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Wastewater and seawater monitoring in Antarctica: Passive sampling as a powerful strategy to evaluate emerging pollution

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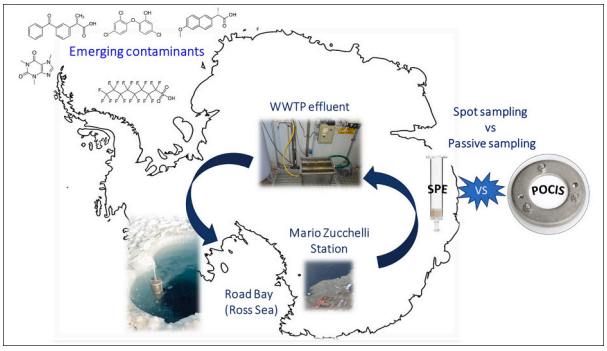
HIGHLIGHTS

- First passive sampling campaign in Antarctic waters for emerging contaminants
- Three-month long assessment in a wastewater effluent and the receiving seawater
- Contaminants of different polarities were detected in both matrices.
- POCIS samplers were compared to classical spot sampling, demonstrating a good agreement.
- A preliminary risk assessment on single analytes showed no significant risk.

GRAPHICAL ABSTRACT



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ABSTRACT

The Ross Sea, among the least human-impacted marine environments worldwide, recently became the first marine protected area in Antarctica.

To assess the impact of the Italian research station Mario Zucchelli (MZS) on the surrounding waters, passive sampling – as well as spot sampling for comparison – took place in the effluent of the wastewater treatment plant (WWTP) and the receiving surface marine waters. Polar Organic Chemical Integrative Samplers (POCIS) were deployed for six consecutive 2-week periods from November to February in a reservoir collecting the wastewater effluent. Passive samplers were also deployed at shallow depth offshore from the wastewater effluent outlet from MZS for two separate 3-week periods (November 2021 and January 2022). Grab water samples were collected alongside each POCIS deployment, for comparison with passive sampling results.

POCIS, used for the first time in Antarctica, demonstrated to be advantageous to estimate time-averaged concentrations in waters and the results were comparable to those obtained by repeated spot samplings. Among the 23 studied ECs – including drugs, UV-filters, perfluorinated substances, caffeine – 15 were detected in both grab and passive sampling in the WWTP effluent and followed similar concentration profiles in both types of sampling. High concentrations of caffeine, naproxen and ketoprofen in the dozens of μg L^{-1} were detected. Other compounds, including drugs and several UV filters, were detected down to sub- μg L^{-1} concentrations. In marine

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waters close to the effluent output, only traces of a drug (4.8 ng L^{-1}) and two UV filters (up to 0.04 μg L^{-1}) were quantified.

1. Introduction

Mario Zucchelli Station (MZS) is a seasonal Italian research base in Antarctica, active during the austral summer. It is located on the coast of Terra Nova Bay in the Ross Sea (74°42′ S and 164°07′ E, altitude 15 m). Since 2017, this region has included the largest marine protected area (MPA) in the world (1,660,000 km^2) with the aim of conserving biodiversity and not interfering with the vulnerable ecosystems of this remote environment (Brooks et al., 2021). While fishing, climate change and tourism are considered the highest threats for the MPA, scientific research activities could also have an impact on the surrounding environment, due to atmospheric emissions (fuel combustion and waste incineration) or by the discharge of treated or untreated sewage into coastal marine water (da Silva et al., 2023). The Annex III of the *Protocol on Environmental Protection to the Antarctic Treaty* regarding the *Waste disposal and waste management* permits the discharge of sewages into the sea provided their dilution and dispersal, and at least a maceration treatment, if produced in large amounts (Annex III to the Protocol on Environmental Protection to the Antarctic Treaty, 1991). However, the Annex IV dealing with the *Prevention of marine pollution* prohibits the input of hazardous substances into the marine environment.

