

Decadal shifts of organic contaminants in oceanic plankton

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Abstract

The ocean is a major reservoir and sink for synthetic chemicals, yet their occurrence in open-ocean biota remains largely uncharted. Plankton forms the base of marine food webs and mediate the export of organic matter-bound contaminants to the deep sea. Here we screened plankton from two global campaigns, MALASPINA (2010–2011; Atlantic, Pacific and Indian Oceans) and ANTOM (2020–2022; Atlantic and Southern Oceans), against 678 organic contaminants using wide-scope target analysis. We detected 78 chemicals (surfactants, pharmaceuticals, UV-filters, biocides, tire additives, plasticizers, OPEs and PFASs) at concentrations from tens to thousands of ng g⁻¹ dry weight in some cases. Atlantic samples collected a decade apart reveal a marked turnover: PFASs, pharmaceuticals, and most aromatic amines decreased in occurrence, consistent with regulatory phase-outs, whereas tire- and plastic-associated chemicals became less frequent but more diverse, with legacy additives replaced by substitutes. Plankton acts as a sentinel of global pollution, showing a shift of novel entities entering food webs and a potential vector for their export to the deep ocean, where contaminants have high persistence.

Introduction

Modern societies produce and use hundreds of thousands of synthetic organic chemicals, which are found in industrial and consumer products, plastics and pharmaceuticals, and are applied extensively across industry and agriculture. A comprehensive assessment of the hazards and risks of all, or a large fraction, of these synthetic chemicals is impossible, as the number is too vast to be covered by laboratory and field assessments. Pollution by synthetic chemicals is considered one of the planetary boundaries and is currently within the broader category of novel entities. This boundary has been surpassed due to their ubiquity, large numbers, and impacts^{1,2}. Because of the overwhelming difficulties in assessing the impact of novel entities, it is important to identify approaches to determine the occurrence and effects of chemical pollution at large scales. In this sense, the widespread presence of a chemical in the open ocean is itself a diagnostic: it signals sufficient persistence and potential for long-range transport to reach regions remote from any source^{3,4}.

The global ocean is a major sink for a wide range of anthropogenic contaminants, including both emerging chemicals and legacy persistent organic pollutants (POPs)^{3,5–7}. Even remote marine regions such as the subtropical gyres or polar oceans, far from relevant direct emission sources, are affected by chemical pollution. Ocean currents and especially long-range atmospheric transport and deposition explain the widespread occurrence of a wide range of contaminants in surface waters and marine biota. To date, most attention has been paid to legacy POPs such as polychlorinated biphenyls, organochlorine pesticides (OCPs)⁸, and dioxins, as well as plasticizers such as phthalates and organophosphate esters (OPEs)^{9,10}, and legacy and current use poly- and perfluoroalkyl substances (PFAS)^{11–13}, among others.

Most previous assessments have relied on highly specific target analysis, sometimes with low-resolution triple quadrupole instruments, which quantify contaminants accurately but only for a small, pre-selected

set of compounds. Wide screening strategies based on high-resolution mass spectrometry (HRMS) overcome this limitation by acquiring full-spectrum data that can be interrogated for thousands of chemicals simultaneously. Among these, wide-scope target screening offers the broadest coverage without sacrificing identification confidence: detections are confirmed against large databases of reference standards previously analyzed on the same instrument, using experimental retention times and fragmentation spectra, whereas suspect and non-target screening extend the search to compounds lacking reference standards, at lower levels of identification certainty. When coupled with cheminformatics workflows, these approaches provide a far more comprehensive view of chemical pollution than conventional specific target-based methods. Their application to the open ocean, however, remains scarce: HRMS screening has been used mainly in terrestrial and coastal matrices and, when applied offshore, is often restricted to a single chemical family such as PFAS¹⁴. Non-targeted HRMS has recently been applied at ocean-basin scale to the dissolved phase⁷, but not to open-ocean biota, where the contaminant burden that enters food webs and settling particles is defined.

Phytoplankton and zooplankton form the base of the marine food web and are excellent sentinels of oceanic pollution. Indeed, plankton drives the biological pump of organic matter and associated contaminants, which has been identified as the key mechanism controlling the sequestration of organic pollution from the surface ocean and subsequent vertical transport in the water column, linking the surface ocean with the deep ocean^{4,6,15–17}. The efficiency of this pump is not spatially uniform, being substantially weaker in oligotrophic gyres than in productive or coastal waters, a heterogeneity that can modulate regional differences in contaminant export. So far, PCBs, OCPs, dioxins, polycyclic aromatic hydrocarbons, OPEs, and PFAS have been reported in oceanic plankton^{11,18–20}. Therefore, finding a given contaminant in phyto- and zooplankton implies that these enter food webs, and due to their role in generating settling particles, it also indicates that pollution is transferred to the deep ocean. The accumulation of hydrophobic organic contaminants, such as PCBs and PAHs, in plankton has been well documented, but amphiphilic and polar contaminants, which have lower hydrophobicity than legacy POPs, have also been found to be ubiquitous in plankton^{11,12,19}. The bioaccumulation factors of PFASs and OPEs in plankton are between one and two orders of magnitude larger than their octanol-water partition coefficient²¹, meaning that the accumulation of polar and water-soluble chemicals can occur; however, this fraction of the chemical space has largely escaped previous screening. Owing to the high surface-to-volume ratio for phytoplankton and large respiration rates for zooplankton, planktonic organisms efficiently accumulate a wide spectrum of contaminants from seawater, thereby facilitating their transfer to higher trophic levels and acting as sensitive indicators of chemical exposure in the marine environment. Then, there is a need to extend the assessment of organic contaminants in plankton to other families of synthetic chemicals.

In this study, a wide-scope target LC-HRMS screening approach was employed to analyze plankton samples collected during two global oceanographic campaigns: MALASPINA (2010–2011) and ANTOM (2020–2022), spanning the Atlantic, Pacific, Indian and Southern Oceans. The Atlantic Ocean was sampled in both campaigns, a decade apart, allowing the exploration of temporal changes. Our

objectives were to (i) identify and quantify organic contaminants in plankton across these four ocean basins, ii) characterize their global distribution and the classes of emerging contaminants present and (iii) evaluate decadal changes (2010 versus 2020) of organic contaminants in the Atlantic Ocean, and get insights into changes in contaminant occurrence and potential impacts of regulatory measures.

