Monitoring contaminants in Lac Bay water samples by applying passive samplers

A combination of target and non-target screening approach

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Contents

Summary

This study applied passive samplers made from polydimethylsiloxane (PDMS) to measure time-integrated concentrations of hydrophobic organic compounds in Lac Bay, a shallow, semi-enclosed bay on the eastern side of Bonaire in the Dutch Caribbean. Characterised by mangroves, seagrass, Halimeda algal beds, and corals, Lac Bay is a popular tourist destination and is vulnerable to anthropogenic stressors, including chemical exposure from human activities.

PDMS samplers offer several advantages: they are cost-effective, require minimal maintenance, and can detect trace levels of contaminants without the need for frequent water sampling. The study primarily targets environmental pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), Polybrominated Diphenyl Ethers (PBDEs), and Organochlorine Pesticides (OCPs) while also gathering baseline data through non-target screening (NTS). NTS enhances the detection of emerging contaminants.

Samplers were deployed at two strategic locations within Lac Bay—near the fishermen's pier and the public toilets at Sorobon and within a coral nursery area—to assess variations in contamination influenced by proximity to human activity. The samplers remained in situ from January to March 2023. Upon retrieval, they were extracted and analysed using Gas Chromatography-Mass Spectrometry (GC-MS) at Wageningen Marine Research in Ijmuiden.

Despite the 'pristine' perception tourists may have of the Lac Bay environment, our analysis detected a diverse array of chemical contaminants influenced by human activities. Non-target screening highlighted emerging concerns, particularly the residues of personal care products, including a UV filter, often overlooked in routine water quality assessments. These chemicals are likely introduced into the water primarily through swimming and grey water influence at Lac Bay. Additionally, higher levels of DEHP, a chemical associated with plastic pollution, were detected in the nursery area, suggesting potential regional contamination.

The targeted analysis identified four contaminants (8.7%) above quantification limits at the Sorobon site and only one in the nursery area. The expansive range of substances identified through non-target screening and the consistent detection of Benzo[a]anthracene confirm the proximity to a point pollution source. Although detected levels were below the Maximum Permissible Concentration (MPC) for seawater, they highlight potential risks by being at similar levels to those at Dutch marine locations and reinforce the need for ongoing monitoring.

Since passive sampling indicates the bioavailable fraction, applying thresholds designed for grab samples (as used in the current study) to assess risks identified through passive sampling might not yield a reliable risk assessment. Analysing these compounds in matrices with established thresholds (e.g., fish, shellfish, sediment) will provide more precise information.

Overall, the findings in this study suggest further investigation into the specific emission rates from pollution sources and their potential risks to aquatic life.

1 Introduction

Despite previous research highlighting the need for a more sustainable management strategy for emissions of anthropogenic chemical pollutants in Bonaire's marine environment—evidenced by the detection of metals in seagrass tissue (Govers et al., 2014; Ouwersloot, 2022) and organic contaminants in sediments (Dogruer et al., 2024) chemical residues in fish (Davidson et al., 2013), personal care products such as UV filters in the water column (Schaap & Slijkerman, 2018), and localised nutrient enrichment (Foekema et al., 2022; Hoekema, 2022; Slijkerman et al., 2014) —comprehensive data on pollutants in Bonaire remains scarce and fragmented.

Lac Bay is a shallow, semi-enclosed bay on the eastern side of Bonaire. It includes mangroves, seagrass, *Halimeda* algal beds, and corals. As a tourist hotspot, Lac Bay is susceptible to anthropogenic stressors and potential exposure to chemicals of anthropogenic activities. Previous research indicates Lac Bay is under eutrophication stress (Slijkerman et al., 2011). Furthermore, gradual changes in the ecosystem with crustose, calcareous algal blooms also point towards the enrichment of nutrients (Eckrich et al., 2011; Eckrich & Engel, 2013). Lac Bay is also affected by repeated sargassum influx (Van der Geest et al., 2024). In response to the concerns expressed by STINAPA, this study monitored organic contaminants within Lac Bay's water column using passive sampling technology.

1.1 Background on passive sampling technology

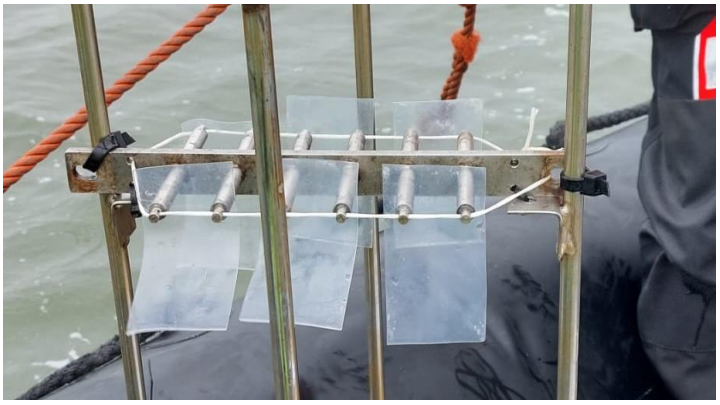

Figure 1.1 *Picture of a set of six polydimethylsiloxane (PDMS) samplers that were used within this present study*

Passive samplers are made of polymeric materials such as polydimethylsiloxane (PDMS) (see Figure 1) and many other materials depending on the physio-chemical properties of the chemicals of interest(Booij et al., 2016). Passive sampler deployment in seawater involves placing the samplers in the water to absorb contaminants over time. These samplers rely on passive diffusion, directly accumulating pollutants like hydrophobic organic compounds from the water column. They are typically anchored securely and left in situ for weeks or months to provide a time-integrated measurement of contaminant concentrations, reflecting average exposure levels (Booij et al., 2016; Burgess, 2012; Smedes & Booij, 2012; Vrana et al., 2005). During the exposure duration, which can range from a few weeks to months, the chemical concentration can be calculated to the volume of water that flows along the passive sampler by application of performance reference compounds (PRCs) (Posada-Ureta et al., 2016, 2017). In contrast, spot sampling entails collecting water samples at a given time and providing a snapshot of exposure without integrating concentration fluctuations over time. Due to the rapidly changing dynamics within the water column, a high sampling frequency for spot sampling is typically required.

Ultimately, these samplers mimic the partitioning behaviour of organic contaminants between water and living organisms. Passive samplers are valuable tools for assessing water quality by detecting the bioavailable fraction of the chemicals in the water column. Bioavailability refers to the portion of a chemical that, once taken up by an organism, is absorbed into its system and can interact with biological processes, potentially causing adverse effects. Measuring the bioavailable fraction of contaminants excludes fractions bound to organic carbon or particulate matter, providing a focused assessment of potential ecological risks. This approach serves as an effective first-tier method in regulatory monitoring, offering early insights into the presence of specific

chemicals in the water column. By identifying bioavailable contaminants, passive samplers facilitate targeted follow-up analyses and more detailed evaluations. However, the absence of established guidelines or regulatory values for passive samplers complicates risk assessments, making comparisons to literature data increasingly important (Allan et al., 2024).

Overall, passive samplers offer several advantages, including cost-effectiveness, minimal maintenance, and the ability to detect trace levels of contaminants without the need for frequent water sampling. Furthermore, these samplers accumulate a wide range of compounds, including hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and pesticides, as well as halogenated organophosphates, synthetic steroids, pharmaceuticals, food additives, and plasticisers.