The release of wastewater, even treated, could be an input of Emerging Contaminants (ECs) such as pharmaceuticals, stimulants and estrogens (Adeleye et al., 2022; Liu et al., 2015), due to inefficient removal by classical wastewater treatment. This input of ECs is exacerbated in Antarctica where sewage treatment is limited and sometimes absent (Gröndahl et al., 2009). ECs, in particular pharmaceuticals and endocrine disrupting compounds, raise concerns due to their possible detrimental effects on aquatic organisms at different trophic levels, even at low concentrations (ng L^{-1} or μg L^{-1}) (Muñoz et al., 2016). In addition, the continuous release of these chemicals due to their frequent usage makes them pseudo-persistent, leading to chronic exposures, with still undisclosed effects. As a consequence, the assessment of the risk posed by ECs on the unique and fragile ecosystems of Antarctica and the prioritization of such pollutants are fundamental steps for the protection of this region, as suggested by Olalla et al. (Olalla et al., 2020). The presence and fate of ECs in Antarctic waters and snow (Balakrishna et al., 2023; Cai et al., 2012; Domínguez-Morueco et al., 2021; Emnet et al., 2015; Esteban et al., 2016; Gao et al., 2018; González-Alonso et al., 2017; Hernández et al., 2019; Postigo et al., 2023; Szopińska et al., 2022; Xie et al., 2020; Xuan et al., 2023), and in other matrices (Duarte et al., 2021; Ferreira et al., 2021; González-Aravena et al., 2022; Magi et al., 2004; Panti et al., 2022) have been object of investigation using mass spectrometry (Magi and Tanwar, 2014). However, in the perspective of a systematic assessment, more intensive water monitoring should be performed. Until now, the presence of ECs has been evaluated in WWTP effluents, freshwater, and seawater by using spot sampling. However, in order to obtain a representative overview of ECs occurrence, frequent or composite samples are required, by combining multiple grab samples or using autosamplers. Considering the severe field conditions in Antarctica, the sampling step might result complex. The use of passive sampling represents a valid alternative, since it avoids the constant attendance of scientific staff, and at the same time reduces costs and energy consumption, compared to active sampling. In fact, by simply deploying the passive samplers for a certain period of time, time-weighted average (TWA) concentrations of target organic compounds over prolonged exposures can be obtained (Huckins and Petty, 2006). Among the most frequently used passive samplers, the Polar Organic Chemical Integrative Sampler (POCIS) was developed for the sampling of hydrophilic organic contaminants (Log Kow < 4) dissolved in water (Alvarez et al., 2014, 2004).

Despite its numerous advantages, passive sampling has rarely been used in polar areas for the detection of ECs. In the Arctic region, silicon rubber (SR), triolein-embedded cellulose acetate membranes (TECAMs) and polyethylene sheets (PE) have been employed as passive samplers for the detection of hydrophobic organophosphorus flame retardants (Carlsson et al., 2018; Gao et al., 2020, 2019; McDonough et al., 2018). Only two studies have reported the use of POCIS and the organic diffusive gradients in thin film (o-DGT) devices for the sampling of more polar compounds, including PFAS, pharmaceuticals and pesticides (Chaves-Barquero et al., 2016; Stroski et al., 2020). In Antarctica, only two examples of passive sampling are reported, involving the use of TECAM and PE for persistent hydrophobic compounds (Gao et al., 2018; Yao et al., 2016). To the best of the authors' knowledge, passive sampling has never been employed in Antarctica for the evaluation of the TWA concentrations of ECs.

A direct anthropic influence on the aquatic environment of Antarctica, due to the introduction of contaminants during research activities, is highly probable, with potential impacts on the unique and fragile ecosystems of these polar regions. Therefore, the main objective of this work as part of the PNRA MATISSE project ('Emerging contaminants in the Ross Sea: occurrence, sources and ecotoxicological risks') was to verify the presence of 23 ECs (pharmaceuticals, estrogens, UV-filters, PFAS, stimulants and artificial sweeteners) in the effluent of MZS' wastewater treatment plant and in the receiving coastal seawater. For the detection of these ECs, passive samplers for semi-polar compounds (POCIS) were deployed for the first time in Antarctica and combined with spot sampling in order to compare the results obtained using these two sampling strategies. To do so, a more intensive and systematic sampling campaign was performed, compared to the vast majority of papers regarding ECs in Antarctica wastewater. Finally, to assess the impact of the scientific station on the surrounding environment, a preliminary risk assessment was conducted for the marine environment near the base.