Results and Discussion

Chemical space of detected contaminants

A total of 77 plankton samples were collected across two oceanographic campaigns: the MALASPINA circumnavigation expedition (42 samples; December 2010-July 2011), covering tropical and temperate regions of the Atlantic, Indian, and Pacific Oceans, and the ANTOM cruises (35 samples; December 2020-February 2022), spanning a latitudinal transect from the North Atlantic to the Southern Ocean. Details about the samples are provided in the Supplementary Tables (**Tables S1-S2**). All samples were analyzed by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS) and subjected to wide-scope target screening against an in-house target database of 678 organic compounds (**Table S3**), all with experimental retention times and MS/MS fragmentation spectra previously acquired from reference standards on the same instrumental setup. This screening detected 78 chemicals across all samples. Detailed information on their concentrations, detection frequencies (DF%), and spatial patterns is provided in **Tables S4 and S5**. Based on their primary uses, compounds were grouped into biocides and agrochemicals, pharmaceuticals and stimulants, tire additives, natural products, personal care products (PCPs, including UV filters and surfactants), and industrial chemicals such as plasticizers, OPEs, PFASs, and other multifunctional substances.

Of these 78 chemicals, 52 were detected in the MALASPINA samples (23 quantified with analytical reference standards and 29 semi-quantified; Fig. 1a) and 47 in the ANTOM samples (20 quantified and 27 semi-quantified; Fig. 1a). Twenty-one were common to both campaigns, while 31 were exclusive to MALASPINA and 26 to ANTOM (Fig. 1b). Overall, 40 of the 78 detected compounds were quantified with reference standards and the remaining ones were semi-quantified. Importantly, this distinction refers exclusively to the quantification approach, not to identification confidence: detections were unambiguously confirmed by the experimental retention times and MS/MS spectra of the corresponding reference standards (see Methods).

The database mainly comprises polar and semi-polar compounds ($\log K_{ow} < 4$), with smaller contributions from highly hydrophilic ($\log K_{ow} < 0$) and highly hydrophobic ($\log K_{ow} > 4$) compounds. While bioaccumulation is governed by multiple physicochemical and biological factors, the octanol-water partition constant ($\log K_{ow}$) provides a first-order indicator of hydrophobicity-driven partitioning to plankton²¹⁻²³. Because the screening relied on liquid chromatography, the database excluded by design legacy POPs such as PCBs and dioxins, as well as hydrocarbons: although highly hydrophobic and readily bioaccumulated in plankton, these compounds require gas chromatography and thus fall outside the analytical window of this study. Within this window, most of the detected compounds (65%) were

moderately hydrophobic ($0 < \log K_{ow} \leq 4$), with molecular weights between 100 and 500 Da. An additional 33% were more hydrophobic ($\log K_{ow} > 4$), while 2% were hydrophilic ($\log K_{ow} < 0$) (Fig. 2a-c). This distribution therefore delineates the chemical space accessible to our LC–HRMS approach (contaminants both amenable to the method and persistent enough to reach the open ocean) rather than the full contaminant burden of plankton. Most detected compounds have low air-water partition coefficients ($\log K_{aw}$, Fig. 2b), consistent with their delivery to the open ocean and the most remote regions through long-range atmospheric transport and subsequent deposition. Sampling closer to the coast would likely have revealed additional chemicals; their absence offshore suggests either insufficient persistence in the marine environment or concentrations below the method's LOQ. Therefore, the fact that the detected compounds had higher hydrophobicity and volatility than the database is consistent with the transport and accumulation processes involved.

Distribution of compounds across ocean basins

Figure 3 and Fig. 4 show the compounds detected in the 2010–2011 MALASPINA and 2020–2022 AN TOM samples expressed as concentrations in ng g^{-1} dry weight (dw). LOQs were derived from procedural and field blanks ($\sim 30\%$ of the sample set) or from minimum detectable areas (see Methods section); only concentrations exceeding this threshold are reported. A complete list of quantified compounds and concentrations registered in samples is reported in **Tables S4 and S5**.

In the MALASPINA campaign, surfactants were among the most frequently detected and most abundant compounds, with concentrations from tens to thousands ng g^{-1} : dioctylsulfosuccinate (DF = 93%; 18.1–1030.4 ng g^{-1} dw), N,N-dimethyltetradecylamine (81%; 53.0–2660.9 ng g^{-1} dw), and benzyldimethylhexadecylammonium (57%; 55.7–3373.8 ng g^{-1} dw). To our knowledge, this is the first report of a quaternary ammonium compound, benzyldimethylhexadecylammonium, in open ocean plankton²⁴; together with the anionic and tertiary-amine surfactants detected here, its widespread occurrence indicates persistence and potential for long-range transport.

Preservatives were also widely registered, with benzoic acid (48%; 267.0–3852.5 ng g^{-1} dw) and methyl paraben (38%; 7.9–36.1 ng g^{-1} dw). Industrial aromatic amines were widespread: 1- and 2-naphthylamine occurred in 86% and 17% of samples, at concentrations up to 33.3 and 31.4 ng g^{-1} dw, respectively. The latter, historically used in dye production and rubber manufacturing and recognized as a human carcinogen, has been largely phased out since the mid-20th century. However, it was still reported as a by-product in some industrial processes in the 2000s²⁵ and is also present in tobacco smoke.

Pharmaceuticals and stimulants were detected at frequencies ranging from 2% to 19%, generally at low concentrations. Epinephrine (19%; 0.05–0.4 ng g^{-1} dw), used in emergency medicine, was registered in the North Atlantic and at single stations in the Indian and Pacific Oceans. 4-Formyl antipyrine (10%; 0.01–0.06 ng g^{-1} dw) occurred in the equatorial and South Atlantic and at one station in the Indian

Ocean. Pilocarpine (10%; 10.2-127.3 ng g⁻¹ dw) was detected in a few hotspots, reaching its highest concentration in the Pacific Ocean.

UV filters such as avobenzone (31%; 20.7–77.1 ng g⁻¹ dw) and octocrylene (50%), persistent and lipophilic compounds frequently reported in coastal and remote areas, were found in all three basins, with octocrylene most frequent in the Atlantic and Indian Oceans and avobenzone in the Indian and Pacific Oceans. Octocrylene was quantified in the Atlantic Ocean at concentrations ranging from 17.2 to 1058.3 ng g⁻¹ dw and in the Indian Ocean at concentrations between 13.6 and 111.8 ng g⁻¹ dw. The bioaccumulation of this UV filter has been previously documented in remote regions^{26,27}, marine organisms, and even in marine mammals²⁸, with tissue concentrations typically ranging from tens to several hundreds of ng g⁻¹ dw^{29,30}.

OPEs, used as flame retardants and plasticizers, occurred at higher frequencies in the Atlantic and the Indian Ocean, with tri-*o*-tolyl phosphate (ToCP, 55%; 10.4-5553.7 ng g⁻¹ dw) and triphenyl phosphate (TPHP, 17%; 63.1-1763.4 ng g⁻¹ dw); TPHP reached its highest concentrations in three stations of the South Atlantic Ocean (M8–M10, 424.9-1763.4 ng g⁻¹ dw) and lower values in four stations of the Indian Ocean (M11, M13, M14, M16; 63.1-268.1 ng g⁻¹ dw). These compounds are semi-volatile and can undergo long-range atmospheric transport, consistent with the reported ubiquity of OPEs in the global ocean^{10,31}.