1.2 The aim of this study

Due to the lack of benchmark data on contaminants for the study area, a **non-target (part 1) and target (part 2) screening** approach was employed in this report.

Part 1. In recent years, suspect and non-target screening (NTS) methodologies have gained prominence within the scientific community and regulatory bodies as complementary to traditional target analysis. Non-target methods allow for identifying a broader range of substances and prioritising those of emerging ecological and regulatory significance. For NTS, data from a Gas Chromatography-Mass Spectrometry (GC-MS) are screened against reference spectra housed within established libraries, such as the National Institute of Standards and Technology (NIST) mass spectral library. The presence and absence of chemicals and their relative abundances are then evaluated. For full confirmation, commercial standards are required. Decisions on the purchase or synthesis of these standards are guided by the relevance of identified compounds based on detection frequency, potential ecological or toxic effects, or peak intensity. Therefore, to further prioritise detected compounds, they are screened against a toxicity database (CompTox Chemicals Dashboard)(Williams et al., 2017). A key advantage of NTS is its capacity for retrospective data analysis and providing baseline data for future research (Alygizakis et al., 2018).

Part 2. Conventional targeted analytical approaches often focus on a limited subset of well-regulated compounds. Therefore, targeted analytical methods are usually optimised for a specific set of compounds with similar physicochemical properties. This study focuses on several groups of known environmental contaminants, including Polycyclic Aromatic Hydrocarbons (PAHs), Polybrominated Diphenyl Ethers (PBDEs), and Organochlorine pesticides (OCPs).

2 Material and Methods

2.1 Location of passive sampler deployment

Figure 2.1 *Lac Bay in Bonaire, including the locations of the passive samplers close to Sorobon and the nursery.*

The deployment locations for the passive samplers were carefully selected based on the limited data currently available for the bay (Figure 2.1). Aside from the deployment in seawater, a set of field blank or procedural blank samplers that underwent the same procedures and handling, except for actual deployment, provides the baseline for any potential background contamination or procedural contamination.

Passive sampler 1
A set of 6 passive sampler sheets (Figure 1.1) was deployed at 'Lac Bay_Sorobon' near the fishermen's pier and the public toilets at Sorobon. This area is anticipated to have higher levels of human impact due to its proximity to these facilities.

- Latitude: 12° 5'37.63"N
- Longitude: 68°14'17.56"W
- Deployment date: Jan 4th, 2023
- Retrieval date: March 22nd, 2023
- Exposure period: 78 days

Passive sampler 2
The second set of 6 passive samplers was deployed at 'Lac Bay_nursery', which was positioned in an area expected to be relatively unpolluted and distant to direct human activities. It is also the location of a coral nursery, with seagrass restoration plots situated slightly south of the sampler. These ecological restoration activities make this location particularly important for monitoring water quality and assessing potential contamination.

- Latitude: 12° 6'2.57"N
- Longitude: 68°13'51.16"W
- Deployment date: Jan 11th, 2023
- Retrieval date: March 22nd, 2023
- Exposure period: 70 days

2.2 Sampler preparation

Polydimethylsiloxane (PDMS) sheets were chosen for passive sampling because they effectively absorb hydrophobic compounds like polychlorinated biphenyls (PCBs). Before the samplers were deployed at their research sites in Bonaire (Figure 2.1), the PDMS sheets were spiked with a standard solution containing PCB 1, 2, 3, 10, 14, 21, 30, 50, 55, 78, 104, 145, and 204. This process ensured that each sheet was uniformly exposed to Performance Reference Compounds (PRC) concentrations. PRCs are non-native chemicals pre-loaded into passive samplers to improve the accuracy of contaminant measurements in aquatic environments by monitoring their desorption rates during deployment. These compounds, chosen for their similarity to target analytes, help account for environmental variability, such as temperature, water flow, and biofouling. PRCs are essential for calibrating the uptake rates of contaminants, enabling the estimation of freely dissolved concentrations of hydrophobic compounds. Following the spiking, the PDMS sheets were placed in a glass jar filled with deionised water (dH2O). To homogenise the concentration of PRCs across all passive samplers, the jar was set on a reciprocal shaker (Stuart SF1, Bibby Sterilin, Stone, UK) for six weeks to ensure a uniform distribution of the PRCs. The PDMS sheets were then carefully removed from the shaker, sealed in solvent-rinsed, chemically inert containers, and stored under controlled conditions until deployment (Figure 2.1).

2.3 Extraction of the passive samplers

After deployment, the surfaces of the passive samplers were cleaned from debris like algae using demi water and an abrasive sponge. The passive samplers were weighed and transferred to a solvent-rinsed glass extraction thimble. A Soxhlet set-up was prepared and solvent cleaned using toluene, acetone, and pentane. Three solvent-rinsed boiling chips and 600 mL of hexane/acetone (3:1) (v/v) mixture were added to a round bottom flask. The soxhlet extraction was performed for a minimum of 12 hours. After extraction, the extract was concentrated to approximately 10 ml using a Rotavapor (Hei-VAP advantage, Hei-VAP expert and Laboratora 4003 control, Heidolph Instruments, Lelystad, The Netherlands). The Rotavapor was set at 40°C and 400 mbar. The 10 ml extract was further concentrated under nitrogen to 5 ml and weighed.

For the non-target screening, 0.5 mL of the extract was transferred to a vial. For the analysis of the PAHs, PCBs, PRC-PCBs, OCPs and BDEs, another 0.5 ml of the extract was weighed and transferred to a test tube. 0.5 ml of each internal standard solution (deuterated PAHs (≈ 70-80 ng/ml), D8-Dicofol (≈ 3 µg/g), BDE 58

(≈ 84 µg/g), PCB 112/207 (≈ 40 ng/ml) were weighed and added to the test tube. The extract was concentrated using nitrogen to 0.5 ml and transferred into a vial.

Details on the chemical analysis are given in annex 1.

2.4 Data processing and evaluation

2.4.1 Data processing- non-target screening (semi-quantitative)

The absence, presence, and relative abundances of chemicals were screened by applying non-target analysis screening (NTS) in seawater samples from Lac Bay. It is important to note that a non-target methodology is a complementary analysis always followed up with a target confirmation of the recommended chemicals. We apply this methodology within this project to prioritise compounds for target analysis. However, a confirmation screening of these chemicals was beyond the scope of this study. Therefore, this approach serves as an exploratory screen for a wide range of chemicals of potential interest.

The data processing flow for a non-target analysis of environmental samples from Lac Bay Sorobon (LB1) and Lac Bay nursery (LB2) are displayed in steps in Figure 2.2. The output of a chemical analysis consists of peaks on a computer that denote certain compounds, and the time and size of the peak identify the compound and its relative concentration. After the NIST database screening of the peaks, each peak can be assigned to multiple compounds with a certain similarity. For each peak, the compound with the highest similarity was chosen in step 1 and step 2. Subsequently, only chemicals with a similarity index of 80 or higher were included in further analyses. Any substances detected in the blank samples (step 3) were excluded from the evaluation, and duplicates were removed.