2. Materials and methods

2.1. Sampling strategies and field deployments

During the 37th Italian Expedition, Mario Zucchelli station had an average of 63 inhabitants with a minimum of 22 people (at the end of the campaign) and a maximum of 100. The wastewater treatment of the station mainly consists of physico-chemical methods.

To assess the anthropic impact of MZS, the WWTP outlet (treated water) and Road Bay coastal water were sampled between November 2021 and February 2022 (see Fig. S3 for the sampling scheme). For both water matrices, two sampling methods were used: passive and spot sampling. The passive samplers used in this study (POCIS) contained the same sorbent type as the one present in the cartridges used for pre-concentration of spot samples (SPE). It is thus expected that the studied contaminants had the same sorption behaviour in both cases.

Passive sampling was carried out using commercial POCIS purchased from E&H services (Prague, Czech Republic). The exposed surface area was of 45.8 cm^2 and the declared mass of the HLB sorbent in the samplers was 220 mg.

The water flow of the WWTP effluent was deviated in a small stainless-steel tank (Fig. 1) and the passive samplers were exposed parallel to the water flux, fixed on brackets. In each sampling, two POCIS protected by stainless-steel grids were deployed for two weeks, for a total of six consecutive sampling periods (Table S1). After each deployment, the devices were rinsed with ultra-pure water to remove organic debris, wrapped in aluminium foil and stored at −20 °C, until

transported to Italy under controlled conditions.

Two samplings of three weeks were carried out in Road Bay marine water (Table S1), using a stainless-steel cage containing two POCIS. The samplings were performed in November 2021 (in presence of the ice pack) and in January 2022 (in absence of the ice pack). The deployment was performed 136 m away from the WWTP discharge point (Fig. 1) at 3–5 m depth (74.69607 S, 164.12037 E, seabed: 15 m). During the first deployment (Fig. S1) the cage was fixed to the ice pack, while during the second one (Fig. S2) a submerged buoy was employed.

In this study, spot sampling was performed at the beginning, in the middle and at the end of each exposure period of the POCIS, to provide a quantitative snapshot of contaminants for comparison. 500 mL of water were withdrawn using glass bottles (WWTP sampling) or Niskin bottles (seawater sampling) and subjected to SPE in the MZS laboratories by using 200 mg HLB cartridges (Supelco, Bellefonte, PA USA). The cartridges were conditioned using 3 mL of MeOH and 5 mL of ultra-pure water and the 500 mL of water sample were loaded. After the extraction, SPE cartridges were stored at −20 °C and transported under controlled conditions. For each type of sampling, blanks samples were performed.

Once transported back to the laboratory in Italy, passive samplers were thawed, the damp sorbent was transferred into an empty SPE cartridge with the aid of approximately 20 mL of ultra-pure water and eluted using 20 mL of MeOH and 5 mL of DCM:IPA (80:20 v/v). The obtained eluate was then reduced to dryness on a rotary evaporator (Rotavapor® R-100, BUCHI, Switzerland), reconstituted in 1 mL of methanol and filtered through a 0.2 μm hydrophilic PTFE filter (Benedetti et al., 2022). Appropriate dilutions were performed before HPLC-MS/MS analysis, in order to detect and possibly quantify the highest possible number of analytes. Different matrix effect (ME) was expected at the different dilutions, thus it was always evaluated by spiking the extracts, in order to obtain reliable data (Matuszewski et al., 2003).