PFASs, including PFHpA, PFHxS, PFHpS, PFNA, PFOS, 10:2-fluorotelomer sulfonic acid, and 8:3-fluorotelomer carboxylic acid, were detected in 7–40% of samples at concentrations between 0.3 and 171.2 ng g⁻¹ dw. PFOS was quantified with reference standards at concentrations ranging from 5.1 to 21.1 ng g⁻¹ dw, consistent with values previously reported for open-ocean plankton during the MALASPINA campaign using targeted analysis¹¹; PFOS bioaccumulation has also been documented in coastal marine biota¹². For PFHpA, PFHxS and PFNA the highest concentrations occurred in the Indian Ocean, in the eastern basin (stations M17 and M18), south of Australia (station M21) and near southern Africa (station M12), as well as in the South Atlantic (stations M5, M6 and M9); the highest single PFAS concentration of the dataset (8:3-fluorotelomer carboxylic acid, 171.2 ng g⁻¹ dw) was measured in the equatorial Pacific (station M28). Comparable offshore enrichments of PFASs in seawater and plankton offshore South America, South Africa, the North Atlantic, and Australia have been reported before^{11,13}, consistent with their known widespread distribution.

Biocides and agrochemicals, including DEET (M8-M10, M22), dinoterb (M22), and propachlor OXA (M41), were detected and quantified in a few stations of the Atlantic Ocean and close to Australian coasts, at concentrations between 0.7 and 31.2 ng g⁻¹ dw.

In the AN TOM samples (Fig. 4), the most frequently detected compounds were industrial chemicals such as methyl paraben (91%; 3.5-573.7 ng g⁻¹ dw), largely used as a preservative in cosmetics and pharmaceuticals, and tris(2-chloroisopropyl) phosphate (TCPP, 66%; 0.3–5.4 ng g⁻¹ dw), used as a

plasticizer and flame retardant. Quinoline (57%; 0.07–1.06 ng g⁻¹ dw) and 2-naphthylamine (51%; 11.5–364.2 ng g⁻¹ dw) were also widely distributed.

Tire additives were also prominent, including 2-benzothiazolesulfonic acid (63%; 3.2–94.8 ng g⁻¹ dw), 2-hydroxybenzothiazole (OHBT) (11%; 19.1–47.7 ng g⁻¹ dw), and diphenylguanidine (23%; 0.03–0.51 ng g⁻¹ dw), which were detected in both the Atlantic and the Southern Ocean. In contrast, 5-chlorobenzotriazole (CBT) (20%; 3.7–242.8 ng g⁻¹ dw) was found exclusively in the Southern Ocean.

Several PCPs including 1-dodecyl-2-pyrrolidone (51%; 0.003–0.04 ng g⁻¹ dw), dodecamethylpentasiloxane (6%; 0.007–0.01 ng g⁻¹ dw), and salicylic acid (37%; 14.0–333.6 ng g⁻¹ dw), plasticizers such as 4-nitrophenol (6%; 24.3–64.6 ng g⁻¹ dw), and dipropyleneglycol dibenzoate (20%; 0.7–26.4 ng g⁻¹ dw) were detected across the Atlantic and Southern Ocean.

Although fewer industrial chemicals were detected overall in ANTOM compared to MALASPINA, plasticizers such as phenols and phthalates, and OPEs were more numerous. As phthalates, OPEs, and phenols are common laboratory and shipboard contaminants, their occurrence was strictly controlled through the extensive blank program of this study (see Methods). Among plasticizers, the phthalate monoesters, which are primary metabolites of phthalate diesters, were detected: mono-isobutyl phthalate (MiBP, 17%; 4.2 to 85.3 ng g⁻¹ dw) and mono-2-ethylhexyl phthalate (MEHP, 9%; 173.4–479.9 ng g⁻¹ dw). 4-Nitrophenol was detected in nearly all ANTOM samples but exceeded the LOQ (20.8 ng g⁻¹ dw) in only two: station A7 in the North Atlantic (24.3 ng g⁻¹ dw) and, at a higher concentration, station A33 in the Southern Ocean (64.6 ng g⁻¹ dw). In MALASPINA, 4-nitrophenol occurred in 10% of samples (21.5–272.0 ng g⁻¹ dw). Other phenolic compounds, including 2,4,6-tribromophenol (TBP, 6%; 221.2–282.3 ng g⁻¹ dw) and 2,4-dibromophenol (2,4-DBP, 6%; 227.3–420.8 ng g⁻¹ dw), were quantified in two Southern Ocean samples (stations A25 and A26). The same compounds occurred in 33% of MALASPINA samples, at markedly higher concentrations (265.1–11460.4 and 67.8–4651.4 ng g⁻¹ dw, respectively). Although TBP is used industrially as a flame-retardant intermediate and biocide, it can also be biogenic. Bromophenols are known secondary metabolites of marine algae, sponges and polychaetes, including species reported in Antarctic ecosystems³². Given the localized occurrence of these compounds, the presence of TBP and 2,4-DBP in the samples may be associated with natural biogenic sources.

Several OPEs were detected across the two campaigns, with distinct occurrence patterns. In ANTOM, OPEs concentrations spanned 0.03–21.1 ng g⁻¹ dw. OPEs have previously been reported in Mediterranean zooplankton at concentrations ranging from 0.4 to 4.6 µg g⁻¹ ¹⁹. Tris(2-butoxyethyl) phosphate (TBEP) was quantified at station A24 and in 45% of Southern Ocean ANTOM samples, with concentrations ranging from 0.06 to 8.6 ng g⁻¹ dw. TCP was quantified in 71% of Atlantic ANTOM samples (0.38–2.26 ng g⁻¹ dw) and 55% of Southern ANTOM samples (0.3–5.4 ng g⁻¹ dw). Triethyl phosphate (TEP) was quantified in 29% of Atlantic ANTOM samples and 27% of Southern ANTOM samples (8.4–21.1 ng g⁻¹ dw), with no latitudinal trend. Its comparatively high LOQ (8.3 ng g⁻¹ dw), derived from procedural blanks, reflects the ubiquity of TEP as a laboratory contaminant and constrains the detection frequency reported here. ToCP and TPHP were detected only in the Southern Ocean, at low

concentrations (0.03–0.95 and 0.8–0.98 ng g⁻¹ dw), as discussed below in the decadal comparison. During the ANTOM campaign, Σ OPEs seawater concentrations at DCM depths averaged 19.3 ng L⁻¹ in the Atlantic Ocean and 14.5 ng L⁻¹ in the Southern Ocean⁹. OPEs decreased toward southern latitudes and were negatively correlated with chlorophyll a, indicating enhanced removal under conditions of higher biological productivity. The dissolved OPEs pool was dominated by chlorinated compounds, with TCP as the most abundant OPE, followed by TPHP, whereas TBEP contributed more substantially in the Southern Ocean. The predominance of TCP and TBEP observed in ANTOM plankton samples supports the role of plankton as an integrative matrix reflecting OPEs distributions.