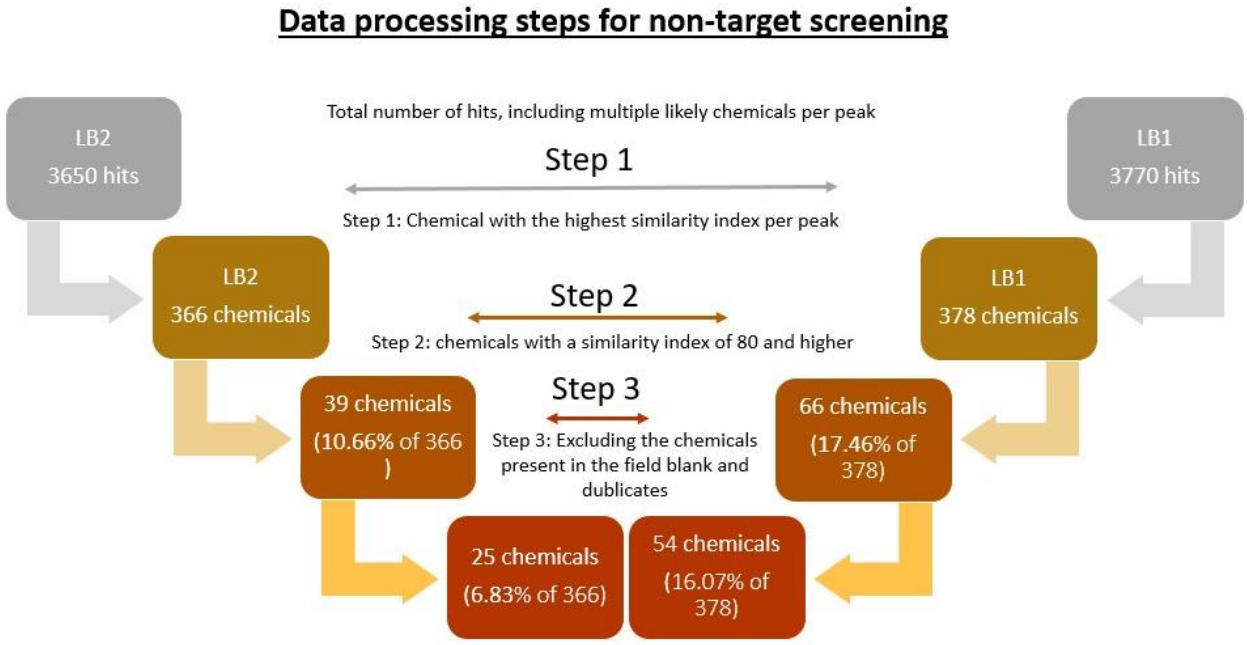

Figure 2.2 *The data processing flow for non-target analysis LB1= Lac Bay Sorobon and LB2= Lac Bay nursery. After the database screening, the number of hits contains multiple chemical options for the same peak with different similarity indexes. Therefore, in the first step, chemicals with the highest similarity index per peak were selected and then included only with a similarity index of 80 or higher. In the last steps, chemicals detected in the blank were excluded, and any duplicates were removed.*

2.4.2 Data prioritisation- non-target screening (semi-quantitative)

The remaining compounds were screened against the CompTox Chemicals Dashboard (https://comptox.epa.gov/dashboard) to cross-reference and validate their environmental relevance and potential health implications.

2.4.3 Calculations to model the water concentration for target analysis (quantitative analysis)

The target analysis follows a step-by-step calculation approach based on the guidelines previously provided by Deltares and other relevant sources. The established calculation sheet, which incorporates partition coefficients and other key parameters, was used for this analysis. The calculation sheet integrates partition coefficients to estimate freely dissolved concentrations of the compounds of interest. The sampler's geometry and volume are also factored into the calculations, as the size, shape, and surface area directly influence chemical uptake. Deployment time is considered, distinguishing between equilibrium and pre-equilibrium uptake conditions, while water flow velocity was incorporated to address its effect on the boundary layer around the sampler and the uptake rate (Smedes & Booij, 2012).

3 Results and discussion

3.1 Non-target screening– a prioritisation approach for a follow-up target screening (semi-quantitative)

A vast range of chemicals was detected, whereby the sampler closer to human activities (LB1, Lac Bay Sorobon) contained more chemicals from anthropogenic activities associated with petroleum, personal care products and other industrial substances of wide use variety (summarised in Annex 4).

Of these various chemicals identified, only octocrylene, cyclotetrasiloxane (D3), and DEHP (Bis(2-ethylhexyl) phthalate) have been extensively studied for their environmental and toxicological impacts, whereby 984 toxicological endpoints (as indicated with the word hits in Table 1), 86 for Cyclotetrasiloxane, octamethyl, 20 for Octocrylene and one endpoint for 2,5 Hexanedione were characterised. Thus, the toxic potency of many chemicals detected within the NTS is undefined. Therefore, risks associated with exposure to these chemicals cannot be defined.

Table 1 *Identified chemicals detected with non-target analysis in both samplers in Lac Bay samples with more than one hit in the database.*

Name	Common Application	Toxicity Database Hits[1]
Bis(2-ethylhexyl) phthalate (DEHP)	Plasticisers in PVC and food packaging material	984
Cyclotetrasiloxane, octamethyl-	Personal care product	86
Octocrylene	Personal care product- UV filter in sunscreens	20

1) CompTox Chemicals Dashboard (https://comptox.epa.gov/dashboard)

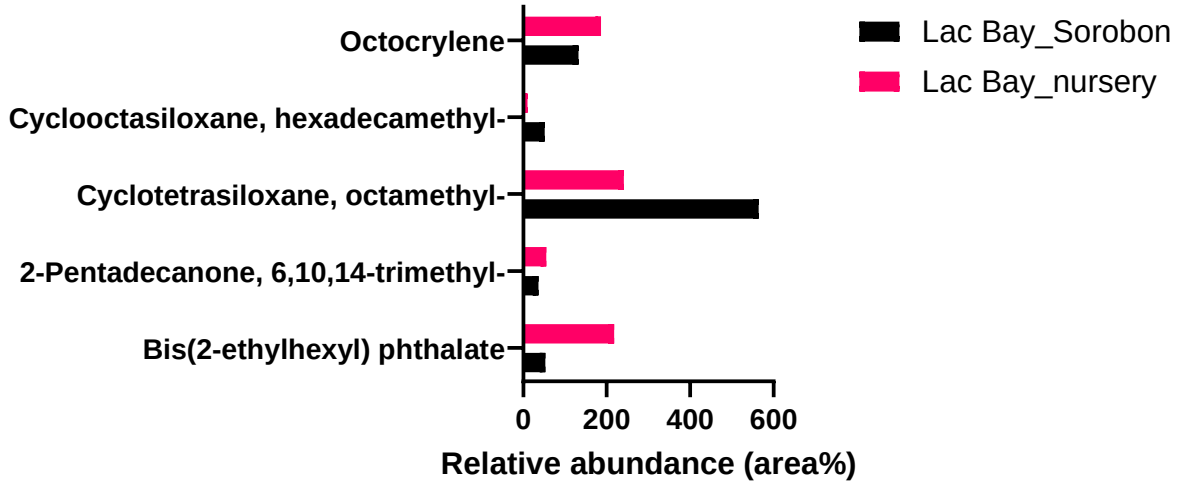

Figure 3.1 *Chemicals detected at both locations to compare the relative abundances.*

Figure 3.1 shows chemicals detected at both locations, where the relative abundance area (given in %) was compared. The relative abundance in NTS provides a semi-quantitative measure of a detected compound's presence, typically represented as peak area or intensity in mass spectrometry data. However, a key limitation of this approach is that relative abundance values do not directly correspond to absolute concentration values.