Some of the studied analytes showed affinity to different extent for PES membranes in previous works (MacKeown et al., 2022; Scapuzzi et al., 2023). Thus, the sorption of target compounds onto the protective polyethersulfone (PES) membranes, part of the POCIS itself, was also assessed. These membranes are generally discarded but are able to behave as passive samplers for some analytes. Therefore, the PES membranes of each POCIS were extracted using MeOH as described elsewhere (Scapuzzi et al., 2023).

Regarding spot sampling, the SPE cartridges were thawed and eluted using the same protocol as for passive samplers, to minimize recovery differences between the two extraction methods.

2.2. Chemicals

Analytical standards were purchased from different suppliers: paraxanthine (PRX), theophylline (TFL), carbamazepine (CARB), benzophenone-3 (BP-3), octyl dimethyl *p*-aminobenzoate (OD-PABA), ethyl hexyl methoxy cinnamate (EHMC), octocrylene (OC), perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), acesulfame (ACS), sucralose (SCL), bisphenol A (BPA), estrone (E1), β-estradiol (E2), 17α-ethinyl estradiol (EE2), ibuprofen (IBU), gemfibrozil (GEM) and triclosan (TCS) from Sigma-Aldrich (St. Louis, MO, USA); caffeine (CAFF), ketoprofen (KETO), naproxen (NAPR), and diclofenac (DCF) from Fluka Analytical (Saint Gallen, Switzerland), while salbutamol (SLBT) from Alfa Aesar (Haverhill, MA, USA). Further details on the solvents used throughout this work are reported in SM.

2.3. LC-MS/MS analysis and quantitation

Analyses were carried out on a 1200 SL Liquid Chromatograph by Agilent technologies (Santa Clara, CA, USA) by using a Kinetex® C18 Polar column (100 mm × 2.1 mm i.d.; 2.6 μm particle size, Phenomenex, Torrance, CA, USA), coupled to an Agilent 6430 Triple Quadrupole mass spectrometer (MS), equipped with an Electrospray Ionization (ESI) ion source. The MassHunter 10.0 software was used for data acquisition and processing.

The target compounds were analyzed by using two different chromatographic methods developed in a previous work (Benedetti et al., 2022). Details of the chromatographic methods are reported in Supporting Material (Table S2).

Dynamic-multiple reaction monitoring (d-MRM) mode was employed to enhance the selectivity and sensitivity of the detection method. The most abundant MRM transition was used for quantification and the others for confirmation purposes. The optimal MS conditions and MRM transitions are reported in Table S3. Limits of detection and quantitation of the overall method are reported in SM (Table S4). The method used was extensively optimized and validated in terms of accuracy, precision, sensitivity and specificity in a previous study (Benedetti et al., 2022).

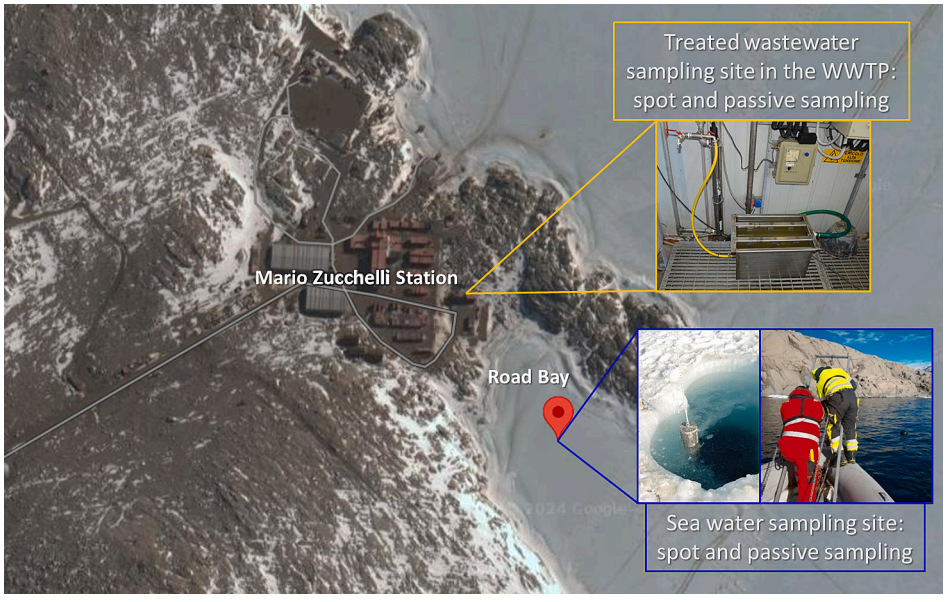

Fig. 1. Mario Zucchelli Station and sampling locations with illustrations of sampling during both seasons.