The large and diverse set of organic classes detected in plankton samples suggests that vertical transport by the biological pump may be relevant for many more chemicals than for those characterized so far, which are generally hydrophobic and semi-volatile compounds such as PCBs, PAHs, polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides. However, polar and water-miscible contaminants such as PFASs and antibiotics have also been reported in the deep ocean, and here we suggest that export on settling particles (zooplankton fecal pellets, phytoplankton aggregates, cells, etc) may involve a larger fraction of the chemical space than previously assumed. This issue will require further research as the conditions found in the deep sea favor the long-term persistence of organic contaminants⁴.

Decadal changes in the occurrence of compounds

Decadal changes were evaluated within the same oceanic region, comparing the Atlantic stations of MALASPINA (M1-M9, M38-M42) with those of the ANTOM Atlantic transect (A1-A24), sampled a decade apart (2010–2011 versus 2020–2022) (Fig. 5a). The comparison reveals differences in both the number and type of detected compounds (Fig. 5b-m).

Several chemical classes declined over time. PFASs (Fig. 5d) were detected exclusively in the 2010 MALASPINA plankton samples, consistent with the progressive reduction of some PFASs emissions following regulatory measures, which contributed to the decreasing environmental concentrations and lower detectability in biota sampled in 2020–2022. Consistently, average Σ PFAS concentrations in Atlantic seawater decreased from 1200 pg L⁻¹ during MALASPINA¹¹ to 204 pg L⁻¹ during ANTOM¹³. Other industrial chemicals (Fig. 5c) also showed reduced occurrence in 2020–2022, particularly aromatic amines, with 2-naphthylamine and methyl paraben being exceptions. Pharmaceuticals (Fig. 5k) were almost absent in ANTOM but more widely present in MALASPINA samples, particularly outside the Caribbean Sea and at several stations in the North Atlantic. Conversely, the composition of plastic and rubber additives changed markedly between the two campaigns, with a larger number of tire additives but lower detection frequencies in the recent samples. Among tire additives (Fig. 5j), 2-benzothiazolesulfonic acid was detected in all MALASPINA samples but only in 14 of the ANTOM1 Atlantic samples, and at markedly lower concentrations (1.6–1136.1 versus 3.2–94.8 ng g⁻¹ dw). 2-Hydroxybenzothiazole occurred along the Atlantic Ocean in ANTOM as well as in the Southern Ocean,

and sporadically in the Indian Ocean in MALASPINA, but not in the Atlantic waters at that time. N,N'-diphenylguanidine was observed only in the Atlantic stations A3 and A11 and in the Southern Ocean. Its limited detection may partly reflect its chemical instability, as degradation during long-term storage cannot be excluded, rather than a reduction in emissions, given that its primary source (tyre use) has not substantially changed. Plasticizers in the Atlantic Ocean (Fig. 5f) declined in occurrence while becoming more diverse in AN TOM samples. Mono-2-ethylhexyl phthalate (MEHP) was widely detected in MALASPINA but absent in AN TOM Atlantic stations, where other phthalates were observed instead: mono-isobutyl phthalate was detected in the North Atlantic (A2, A6, A7), while monomethyl phthalate occurred at one equatorial and two subtropical South Atlantic stations (A9, A17 and A19). MEHP was detected only in Southern Ocean stations (A27, A33 and A34). The observed decline in MEHP detection frequency likely reflects the progressive reduction in the use of its precursor, bis(2-ethylhexyl) phthalate (DEHP), which has been regulated under REACH and the EU Water Framework Directive (European Commission, 2011³³, 2012³⁴) and so replaced by higher-molecular-weight phthalates. OPEs (Fig. 5e) were more diverse in AN TOM1 but not more frequent overall. TPHP occurred at markedly higher concentrations during the MALASPINA campaign, particularly in the South Atlantic (M8 and M9; 424.89–1324.40 ng g⁻¹ dw), whereas in AN TOM it was only detected in the Southern Ocean at low concentrations (0.77–0.98 ng g⁻¹ dw). ToCP was detected in 50% of MALASPINA Atlantic samples (10.42–796.65 ng g⁻¹ dw), while in AN TOM it occurred in only four samples of the Southern Ocean (A25, A31, A33–A34) and at much lower concentrations (0.03–0.95 ng g⁻¹ dw). The lower detection frequencies observed in 2020–2022 are consistent with a decrease in the occurrence of these two OPEs in open ocean plankton.

In general, the recent samples show a changed composition of these plastic and rubber additives, with legacy compounds (MEHP, ToCP, TPHP) largely replaced by a broader set of substitutes. This turnover is consistent with the continued growth in plastic production, which has a doubling time of about 15 years³⁵, combined with the regulatory phase-out of individual compounds, and suggests that the plankton contaminant profile tracks changes in chemical use rather than a simple accumulation of contaminants in the surface ocean.

Methods

Sampling

Plankton samples were collected during two oceanographic campaigns conducted in 2010–2011 and 2020–2022 following analogous sampling protocols. The historical series (42 samples) was obtained aboard the *R/V Hespérides* between December 2010 and July 2011 during the MALASPINA 2010 circumnavigation expedition covering tropical and temperate regions between 32.85°N and 40.5°S across eight consecutive transects: Cádiz (Spain) → Rio de Janeiro (Brazil) → Cape Town (South Africa) → Perth (Australia) → Sydney (Australia) → Auckland (New Zealand) → Honolulu (Hawaii, USA) → Cartagena de Indias (Colombia) → Cartagena (Spain). Details on station locations and ancillary

oceanographic data are provided in the Supplementary Tables (**Table S1**). The samples used here are duplicates of those used before for the analysis of PAHs, PCBs, dioxins, and PFAS^{11,20,23}. The recent series of plankton samples was collected during the ANTOM 1 (December 2020–January 2021) and ANTOM 2 (January–February 2022) cruises. During ANTOM 1, 24 stations were sampled along a latitudinal transect from Vigo (Spain) to Punta Arenas (Chile) in the Atlantic Ocean aboard the *R/V Sarmiento de Gamboa*. During ANTOM 2, an additional 11 stations were sampled in the Bransfield Strait and Bellingshausen Sea, west of the Antarctic Peninsula, aboard the *R/V Hespérides* (**Table S2**).