The relatively higher abundance of cyclotetrasiloxane, octamethyl- (D3) at the Sorobon location likely reflects the proximity to beach activities and/or surface or sewage run-off, confirming the expected difference between the two locations. Recognised in the European Union as a substance of very high concern for its persistent, bioaccumulative, and toxic characteristics, its inclusion in personal care products has been effectively banned there since 2018. However, this restriction does not apply elsewhere, for example, in the United States, where D4 continues to be used. A recent review, however, concludes that typical concentrations of D3 in the aquatic environment are usually below the no-effect concentrations proposed for freshwater and marine species; thus, this compound may not pose an acute threat to the aquatic environment at Lac Bay (Kumari et al., 2024). Nevertheless, the toxicity, thus the associated risk of exposure to aquatic organisms, of many personal care products detected at this location (Annexe 4) is unknown.

As one of the two most widely used plasticisers, DEHP is frequently detected in environmental samples due to its extensive applications in products like PVC plastics, building materials, and food packaging (He et al., 2020; Zhang et al., 2019b). DEHP's prevalence is of particular concern because of its known endocrine-disrupting effects, including estrogenic disruption in zebrafish embryos (Chen et al., 2014). The levels detected in this study indicate more regional contamination, with the Lac Bay nursery area showing relatively higher levels of DEHP. It enters ecosystems through wastewater effluents during production, leaching, and volatilisation from products during use and disposal.

Octacyrlene has previously been detected to be widely spread throughout the bay at concentrations exceeding the protective limits suggested in the literature (Schaap & Slijkerman, 2018). Despite this, a continuous monitoring program is still not in place. Thus, considering what is known about octocrylene, the findings from the non-target screening can be seen as reliable. In this study, levels were comparable at both locations. Although these results are preliminary and require validation through targeted analysis, efforts to address contamination from personal care products containing harmful UV filters are warranted. They could include raising visitor awareness and promoting environmentally safe alternatives. Monitoring the success of these initiatives through seawater testing would provide valuable insights.

3.2 Quantitative targeted analysis- modelled water concentrations using PDMS samplers

Several groups of known environmental contaminants, including Polycyclic Aromatic Hydrocarbons (PAHs, n=16), Polybrominated Diphenyl Ethers (PBDEs, n=14), and Organochlorine pesticides (OCPs, n=16), were analysed. The concentrations of these chemicals are given in Annex 3. Analysis revealed that only four chemicals (8.7% of all sampled chemicals) were detected above the detection limit in Sorobon (Figure 3.2). In contrast, only one chemical exceeded detection levels at the Lac Bay nursery (Figure 3.2). Elevated blank levels for some chemicals suggest that many compounds may have been excluded due to procedural errors and quality control measures. Thresholds for whole water concentrations were provided for comparison in the figure from the literature (Moermond & Verbruggen, 2011; Verbruggen, 2012; Verbruggen & Van Herwijnen, 2012). Since passive sampling indicates the bioavailable fraction, applying thresholds designed for grab samples to assess risks identified through passive sampling might not yield a reliable risk assessment. However, it provides a perspective on potential risks.

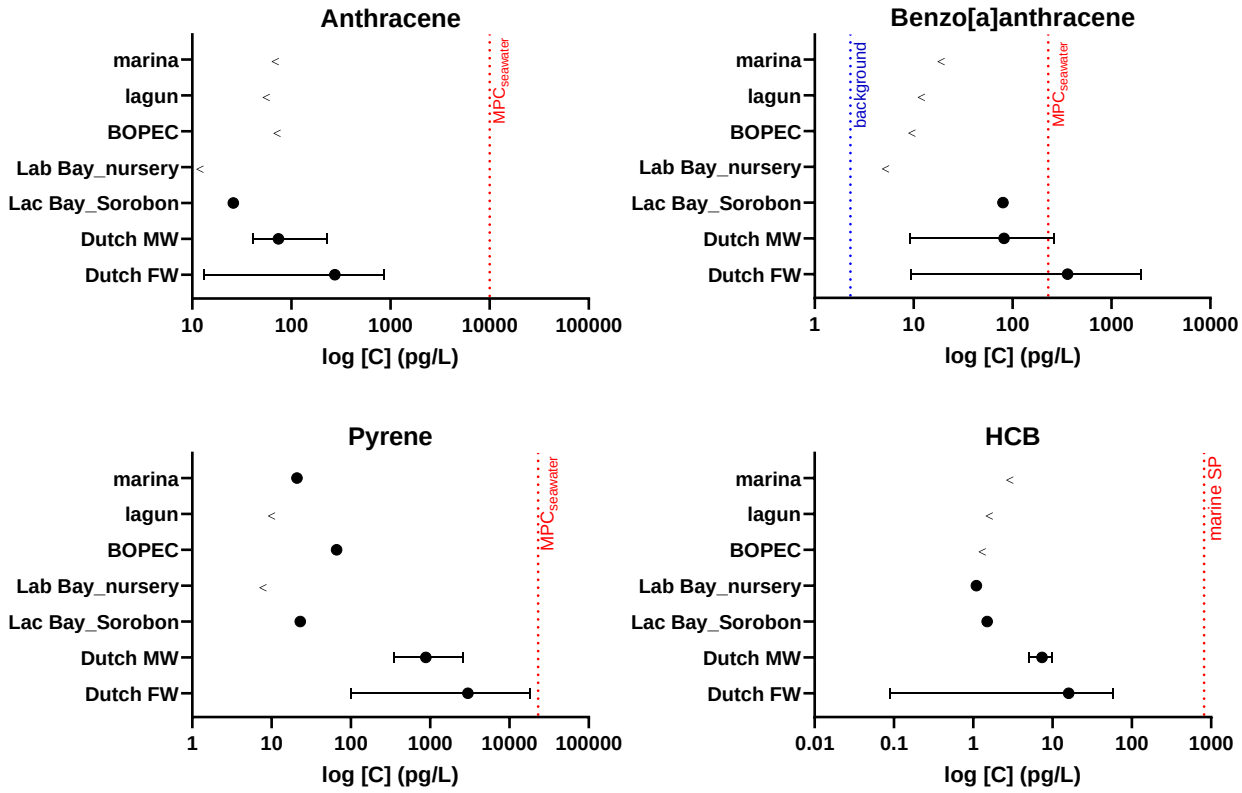

Figure 3.2 *Results of the targeted analysis from two locations in Lac Bay, sampled from January to March 2023 using passive samplers. The x-axis provides the calculated water concentration in the logarithmic scale [pg/L]. The range from minimum and maximum concentrations (the line) and the dot indicating the average concentration over the 6 locations in Dutch Marine Water (MW) and 9 locations from Fresh Water (FW) were provided for comparison. Results below the limit of quantification are indicated with the symbol <. Maximum Permissible Concentration (MPC) in water for PAHs and secondary poisoning (SP) limit HCB are indicated with vertical lines.*

Hexachlorobenzene (HCB), a persistent organic pollutant recognised under the Stockholm Convention, concentrations in Lac Bay were lower than those in more contaminated sites, measured at 1 pg/L in the nursery area and 1.5 pg/L in the Sorobon area. The secondary poisoning concentration in seawater is suggested to be 820 pg/L (Moermond & Verbruggen, 2011), indicating that the detected concentrations are approximately 100-fold below this threshold. Similarly, anthracene and pyrene concentrations detected in this study are below the proposed marine threshold in the literature (Verbruggen, 2012).