2.4. Multivariate analysis

When dealing with big data matrices, a multivariate approach is recommended to highlight relations among groups of data. Thus, statistical analysis was performed through a free software, Chemometric Agile Tool (CAT) (Leardi et al., 2023). Concentration values were used for the statistical evaluations; when levels were below the detection limit, they were set to be equal to half of the limit of detection itself.

Firstly, a Principal Component Analysis (PCA) was computed, to contemporarily highlight correlations among both variables and samples, by graphically reporting data with respect to new variables along which variance is maximized.

Secondly, to investigate bivariate correlations among the concentrations of the target compounds and/or with the number of people within the MZS, correlation matrices were computed both between single SPEs results and 2-weeks averaged SPE with POCIS data, obtained from both the HLB sorbent and the PES membranes (Tables S5 and S6). The Pearson Correlation Coefficients obtained display the linear relationship between two variables (r_{xy}). These coefficients range between $-1 \leq r_{xy} \leq +1$, where negative values mean anticorrelation between the variables, 0 no correlation, and positive values indicate a correlation. The higher the absolute value of the coefficient, the stronger the relation considered.

2.5. Risk assessment

The risk that the detected ECs may pose to marine organisms was assessed with the hazard quotient (HQ) method. HQs are calculated as the ratio between the Measured Environmental Concentration (MEC) and the marine Predicted No Effect Concentration (PNEC) for each compound. Using the highest MEC, a worst-case scenario environmental risk assessment was conducted for the surveyed ECs.

In many instances in the literature, reported PNEC values differ between studies, especially due to inconsistencies in the attribution of an assessment factor to take into account the differences between laboratory conditions and natural conditions (Carve et al., 2021). For simplicity, the lowest PNECs from the NORMAN Ecotoxicology Database were used in this study (downloaded in September 2023). Often the lowest PNEC for marine water is set at the lowest PNEC for fresh water divided by a factor of 10 (NORMAN, 2024).