Across all campaigns, samples were obtained through vertical tows from 20 m below the deep chlorophyll maximum (DCM) depth to the surface, with sampling depths varying by station: 20–150 m during MALASPINA, 29–155 m during ANTOM 1, and 40–80 m during ANTOM 2. The plankton net had a mesh size of 50 or 100 µm, depending on the region. The plankton samples studied comprise both phyto- and zooplankton²³, except for the Southern Ocean samples that are dominated by phytoplankton, especially diatoms. Samples were filtered on board by using pre-combusted and pre-weighed GF/D filters (Whatman) and immediately stored at – 20°C wrapped in aluminium foil and in air-tight bags until further analysis.

Sample treatment

Once in the laboratory, samples were analyzed in a clean lab with positive pressure and prefiltered (activated carbon) air. Plankton samples from all campaigns were extracted following a standardized procedure. Briefly, the filters containing plankton were lyophilized for 8–12 h, depending on biomass, and then weighed to determine the dry weight of each sample. The biomass was determined by the difference between the weight of the filter before sampling and the weight after lyophilisation. The filters were transferred into glass centrifuge tubes and extracted using MeOH (LiChrosolv® LC/MS grade, Merck). For each extraction cycle, samples were sonicated with a sonication probe (2 minutes, 40% power) and subsequently centrifuged at 8000 rpm for 10 minutes. The resulting supernatant was collected in clean glass tubes. This procedure was repeated three times per sample, yielding a total of 40 mL of MeOH extract, which was then evaporated to dryness using a Turbovap system. The dry residue was reconstituted with 3 mL of MeOH to rinse the tube, and the extract was cleaned up in a sodium sulphate column to remove any particulate material, filter debris, or non-dissolved residues. The extract was then transferred into LC vials, evaporated until dryness and reconstituted in 500 µL MeOH:HPLC grade water (1:1).

Instrumental analysis

MALASPINA and ANTOM samples were analyzed by liquid chromatography–high-resolution mass spectrometry (LC-HRMS) using a Q-Exactive Orbitrap system (Thermo Fisher Scientific) operated in both positive (ESI⁺) and negative (ESI[–]) electrospray ionization modes, at 3000 V and 2800 V, respectively. Full-scan MS data were acquired over an *m/z* range of 67–1000 Da at a resolving power of 70,000, with parallel data-independent acquisition (DIA) of MS² spectra.

Chromatographic separation was performed on a Cortecs C18 + reversed-phase column (2.1 × 100 mm, 2.7 µm; Waters) equipped with a matching guard column (2.1 × 5 mm, 2.7 µm). In ESI⁺ mode, the mobile phases consisted of water with 0.1% formic acid (aqueous) and methanol with 0.1% formic acid (organic). In ESI⁻ mode, the aqueous mobile phase was water containing 5 mM ammonium acetate, while the organic phase was methanol with 5 mM ammonium acetate. The flow rate was 0.3 mL/min, and the injection volume was 5 µL.

A pool quality-control sample (QC) was additionally injected under data-dependent acquisition (DDA) to obtain compound-specific MS² spectra for structural confirmation. In DDA mode, the five most intense precursor ions were isolated and fragmented at a normalized collision energy of 35 eV and a resolving power of 35,000.

Wide scope target screening, confirmation, and quantification

HRMS data acquired from both campaigns were screened using an in-house database containing 678 compounds (**Table S3**) as described elsewhere³⁶. Reference standards of all chemicals had been previously injected and analyzed on the same instrumental setup, so that compound-specific experimental retention times and MS/MS fragmentation spectra were available for every entry in the database. The database included organic contaminants from diverse chemical classes and sources, such as pharmaceuticals, personal care products (PCPs), biocides, plant protection products, and industrial chemicals, including plasticizers, tire additives, OPEs, and PFAS. Peak detection was performed with TraceFinder™ 5.2 SP1 (Thermo Fisher Scientific), and compounds were identified using strict criteria: mass accuracy within 5 ppm, retention-time deviation below 0.30 min, isotopic pattern matching, and MS2 fragment-spectra matching.

Two complementary approaches were used to determine the concentrations of the 78 detected compounds. For 40 of them, matrix-matched calibration curves were prepared with the corresponding analytical reference standards and analyzed on the same instrument under identical conditions as the samples, allowing their accurate quantification (**Table S8**). These comprised compounds included in the calibration set of approximately 100 reference standards, complemented with standards specifically purchased for additional compounds detected in the samples. The remaining detected compounds, for which no calibration curve could be established, were semi-quantified using an ionization efficiency-based prediction model. Concentrations were derived from peak areas and model-predicted responses (**Figure S1**), and corrected for the matrix effect estimated from retention time (**Figure S2**). More details on the semi-quantification protocol can be found in the Supplementary Information. All reported concentrations are expressed on a dry-weight (dw) basis of the analyzed plankton.

Blanks and quality control procedures

Quality control and quality assurance (QC/QA) procedures were implemented throughout sampling, extraction, and instrumental analysis. All samples were processed in an ultraclean laboratory, and all

glassware was cleaned with deionized water, MeOH, and acetone and subsequently heated at 450°C before use.

Approximately 30% of the processed samples consisted of field blanks, filters that underwent the same treatment as the real samples from the ship to the laboratory. Specifically, these were pre-combusted and pre-weighed GF/D filters that were passed through the onboard filtration system without any sample material, transported with the samples, and then extracted following the same procedure applied to environmental samples. Mean concentration of compounds detected in the blanks are reported in **Tables S6-S7**.

During instrumental analysis, solvent blanks were injected every 10 injections to monitor potential carryover and background signals. All samples were spiked with the surrogate standard clothianidin-d3 before extraction to verify extraction efficiency. Additionally, a mixture of 10 isotopically labeled internal standards (**Table S9**) was added before instrumental analysis to ensure accurate injection and signal stability in the HRMS system. Additional experiments were performed to evaluate recoveries and matrix effects. Specifically, one plankton filter was spiked with the mix of target compounds and internal standards and extracted following the same procedure as for the samples, while another non-spiked filter was extracted to assess background levels. Furthermore, post-extraction spiked samples (i.e., filters spiked after extraction but before instrumental analysis) were prepared to evaluate ionization suppression or enhancement.

