB104, $_{13}C^{12}$PCB178, $_{13}C^{12}$p,p'-DDE, $_{13}C^{12}$p,p'-DDD, $_{13}C^{12}$p,p'-DDT, $_{13}C^{6}$ β-HCH, $_{13}C^{6}$γ-HCH, $_{13}C^{6}$HCB: 10 ng/sample, Cambridge Isotope Laboratories, MA, USA) solvent extracted with hexane in ultrasonic bath (3x 15 mL of hexane), preconcentrated under N_2 stream to 10 mL and split into three fractions by weighing (10 % for PAHs analysis, 45 % for PCBs+OCPs analysis, 45 % archived). 10% fraction for PAHs analysis was cleaned by column clean-up with activated silica gel and sodium sulfate. PAHs were analyzed on 7890 GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 µm Rxi-5Sil-MS column (Restek, FR) coupled to a 7000B MS (Agilent, USA).
PCBs and OCPs were quantified with an external calibration of eight points with concentrations from 1 ng/ml to 1000 ng/ml, linearity was maintained in the whole range (LGC)





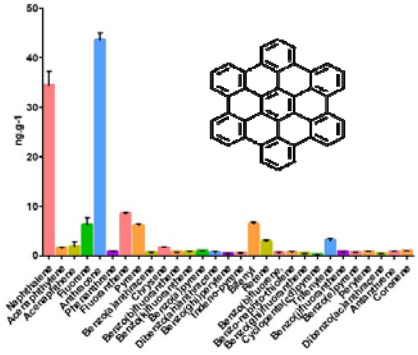
Schematic sampling design along the beach sediments of the Bahía Blanca Estuary with the averaged microplastic distribution by beach zone. Orange squares represent the sampling point distribution along the three sampled beaches.



POPs concentrations (organochlorine pesticides and PCBs, ng.g-1 pellet) in Bahía Blanca Estuary, Argentina (Galvan port).

All 7 indicator PCBs studied were found in the collected plastic pellets in concentrations above the detection limit (in triplicate analyses). The overall media for the sum of congeners was 4.03±0.89 ng/g pellet (∑7PCBs). The three main congeners in terms of abundance were CB28, CB52 and CB101; from these only CB28 exhibit dioxin-like activity (van den Berg et al., 2006). Although PCBs production and use has been banned in Argentina since 2002 (Law 25670); they might still be in use in several closed systems (capacitors, transformers, electronic equipment, etc.) and they continue to circulate as long-range transport processes (Stockholm Convention).

The pellet´s resin, the α-HCH/γ-HCH ratio was 0.25 which assuming equal partitioning coefficients for these compounds, pointed to aged technical mixture signatures and/or lindane usage. Lindane sorbed to resin pellets could be associated with the runoff or sewage effluents containing the insecticide, which is has been a common vector control product on agricultural lands, forest products, timber applications and is still allowed in shampoos for treating head lice.



PAHs concentrations (ng.g^{-1} plastic pellet) in Bahía Blanca Estuary, Argentina (Galvan port)

From the 29 PAHs studied, the overall mean in the composite pellet samples was 108.76 ± 12.88 ng/g pellet for the ∑16 PAHs and 122.79 ± 11.13 g/g pellet for ∑29 PAHs. The most abundandt congeneres were Phenanthrene, Naphtalene, Fluoranthene, Bifenyl, Fluorene, Pyrene and Tryphenylene. On the other side, Benzo(k)fluoranten, Benzo(b)fluoranten, Benzo(a)pyren, Indene-1,2,3,c-d-pyrene, Dibenzo(ah)antracene, Benzo(ghi)perylene were not detected in the samples.

Conclusions

- *MPs fragments accounted for the most abundant (74%) followed by films (13%) and pellets (11.3%)*
- *The pellets Microplastic Impact Coefficient defined this shape as probably the most problematic for the area*
- *MPs are playing a role in the movement of other organic pollutants, namely PAHs, PCBs and OCPs*
- *MPs serve as good proxy indicators of exposure to pollutants at coastal environments.*

Cited Ref: Rangel-Buitrago, N., Arroyo-Olarte, H., Trilleras, J., Arana, V. A., Mantilla-Barbosa, E., Gracia, A., ... & Micallef, A. (2021). Microplastics pollution on colombian Central Caribbean beaches. Marine Pollution Bulletin, 170, 112685.