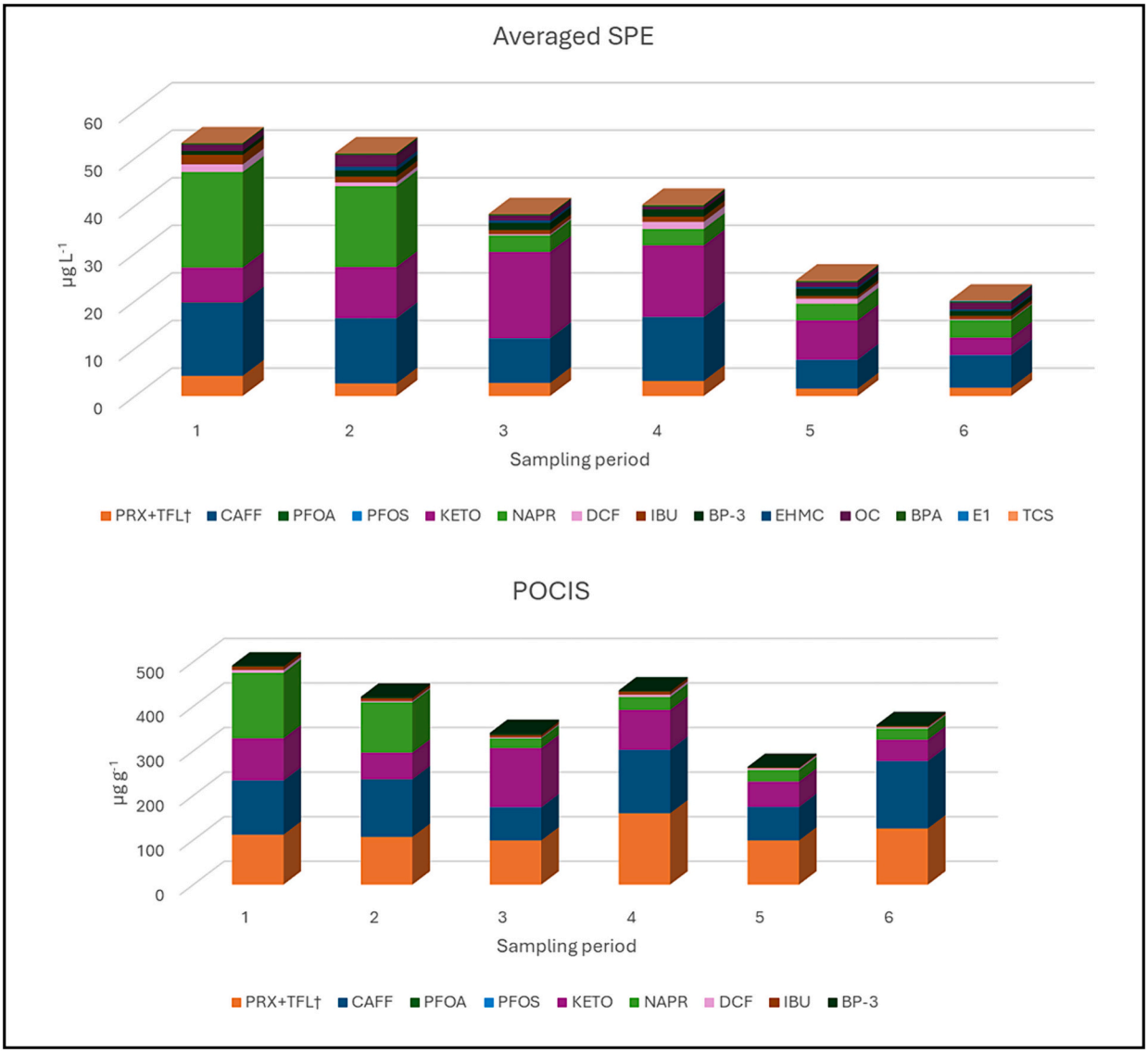

Fig. 2. Concentration profiles for each sampling period for a) 2-week averaged SPE concentrations, b) POCIS sorbent concentrations.

3. Results and discussion

3.1. Wastewater treatment plant of Mario Zucchelli Station

3.1.1. Spot sampling

The thirteen spot samples were collected weekly from the WWTP of MZS, to cover the whole period of the station research activities. The concentrations of the analytes obtained for each SPE sample are reported in Table S7, and their 2-week average is graphically presented in Fig. 2.

Method detection limits (MDLs) are reported in Table S4 and ranged between 1.2 and 30 ng L^{-1} for most of the analytes except for PRX-TFL, CAFF, KETO, NAPR, EHMC, OC, E2 and EE2 which ranged from 50 up to 300 ng L^{-1} (median 26 ng L^{-1}).

Fourteen analytes were quantified in at least one sample. The highest concentrations observed during the whole campaign were for NAPR, CAFF and KETO (>10 μg L^{-1}), which were followed by OC, IBU, DCF, BP-3, and PRX-TFL (1–10 μg L^{-1}), EHMC, BPA, TCS and E1 (0.1–1 μg L^{-1}), PFOS and PFOA (<0.01 μg L^{-1}). Besides them, ACS was detected, but water concentrations could not be calculated, due to its poor recovery.

The 12-week averaged concentrations for the whole campaign followed a very similar profile: the most abundant ECs present in all samples were CAFF, KETO and NAPR (ranging from 9 to 12 μg L^{-1}), followed by PRX-TFL, OC, BP-3, IBU and DCF (0.9–2.8 μg L^{-1}). BPA, and TCS presented lower concentrations (0.1–0.3 μg L^{-1}), while EHMC, E1, PFOA, PFOS, ACS were detected occasionally and often under the LOQs, thus average concentrations were not reported.