The limits of detection (LOD) and quantification (LOQ) were estimated based on standard addition calibration curves and blank responses. When no analyte signal was observed in the field blanks, the LOQ was set at the lowest concentration level of the calibration curve, and the LOD was extrapolated accordingly. In case measurable blank responses were detected, LOD and LOQ were calculated from the variability of the blank response, with LOD defined as the mean blank signal plus three times its standard deviation, and LOQ as the mean blank signal plus ten times its standard deviation. For semi-quantification, the same approach was applied to determine the LOQ of compounds with a measurable response in the blanks. For those absent in the blanks, the LOQ was derived from the minimum peak area required for compound confirmation on the instrument, which differed between ionization modes. Minimum areas of 5×10^4 and 1×10^5 were set for negative and positive ion mode, respectively, in MALASPINA, and 6×10^4 and 7×10^4 in AN TOM. Detailed information on calibration curves, target compounds, recoveries, matrix effects, and limits of detection and quantification is provided in **Table S8**.

Declarations

Acknowledgements

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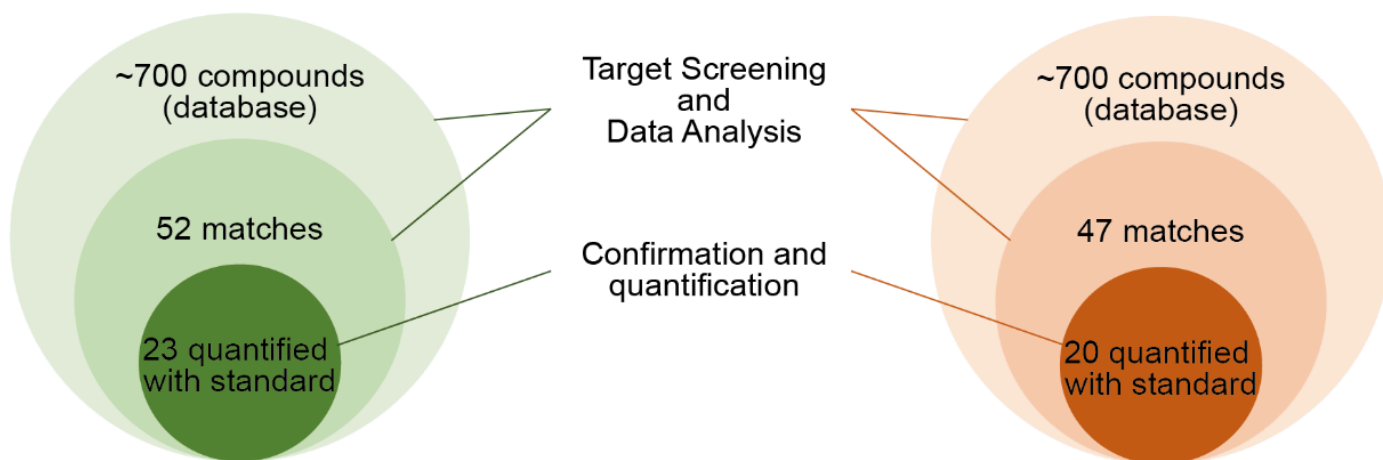
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Figures

MALASPINA CAMPAIGN

ANTOM CAMPAIGN

a



b

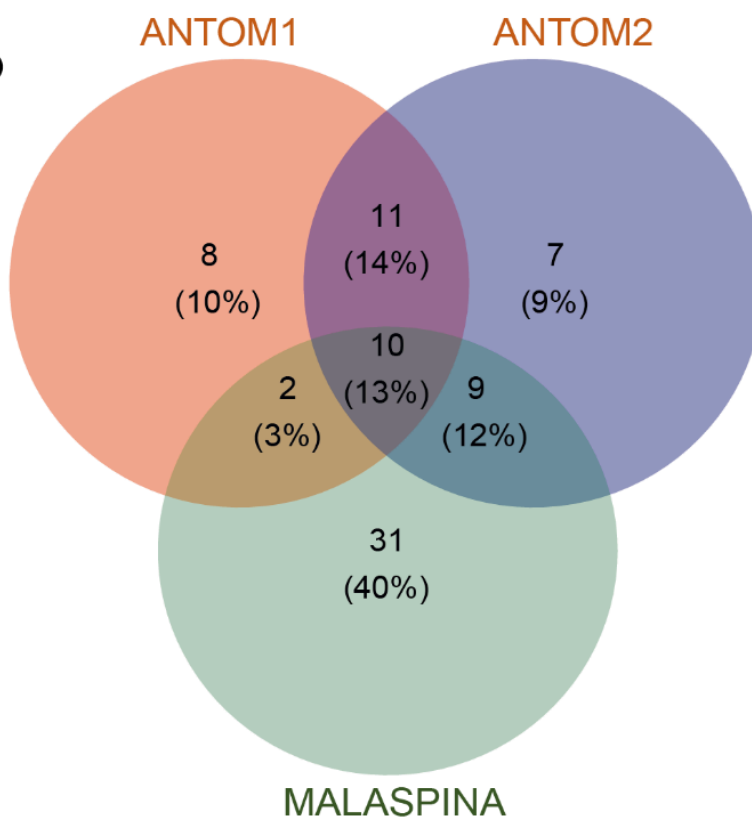


Figure 1

Screening workflow and overlap of the compounds detected in the MALASPINA and ANATOM campaigns.

a) Analytical workflow. Plankton extracts from both campaigns were screened by wide-scope target analysis against an in-house database of 678 reference standards; detections were confirmed by experimental retention time and MS/MS matching, and either quantified with matrix-matched calibration curves or semi-quantified with an ionization-efficiency prediction model. **b)** Venn diagram showing the overlap of detected compounds among MALASPINA, ANATOM 1 (Atlantic Ocean),

and ANTOM 2 (Southern Ocean) campaigns; numbers indicate the total compounds detected exclusively or shared between datasets, with percentages relative to the total number of detected compounds.