The no-effect level for seawater concentration for Benzo[a]anthracene is 2.3 pg/L, while the Maximum Permissible Concentration (MPC) in seawater is 230 pg/L (Verbruggen & Van Herwijnen, 2012). The dissolved concentration detected at Lac Bay Sorobon was 80 pg/L, over one-third of the MPC suggested by RIVM for seawater. Despite being above the negligible level, the detected concentrations for Benzo[a]anthracene remain below the MPC. Furthermore, the concentration of Benzo[a]anthracene in Lac Bay's Sorobon area was comparable to those observed in some Dutch marine waters. The highest concentrations for all studied compounds were consistently recorded in freshwater locations in the Netherlands, reflecting their proximity to anthropogenic sources. Marine waters generally exhibit more diluted contaminant concentrations than freshwater systems due to their larger volume and dynamic mixing processes.

The analysed chemicals in the water column have hydrophilic properties, facilitating their rapid adsorption onto sediments and uptake by biological organisms. Therefore, investigating these compounds within sediment or biological matrices may provide a more comprehensive and precise understanding of their risks to aquatic organisms.

4 Conclusions

Even in environments perceived by tourists as 'pristine', tourism can introduce invisible chemical pollutants. Our analysis of chemical contaminants in Lac Bay has unveiled the presence of a wide array of substances, the presence of many of those is influenced by the proximity to human activities. Non-target screening has highlighted significant emerging concerns, particularly the residues of personal care products, including a UV filter. Such compounds are often overlooked in routine water quality assessments. Our findings also indicate the co-occurrence of chemicals associated with plastic pollution in Lac Bay.

At the Sorobon site, the expansive range of substances identified through non-target screening and the consistent detection of Benz[a]anthracene suggest a continuous presence of these contaminants throughout the sampling period. These results point towards further investigation into the specific emissions rates from pollution and their potential risks to aquatic life. Implementing monitoring and management structures to assess acceptable emission rates and concentrations from local and regional pollution sources is crucial for enhancing ecosystem resilience.

5 Quality Assurance

Wageningen Marine Research utilises an ISO 9001:2015 certified quality management system. The organisation has been certified since 27 February 2001. DNV issued the certification.

The Chemical and Benthos laboratory has an EN-ISO/IEC 17025:2017 accreditation for test laboratories with number L097. The Dutch Accreditation Council has granted this accreditation. As a result, the Chemical and Benthos laboratory has demonstrated its ability to provide valid results in a technically competent manner and to work in accordance with the ISO17025 standard. The scope (L097) of de accredited analytical methods can be found at the website of the Council for Accreditation (www.rva.nl).

The quality of the test methods is ensured in various ways. The accuracy of the analysis is regularly assessed by participation in proficiency tests.
In addition, a first-level control is performed for each series of measurements. If the quality cannot be guaranteed, appropriate measures are taken.

Information regarding the performance characteristics of the analytical methods can be obtained upon request.

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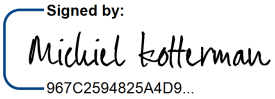
Justification

Report: C002/25
Project Number: 4316100313

The scientific quality of this report has been peer reviewed by a colleague scientist and a member of the Management Team of Wageningen Marine Research

Approved: Dr. Ir. M.J.J. Kotterman
Senior Researcher

Signature: 

Date: 10 January 2025

Approved: Dr. A.M. Mouissie
Business Manager Projects

Signature: 

Date: 10 January 2025

Annex 1 Materials and methods of the chemical analysis

Solvents and Standards

The solvents acetone and n-hexane were obtained from Boom (Meppel, The Netherlands), toluene from VWR (Amsterdam, The Netherlands) and pentane from Actu-all (Oss, the Netherlands)

Standard solutions for the PAH were obtained from Agilent Technologies (Abcoude, The Netherlands). The internal standard solutions for the deuterated PAH were obtained from LGC Standards (Wesel, Germany). Deuterated anthracene, a standard solution of dicofol and an internal standard solution of D8-dicofol were obtained from Merck (Amsterdam, The Netherlands).

Standard solutions of BDEs, PRC-PCBs, OCPs and the internal standard solution of the BDE58, PCB112/207 were used. Those standard solutions were obtained from Da Vinci Laboratory Solutions (Rotterdam, the Netherlands).

Instrumental analysis

Non-target screening

The analysis of the non-target screening was performed on a Shimadzu GC-2010Plus (Shimadzu, 's-Hertogenbosch, The Netherlands) coupled with a Shimadzu QP2010 Ultra MS and AOC-20i Auto Injector. A Negative Chemical Ionisation (NCI) source and an Electron Ionization (EI) source were used. Separation was performed on a CPsil8 (50 m x 0.25 mm, 0.25 µm) column (Agilent Technologies, Abcoude, The Netherlands). Hydrogen gas was a carrier gas with a constant pressure of 70.5 Kpa. Injected was 1 µl of sample in splittles mode with a sampling time of 1.5 minutes. The GC oven temperature was set to 50°C for 1 minute and then increased to 110°C at 30°C/min and then programmed to 320°C at 5°C/min. The injector temperature, interface and ion source were set to 270, 250 and 200°C, respectively. The MS data was acquired in full scan mode from m/z 30-550.

Analysis of PAHs

A Shimadzu NEXIS GC2030 (Shimadzu, 's-Hertogenbosch, The Netherlands) coupled with a Shimadzu GCMS-TQ8050NX and AOC-20i Auto Injector was used for the analysis of the PAHs. An Electron Ionization (EI) source was used. A ZB-PAH-CT (30 m x 0.25 mm, 0.20 µm) column (Phenomenex, Woerden, The Netherlands) was used to separate the compounds. Hydrogen gas was used as a carrier gas with a constant pressure of 17.7 Kpa.

To analyse naphthalene and acenaphthylene, 1 µl of the sample was injected in splittles mode with a sampling time of 1.5 minutes. The GC oven temperature was set to 90°C for 3 minutes and then increased to 130°C at 20°C/min, then programmed to 160°C at 5°C/min and then programmed to 320°C at 200°C/min with a hold time of 15 minutes. The injector temperature, interface and ion source were set to 250, 300 and 290°C, respectively.

For the analysis of the other PAHs, 5 µl of the sample was injected in splitt mode with a sampling program set at 40°C for 1 minute and then increased to 320°C at a rate of 200°C/min with a hold time of 33 minutes. The GC oven temperature was set to 45°C for 1 minute and then increased to 200°C at a rate of 45°C/min, then programmed to 266°C at 3°C/min and then programmed to 320°C (rate 10°C /min) with a hold time of 5 minutes. The interface and ion source were set to 300 and 290°C, respectively. In Table 3 the used masses and collision energies are presented for the PAHs.