In most cases, completely acceptable ME were observed (80 % < ME < 120 %), except for PRX-TFL and CAFF which presented a moderate signal suppression (Rutkowska et al., 2019). However, all the results were corrected for the obtained ME (detailed values are reported in Table S8).

As shown in Fig. 2a, the 2-week averaged concentrations showed an overall downward trend, except for KETO, with higher concentrations in the middle periods. At least in part, the observed trend was due to the great decline in NAPR concentrations after the first two periods.

Even though informative, the values obtained from the grab sampling may be not representative of the whole period, since relevant short-term variations are expected in WWTPs. Indeed, intermittent flushing 'events' and variability in what is discharged were expected (toilet flushing, showers, dishwashers, washing machines…) (Ort et al., 2010), also exacerbated by the small dimension of the wastewater treatment facility. Thus, the high temporal variation of many of the compounds' concentrations (up to 2 orders of magnitude for NAPR), was not surprising. For this reason, passive sampling was applied to obtain TWA concentrations, probably providing more 'realistic' mean values than those calculated from only 3 spot samples along the 2-weeks period.

3.1.2. Passive sampling

3.1.2.1. POCIS and PES concentrations. The concentrations of the analytes obtained for each POCIS sampling period are reported in Table S9 and graphically presented in Fig. 2b.

MDLs for concentrations in the HLB phase ranged between 7 and 140 ng g_{HLB}^{-1} for half of the analytes and up to 1400 ng g_{HLB}^{-1} for the others (median 200 ng g_{HLB}^{-1}). As already discussed for SPE samples, ME was evaluated at the different dilutions tested, showing moderate suppression only for PRX-TFL, CBZ and OC at lower dilution (Table S8). Thirteen compounds were detected at least once in the POCIS sorbent. The RSDs between duplicate POCIS HLB extracts were <30 % for the majority of compounds detected in the sorbent, with the exception of CAFF and PRX-TFL (49 and 57 %). In the POCIS membranes, the RSDs for the detected compounds (3 UV filters, BPA and TCS) were below 25 % except for BP-3 in one deployment (57 %). Fifteen ECs were detected at least once by the POCIS when considering not only the HLB sorbent but also the PES membranes (Table S10); all these analytes were also detected in the SPE eluates. After 2 weeks of exposure in the WWTP, most contaminants preferentially partitioned in the POCIS sorbent rather than in the PES membranes, except for the UV filters and TCS. Indeed, the concentrations of BP-3 and TCS were much higher in the membranes, with a C_{PES}/C_{HLB} ratio ranging from 3.1 to 8.3 and 5.8 to 9.1, respectively; the more hydrophobic UV filter OC was detected in the PES membranes only. This result agrees with our previous findings regarding repartition of different chemicals between the POCIS sorbent and membrane (MacKeown et al., 2022).

While the number of compounds detected at least once was nearly the same as with spot sampling, passive sampling was better for the detection of certain analytes, since PFOA, PFOS and ACS were not detected on certain dates by spot sampling. By choosing different days for the spot samples, these analytes may not have been detected at all.

3.1.2.2. Median sampling rates from the literature and derived TWAs. Accurate quantitation using POCIS data from field deployment is not straightforward, since calibration of passive samplers is required to obtain the specific Rs of each compound. For rough estimations, a default value of approximately 0.2 L d^{-1} could be theoretically used for contaminants which accumulate on the POCIS but with no experimentally derived Rs (Mathon et al., 2022; Toušová et al., 2019). However, this method usually leads to higher uncertainties on estimated TWA concentration (Mathon et al., 2022). Generally, lab derived Rs are applied to in situ exposures and various Rs values are already available in the literature for different molecules and exposure conditions (Mathon et al., 2022). Still, these Rs may not accurately reflect field Rs, due to several site-specific parameters such as (bio)fouling and flow rate that affect analyte diffusion. The use of performance reference compounds (PCR) has been proposed to account for site-specific water matrix and flow conditions (Harman et al., 2011), but the strong retention of analytes on the HLB sorbent greatly limits the use of this approach for POCIS. A more reliable strategy is to calibrate Rs in situ by analysing spot water samples collected during the same period of deployment. Nevertheless, in situ calibration is a costly and time-consuming approach and may not be appropriate for the wastewater treatment plant effluent, due to highly varying concentrations.