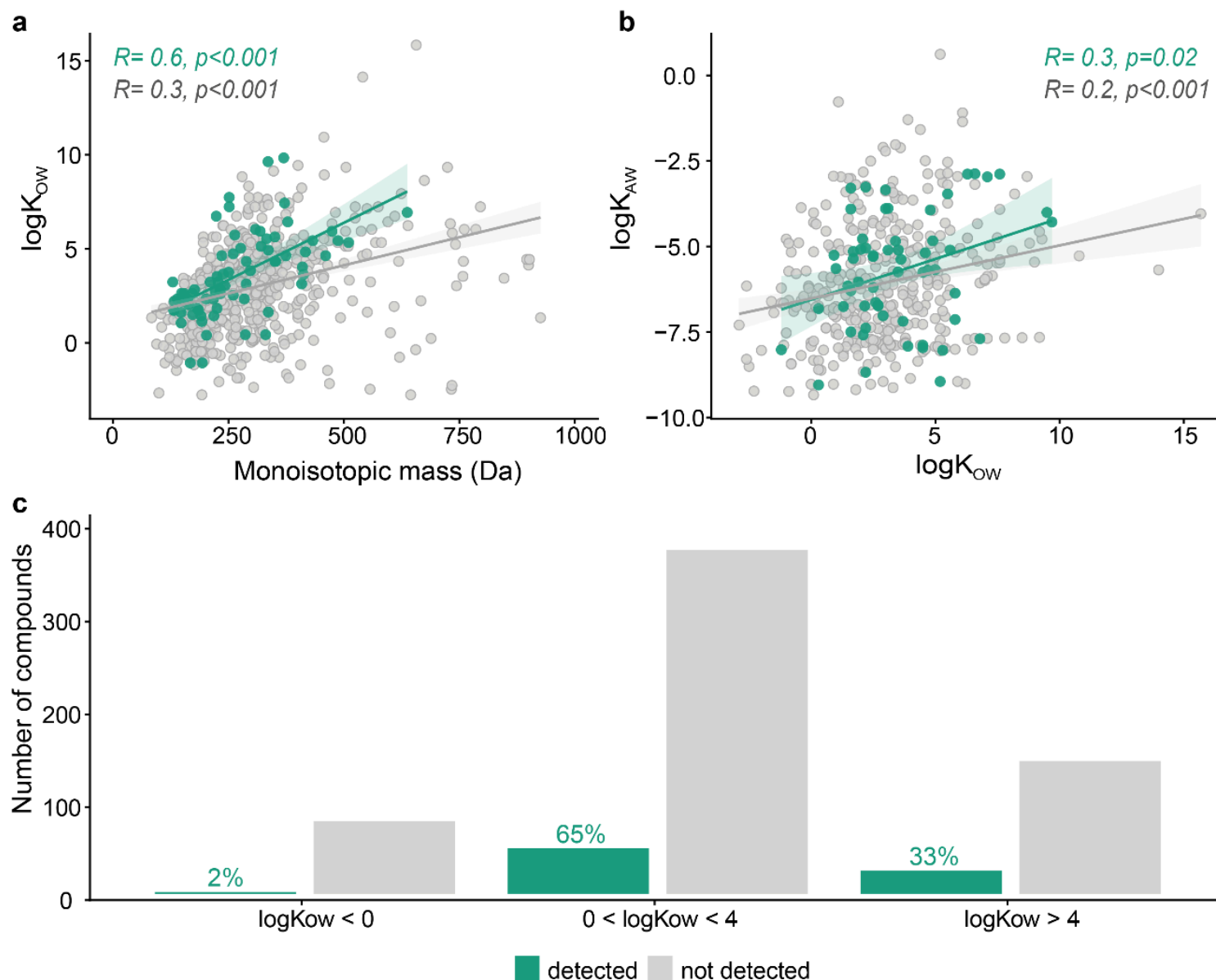


Figure 2

Overall distribution of physicochemical properties ($\log K_{ow}$ and $\log K_{aw}$) of the compound database and the detected compounds. **a)** $\log K_{ow}$ values as a function of monoisotopic mass for all compounds in the database. Compounds detected in the samples are highlighted in green, while non-detected compounds are shown in grey. Both groups show a significant positive Pearson correlation between $\log K_{ow}$ and monoisotopic mass (detected: $r = 0.67, p < 0.05$; non-detected: $r = 0.31, p < 0.05$). **b)** $\log K_{aw}$ values as a function of $\log K_{ow}$. Both groups (detected and non-detected compounds) show a positive Pearson correlation between $\log K_{aw}$ and $\log K_{ow}$ (detected: $r = 0.27, p = 0.055$; non-detected: $r = 0.21, p = 2.7e-05$). **c)** Compound distribution within $\log K_{ow}$ classes (from $\log K_{ow} < 0$: low hydrophobic to $\log K_{ow} > 4$: highly hydrophobic). Bars report absolute counts for the entire database (grey) and for the detected fraction

(green). Percentages displayed within the green bars indicate the proportion of all detected compounds falling in each hydrophobicity class.