Table 2 *Used masses (m/z) and collision energies (CE) for the analysis of the PAHs using GC-MS/MS.*

PAHs				
	target ion (quantification)	**CE target ion (v)**	**qualifier ion**	**CE qualifier ion (v)**
Internal standard				
D8-Naphtalene	136.00>134.00	10	136.00>108.00	20
D10-Acenaphtylene	160.10>159.10	10	161.10>160.10	10
D10- Acenaphtene	164.00>162.00	20	164.00>160.00	30
D10-Fluorene	176.00>174.00	20		
D10-Phenanthrene	188.00>160.00	20	187.00>159.00	30
D10-Anthracene	188.00>160.00	20	187.00>159.00	30
D10-Fluoranthene	212.00>210.00	20	212.00>208.00	30
D10-Pyrene	212.00>210.00	20	212.00>208.00	30
D12-Benzo(a)anthraceen	240.00>238.00	10	240.00>236.00	30
D12-Chrysene	240.00>238.00	10	240.00>236.00	30
D12-Benzo(b)fluoranthene	264.00>260.00	45	264.00>236.00	30
D12-Benzo(k)fluoranthene	264.00>260.00	45	264.00>236.00	30
D12-Benzo(a)pyrene	264.00>260.00	45	264.00>236.00	30
D14-Dibenzo(ah)anthracene	292.00>288.00	35		
D12-Indeno(1,2,3-cd)pyrene	288.00>286.00	20	288.00>284.00	45
D12-Benzo(ghi)perylene	288.00>286.00	20	288.00>284.00	45
Component				
Naphtalene	128.10>102.00	20	128.10>126.10	20
Acenaphtylene	152.10>151.10	10	153.10>152.10	10
Acenaphtene	152.10>151.10	10	153.10>152.10	10
Fluorene	166.10>165.10	10	165.00>163.00	20
Phenanthrene	178.10>176.10	20	178.10>152.10	30
Anthracene	178.10>176.10	20	178.10>152.10	30
Fluoranthene	202.10>200.10	20	202.10>198.10	30
Pyrene	202.10>200.10	20	202.10>198.10	30
Benzo(a)anthracene	228.10>226.00	30	228.10>202.10	30
Chrysene	228.10>226.00	30	228.10>202.10	30
Benzo(b)fluoranthene	252.10>250.10	30	252.10>226.10	30
Benzo(k)fluoranthene	252.10>250.10	30	252.10>226.10	30
Benzo(a)pyrene	252.10>250.10	30	252.10>226.10	30
Dibenzo(ah)anthracene	276.10>274.10	30	276.00>275.00	20
Indeno(1,2,3-cd)pyrene	278.00>277.00	20	278.10>276.10	25
Benzo(ghi)perylene	276.10>274.10	30	276.00>275.00	20

Analysis of dicofol

The analysis of dicofol was performed on a Shimadzu GC-2010Plus (Shimadzu, 's-Hertogenbosch, The Netherlands) coupled with a Shimadzu QP2010 Ultra MS and AOC-20i Auto Injector. A Negative Chemical Ionisation (NCI) source was used. Separation was performed on a CPsil8 (50 m x 0.25 mm, 0.25 µm) column (Agilent Technologies, Abcoude, The Netherlands). Hydrogen gas was used as a carrier gas with a constant pressure of 80 Kpa. 1 µl of sample was injected in splittles mode with a sampling time of 2.0 minutes. The GC oven temperature was set to 90°C for 1 minute and then increased to 180°C at 30°C/min, then programmed to 225°C at 5°C/min, then the temperature increased to 290°C at 30°C/min. The injector temperature, interface and ion source were set to 270, 150 and 150°C respectively. In Table 4 the used masses and collision energies are presented for dicofol.

Table 3 *Used masses (m/z) and collision energies (CE) for the analysis of the dicofol using GC-MS.*

Dicofol		
	target ion (quantification)	**qualifier ion**
Internal Standard		
D8-dicofol	258	260
Component		
Dicofol	250	252

Analysis of PBDEs

PBDEs were analysed on a Shimadzu GC-2010Plus (Shimadzu, 's-Hertogenbosch, The Netherlands) with AOC-20i Auto Injector, coupled with a Shimadzu QP2010 Ultra MS with Negative Chemical Ionisation (NCI) source. A CPsil8 (50 m x 0.25 mm, 0.25 µm) column (Agilent Technologies, Abcoude, The Netherlands) was used for separation. Hydrogen gas was used as a carrier gas with a constant pressure of 120 Kpa. 1 µl of sample was injected in splittles mode with a sampling time of 1.5 minutes. The GC oven temperature was set to 150°C for 1.50 minutes and then increased to 210°C at 5°C/min, then programmed to 320°C at 5°C/min. The injector temperature, interface and ion source were set to 270, 290 and 200°C respectively. In Table 5 the used masses and collision energies are presented for the PBDEs.

Table 4 *Used masses (m/z) and collicion engergyes (CE) for the analysis of the PBDEs using GC-MS*

PBDEs		
Component	**target ion (quantification)**	**qualifier ion**
Internal Standard		
PBDE 58	79	81
Component		
PBDEs	79	81

Analysis of OCPs

OCPs were analysed on a Shimadzu NEXIS GC2030 (Shimadzu, 's-Hertogenbosch, The Netherlands) coupled with a Shimadzu GCMS-TQ8050NX and AOC-20i Auto Injector. An Electron Ionization (EI) source was used. Separation was performed using a ZB-PAH-CT (30 m x 0.25 mm, 0.20 µm) column (Phenomenex, Woerden, The Netherlands). Hydrogen gas was used as a carrier gas with a constant pressure of 14.1 Kpa. Injected was 5 µl of sample in splitt mode with a sampling program was set on 40°C for 1 minute and then increased to 320°C at 200°C/min with a hold time of 33 minutes. The GC oven temperature was set to 45 °C for 1 minute and then increased to 170°C at 30°C/min, then programmed to 255°C at 2°C/min and then programmed to 320°C at 30°C/min with a hold time of 10 minutes. The interface and ion source were set to 225 and 225°C, respectively. In Table 6 the used masses and collision energies are presented for the OCPs.

Table 5 *Used masses (m/z) and collision energies (CE) for the analysis of the OCPs using GC-MS/MS*

OCPs				
Component	**target ion (quantification)**	**CE target ion (v)**	**qualifier ion**	**CE qualifier ion (v)**
Internal standard				
13C4 HCBD (Hexachlorobutadiene)	263.90>228.90	18	265.90>230.90	18
13C4 HCB (Hexachlorobenzene)	290.80>256.80	19	292.80>258.80	20
Component				
HCBD (Hexachlorobutadiene)	224.80>189.90	18	226.80>191.90	18
HCB (Hexachlorobenzene)	285.80>250.80	20	283.80>248.80	19
Heptachlor	271.80>236.90	18	273.85>238.85	18
Cis-heptachloro epoxide (b-HEPO)	352.80>262.90	20	350.85>260.85	18
Trans-heptachloro epoxide (a-HEPO)	288.85>253.00	10	290.90>254.85	10

Analysis of PRC-PCBs

The analysis of the PRC-PCBs was performed on a Shimadzu GC2010 plus (Shimadzu, 's-Hertogenbosch, The Netherlands) coupled with a Shimadzu TQ8040 and AOC-20i Auto Injector. An Electron Ionization (EI) source was used. Separation was performed on an HT8 (30 m x 0.25 mm, 0.25 µm) column (Da Vinci Laboratory Solutions, Rotterdam, the Netherlands). Helium gas was a carrier gas with a 26 cm/sec linear velocity.

Injected was 1 µl of sample in splittles mode with a sampling time of 2.0 minutes. The GC oven temperature was set to 95°C for 3 minutes and then increased to 170°C at 25°C/min, then programmed to 270°C at 2.5°C/min with a hold time of 10 minutes and then programmed to 325°C at 45°C/min. The injector temperature, interface and ion source were set to 280, 290 and 230°C, respectively. In Table 7 the used masses and collision energies are presented for the PRC-PCBs.

Table 6 *Used masses (m/z) and collision energies (CE) for the analysis of the PRC-PCBs using GC-MS/MS*

PRC-PCBs				
Component	**target ion (quantification)**	**CE target ion (v)**	**qualifier ion**	**CE qualifier ion (v)**
Internal standard				
PCB 112	323.90>253.90	24	325.90>255.90	24
PCB 207	461.80>391.80	30	463.80>393.80	30
Component				
PCB 1	188.00>152.00	24	190.00>152.00	24
PCB 2	188.00>152.00	24	190.00>152.00	
PCB 3	188.00>152.00	24	190.00>152.00	
PCB 10	222.00>152.00	24	224.00>152.00	24
PCB 14	222.00>152.00	24	224.00>152.00	24
PCB 30	256.00>186.00	24	258.00>186.00	24
PCB 50	289.90>219.90	24	291.90>221.90	24
PCB 21	256.00>186.00	24	258.00>186.00	24

PCB 104	323.90>253.90	24	325.90>255.90	24
PCB 55	289.90>219.90	24	291.90>221.90	24
PCB 145	357.90>287.90	27	359.90>289.90	27
PCB 78	289.90>219.90	24	291.90>221.90	24
PCB 204	427.80>355.80	30	429.80>357.80	30

QA/QC

The measurement range of the calibration curve of PAHs, dicofol, pBDEs, PRC-PCBs and the OCPs were approximately 0.06-700, 19-2100, 0.06-250, 0.9-400 and 0.3-220 ng/g IS respectively. An r^2>0.996 for all calibration curves was required and achieved.

For each compound, both a quantifier and a qualifier peak were measured. The ratio of quantifier to qualifier in the standards should be the same as in the sample, with a maximum deviation of 20%.

The lowest standard and the concentration found in the blank sampler were used to determine the Limit of Quantification (LOQ shown with a '<'-sign). If the concentration found in the blank sampler was higher than the lowest standard, the concentration in the blank sampler was used for the LOQ. Otherwise, the lowest standard measured was used.

Annex 2 Results of the non-target screening

Name	Common Source	Common Application
Chemicals detected at both locations- Lac Bay_Sorobon and Lac Bay_nursery		
Bis(2-ethylhexyl) phthalate (DEHP)	Plasticisers	Plasticisers in PVC and other plastics
2-Pentadecanone, 6,10,14-trimethyl-	Personal care products	Fragrance industry, personal care products
Cyclotetrasiloxane, octamethyl-	Personal care products	Cosmetics, personal care products, electronics, textiles
Cyclooctasiloxane, hexadecamethyl-	Personal care products	Personal care products, lubricants
Octocrylene	Personal care products	UV filter in sunscreens, cosmetics
Chemicals detected at Lac Bay_Sorobon		
Betulin	Personal care products	Pharmaceuticals, cosmetics
3-Pentanone,2-nitro-4-methyl-1-(tetrahydro-2H-2-pyranyloxy)	Industrial chemical	Synthetic chemical
Oleyl alcohol, chlorodifluoroacetate	Personal care products	Surfactants, cosmetics, pharmaceuticals
2-Nitrohept-2-en-1-ol	Chemical synthesis	Synthetic chemical
2-Decen-1-ol, (E)-	Personal care products	Fragrance industry, flavour agent
2-Dodecen-1-yl(-)succinic anhydride	Personal care products	Used in the manufacture of surfactants and lubricant additives
2-Heptanol, 5-ethyl-	Chemical synthesis	Synthetic chemical
2-Heptanol, 3-methyl-	Chemical synthesis	Synthetic chemical
4-Octanone	Chemical synthesis	Solvent, flavour ingredient
Oxirane, [(hexyloxy)methyl]-	Chemical synthesis	Epoxy resin production
3-Hexanol	Personal care products	Fragrances, flavourings
Bicyclo[9.3.1]pentadeca-3,7-dien-12-ol, 4,8,12,15,15-pentamethyl-, [1R-(1R*,3E,7E,11R*,12R*)]-	Personal care products	Fragrance compound research ambrein.
3,7-Dimethyloct-6-en-1-yl palmitate	Personal care products	Cosmetics, skincare products
[1,1'-Bicyclohexyl]-4-carboxylic acid, 4'-pentyl-, 4-fluorophenyl ester	Personal care products, Pharmaceutical	Pharmaceutical and chemical intermediates
Pentafluoropropionic acid, pentadecyl ester	Industrial chemical	Synthetic chemical
Phenanthrene, 3,9-bis(1,1-dimethylethyl)-	Coal tar, petroleum	A polycyclic aromatic hydrocarbon
Sulfurous acid, isohexyl hexyl ester	Plasticiser	Plasticiser
2,5-Hexanedione	Industrial chemical production	Solvent, Industrial chemical
Cycloheptasiloxane, tetradecamethyl-	Personal care products , industrial chemical	Cosmetics, lubricants gc, coatings, silicone
Hexadecanoic acid, 2-methylpropyl ester	Natural fats and oils	Food industry, cosmetics
Octadecanoic acid, butyl ester	Natural fats and oils	Food industry, personal care products
Hexadecanoic acid, octadecyl ester	Natural fats and oils	Cosmetics, pharmaceuticals, food additive
Octadecanoic acid, 2-methylpropyl ester	Natural fats and oils	Pharmaceuticals, cosmetics
Eicosane, 1-iodo-	Personal Care Products	surfactants, lubricants, a
3-Eicosyne	Natural sources (plant oils)	Natural product