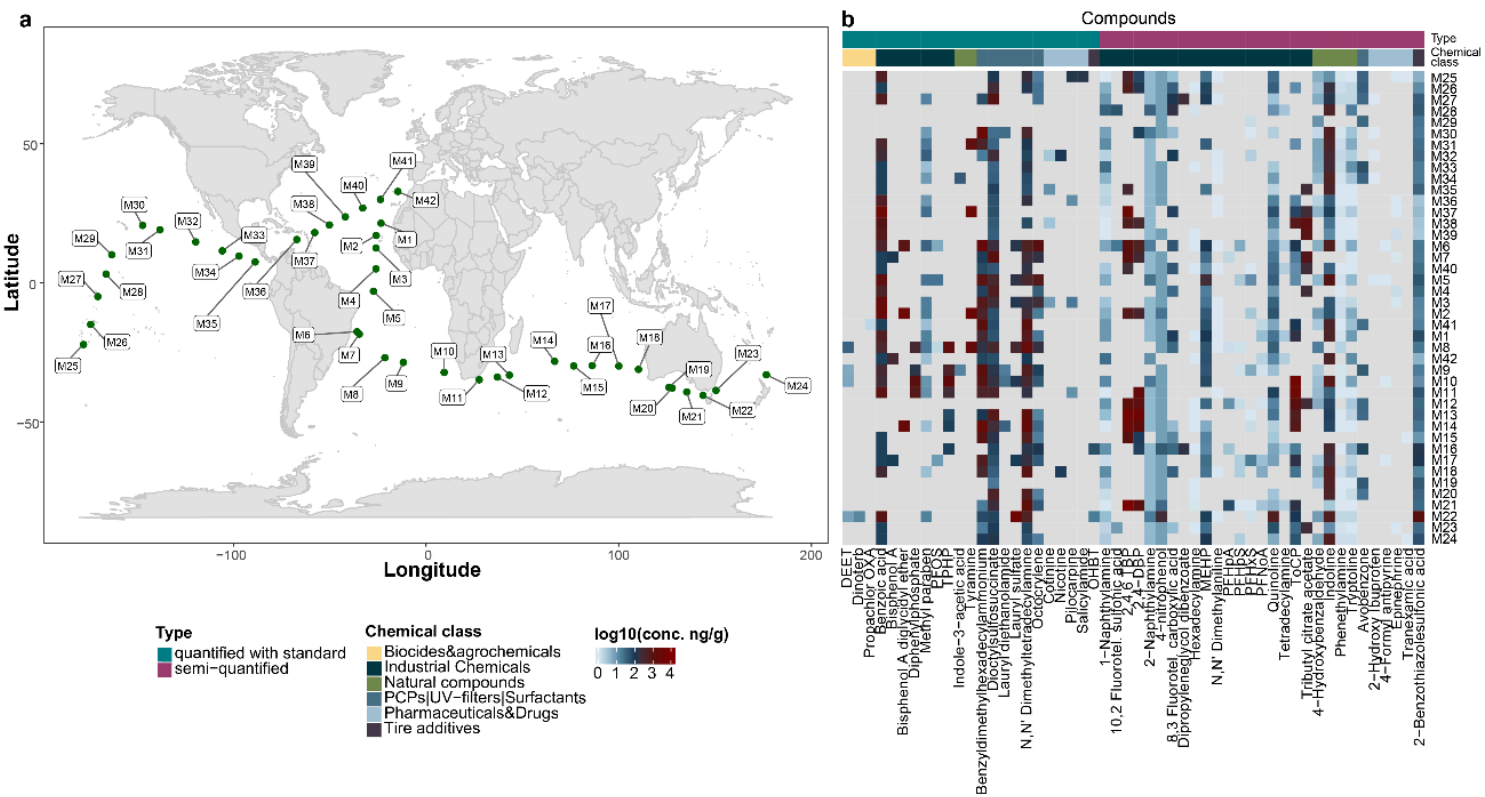


Figure 3

Spatial distribution of MALASPINA samples and associated chemical characterization. **a)** Geographic location of MALASPINA sampling stations. **b)** Heatmap of compound concentrations across samples, expressed as the logarithm of the concentration (ng g⁻¹); grey cells indicate compounds not detected in that sample. Compounds are ordered by quantification approach (quantified with standards vs. semi-quantified) and by chemical class (Industrial Chemicals; PCPs, UV-filters and Surfactants; Natural compounds; Biocides and agrochemicals; Tire additives; Pharmaceuticals and Drugs). Rows are ordered according to the longitudinal gradient of the sampling stations.

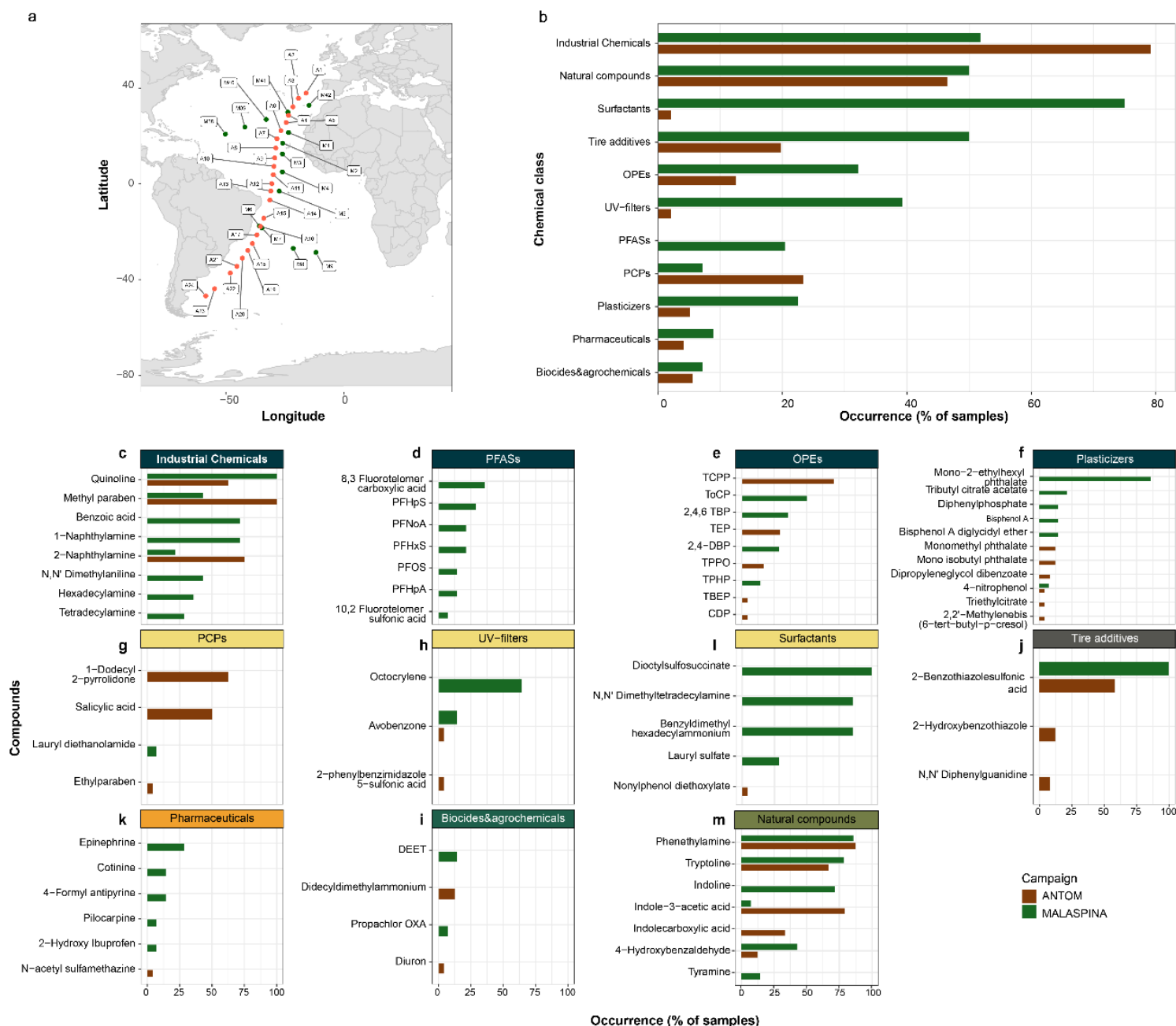


Figure 5

Occurrence of the different chemical classes in the ANTOM and MALASPINA samples collected in the Atlantic Ocean. **a)** Map of the sampling stations located in the Atlantic Ocean during the two campaigns. **b)** Bars represent the normalized occurrence of compounds within each chemical class detected at least twice in each campaign. Occurrence values were calculated as the total number of detections per class, normalized by the number of samples and the number of compounds in each class. Chemical classes are shown on the y-axis and ordered by decreasing mean normalized occurrence across campaigns. **c-m)** Distribution of compound occurrence across chemical classes in the ANTOM and MALASPINA samples collected in the Atlantic Ocean. Bar plots show the occurrence of individual compounds grouped into chemical subclasses and faceted accordingly. Subclasses are organized into five major chemical classes: **c-f)** Industrial Chemicals (industrial chemicals, PFASs, OPEs, plasticizers), **g-i)** PCPs,

UV-filters and Surfactants, **j**) Tire additives, **k**) Pharmaceuticals, **l**) Biocides and agrochemicals, **m**) Natural products.

Supplementary Files

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