2-Nonadecanone	Natural sources (plant waxes)	Fragrance, flavouring agent, biofuels, insecticides, pharmaceuticals
Pentacosane	Natural sources (plant waxes)	Chemical research, lubricants
Hexatriacontane	Natural sources (plant waxes)	Coatings, lubricants
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	Natural sources, biosynthesis	Natural product
Tetratriacontane	Natural waxes	Lubricants, waterproof coatings
Dotriacontane	Natural waxes, petroleum , industrial chemical	Coatings, lubricants, solvent
Triacontane	Natural waxes, petroleum industrial chemical	Coatings, lubricants , electrodes
Tetracosane	Natural waxes, petroleum,	Industrial lubricants, paraffin waxes, fuel
Dipyrido[1,2-a:2',1'-c]quinoxaline-7,8-dicarbonitrile, 1,2,3,4,11,12,13,14,14a,14b-decahydro-	Organic synthesis	Organic electronics, photonics
5,15-Dimethylnonadecane	Petroleum distillation	Industrial lubricants
Octane, 2-methyl-	Petroleum distillation	Solvent, chemical feedstock , fuel
Hexadecane, 2,6,10,14-tetramethyl-	Petroleum distillation	Solvents, fuel additives, lubricants
Octane, 2,3-dimethyl-	Petroleum distillation	Solvent, chemical feedstock
Undecane, 3-methyl-	Petroleum processing	Solvent, fuel component, research
Pentadecane, 2,6,10,14-tetramethyl-	Petroleum processing	Industrial solvents, chemical intermediate
Lup-20(29)-en-3-one	Plant extracts	Natural product
Octacosyl acetate	Plant waxes	Cosmetics, food packaging
Cyclohexasiloxane, dodecamethyl-	Personal care product	Personal care products, lubricants
Cyclopentasiloxane, decamethyl-	Personal care product	Personal care products, lubricants, cosmetics
Cyclononasiloxane, octadecamethyl-	Personal care product	Personal care products, lubricants, antibacterial agent
Cyclodecasiloxane, eicosamethyl-	Personal care product/Industrial chemical	Personal care products, lubricants, Sealants and adhesives
Tetracosamethyl-cyclododecasiloxane	Personal care product/Industrial chemical	Personal care products, lubricants, textile enhancements
2-(1,1-Dimethylethyl)-5-oxohexanal	Industrial chemical	Fragrance industry
Supraene	Synthetic organic chemistry	Research chemical
Betulin	Personal care product/Industrial chemical	Pharmaceuticals, cosmetics
3-Pentanone,2-nitro-4-methyl-1-(tetrahydro-2H-2-pyranyloxy)	Industrial chemical/pharmaceuticals	Intermediate in pharmaceuticals
Oleyl alcohol, chlorodifluoroacetate	Personal care product/Industrial chemical	Surfactants, cosmetics , solvants
2-Nitrohept-2-en-1-ol	Personal care product/Industrial chemical	Intermediate in organic synthesis
Chemical detected at Lac Bay_Nursery		
1-Pentanol, 2-ethyl-4-methyl-	Industrial chemical	Solvent, chemical intermediate
2-Hexanone, 6-hydroxy-	Industrial chemical	Solvent, industrial applications
2-Bromophenazine 10-oxide	Industrial chemical	Biomedical research
Guanidineacetic acid	Industrial chemical	Animal feed additives, pharmaceuticals
1H-Cyclopropa[a]naphthalene, 1a,2,3,3a,4,5,6,7b-octahydro-1,1,3a,7-tetramethyl-, [1aR-(1a.alpha.,3a.alpha.,7b.alpha.)]-	Industrial chemical /Natural sources	Fragrance ingredients, research chemicals
2-Cyclohexen-1-one, 5-methyl-2-(1-methylethyl)-	Industrial chemical	Fragrances, flavours

4,7-Methano-1H-indene, octahydro-5-(2-octyldecyl)-	Industrial chemical	Industrial lubricants, synthetic rubber processing
6,10,14-Trimethyl-pentadecan-2-ol	Industrial chemical	Cosmetics, skin care products, pharmaceuticals
Pentafluoropropionic acid, heptadecyl ester	Industrial chemical	
Batilol	Marine organisms (algae, sponges)	Research, potential medicinal applications
Docosahexaenoic acid, 1,2,3-propanetriyl ester	Marine sources (fish oil)	Nutritional supplements
Undecanal, 2-methyl-	Natural sources, Industrial chemical	Fragrance industry
1,19-Eicosadiene	Natural sources, Industrial chemical	Research, industrial applications
5-Eicosene, (E)-	Natural sources, Industrial chemical	Industrial applications, research
Decane, 3,8-dimethyl-	Petroleum distillation	Fuel, solvent, extractant, cosmetics, personal care
Heptane, 2,3,5-trimethyl-	Petroleum distillation	Solvent, laboratory reagent
Octane, 2,2,6-trimethyl-	Petroleum distillation	Solvent, fuel additive
Octadecane, 5-methyl-	Industrial chemical	Lubricant, paraffin wax component
Octadecane	Petroleum processing	Lubricants, paraffin waxes, gc stationary liquid, solvent
1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	Plastic production	Plasticizer in PVC and other plastics
1-Pentanol, 2-ethyl-4-methyl-	Industrial chemical	Solvent, chemical intermediate
2-Hexanone, 6-hydroxy-	Industrial chemical	Solvent, industrial applications
2-Bromophenazine 10-oxide	Industrial chemical	Biomedical research
Guanidineacetic acid	Industrial chemical	Animal feed additive, pharmaceuticals

Annex 3 Results of the targeted analysis

Table 7 Chemical analysis results of the passive samplers deployed in Lac Bay, Bonaire in January-March 2023 in ng/L.

Group	Chemical name	Lac Bay_nursery	Lac Bay_Sorobon
PAHs	Acenaphtene	<0.092	<0.084
	Acenaphtylene	<0.1	<0.096
	Anthracene	<0.012	**0.026**
	Benzo(a)anthracene	<0.0052	**0.079**
	Benzo(a)pyrene	<0.0039	<0.0039
	Benzo(b)fluoranthene	<0.0039	<0.0038
	Benzo(g,h,i)perylene	<0.0018	<0.0018
	Benzo(k)fluoranthene	<0.0038	<0.0038
	Chrysene	<0.0057	<0.0055
	Dibenz(a,h)anthracene	<0.0018	<0.0018
	Fluoranthene	<0.039	<0.04
	Fluorene	<0.031	<0.028
	Indeno(1,2,3-cd)pyrene	<0.0036	<0.0036
	Naphthalene	<1.8	<1.7
	Phenanthrene	<0.13	<0.14
	Pyrene	<0.0078	**0.023**
PBDEs	PBDE28	<0.00012	<0.00013
	PBDE47	<0.00012	<0.00013
	PBDE49	<0.00012	<0.00013
	PBDE71	<0.00012	<0.00013
	PBDE75	<0.00012	<0.00013
	PBDE85	<0.00019	<0.00021
	PBDE99	<0.0002	<0.00021
	PBDE100	<0.00019	<0.00021
	PBDE119	<0.00019	<0.00021
	PBDE138	<0.00028	<0.00029
	PBDE153	<0.00028	<0.00029
	PBDE154+BB153	<0.00028	<0.00029
	PBDE183	<0.00036	<0.00039
	PBDE190	<0.00036	<0.00039
OCPs	Heptachlor	<0.00014	<0.00013
	trans-heptachlor-epoxide	<0.005	<0.0049
	cis-heptachlor-epoxide	<0.0015	<0.0015

Dicofol	<0.13	<0.12
HCB (Hexachlorobenzene)	**0.0011**	**0.0015**
HCBD (Hexachlorobutadiene)	<0.0011	<0.00094

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With knowledge, independent scientific research and advice, **Wageningen Marine Research** substantially contributes to more sustainable and more careful management, use and protection of natural riches in marine, coastal and freshwater areas.

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