A total of 209 Rs values were compiled for 13 of the studied contaminants, by selecting those satisfying specific criteria for reliability (as

Table 1
Median Rs values built from the literature.

Compound	Rs median all values (number of Rs values selected)	10 %–90 % percentile range of Rs
BPA	0.12 (8)	0.02–0.26
CAFF	0.13 (19)	0.03–0.17
CBZ	0.31 (18)	0.20–0.41
DCF	0.12 (24)	0.03–0.31
E1	0.16 (6)	0.11–0.21
E2	0.12 (6)	0.08–0.19
EE2	0.17 (6)	0.08–0.24
GEM	0.34 (17)	0.23–0.78
IBU	0.12 (31)	0.06–0.35
KETO	0.08 (21)	0.04–0.21
NAPR	0.13 (23)	0.04–0.39
PFOA	0.21 (15)	0.06–0.25
PFOS	0.07 (15)	0.04–0.08

References for the Rs used in the calculations: (Amdany et al., 2014; Arditsoglou and Voutsa, 2008; Bartelt-Hunt et al., 2011; Bayen et al., 2014; Belles et al., 2014; Di Carro et al., 2014; Elkayar et al., 2022; Gobelius et al., 2019; Guibal et al., 2020; Hahn et al., 2022; Kim and Homan, 2020; Li et al., 2010, 2011; MacKeown et al., 2022; MacLeod et al., 2007; Magi et al., 2018; Miège et al., 2012; Mirasole et al., 2016; Morin et al., 2013; Niemi et al., 2022; Shi et al., 2014; Zhi et al., 2023).

described in Supplementary Material). Table 1 presents the 13 median POCIS Rs values and their associated standard deviation, as well as the number of individual Rs that respected the criteria for the calculation.

For some compounds, no Rs could be found (UV filters), while among the several Rs reported for TCS, none respected the chosen criteria. Therefore, no TWA could be estimated for the above-mentioned compounds. For several analytes that were not detected in the POCIS but for which acceptable Rs were found in the literature (CBZ, GEM, E2, EE2), the median Rs were calculated to estimate TWA limits of detection in the WWTP effluent.

Using these median Rs, TWA were estimated (Table 2): among all target ECs, CAFF and KETO were present at the greatest concentrations (8.4–17 μg L^{-1} and 5.9–16 μg L^{-1}, respectively) in treated wastewater. Also NAPR was found at high TWA concentrations, but just in the first two deployment periods. This could be due to a periodic selective prescription of this NSAID.

Neither CARB nor GEM, which are drugs for very specific illness, was detected in the WWTP effluent despite low TWA LODs (0.33 and 0.71 ng L^{-1} respectively).

3.1.3. Correlations between individual compounds

As a first exploratory tool, PCA was performed on quantitation results of SPE and POCIS, by considering the 6 POCIS deployments as the objects, and associating to each deployment the average results of the spot samples collected during the same period. Besides the analytes' concentrations, also the number of people present at the base was considered as a variable. The first 3 principal components explained up to 78.2 % of the experimental variance, indicating a strong correlation among the variables. The biplots of the model (including loading and score values) are reported in Fig. 3. These biplots simultaneously highlight all the correlations among the experimental responses: for example, Fig. 3a) shows how PFOA, IBU and NAPR content were all correlated with the number of people at the MZS and among each other; Fig. 3b) shows how PC3 loadings imply an anticorrelation concerning the UV filters BP-3 and the couple EHMC-OC. Even though the variables resulted correlated, no particular pattern was found for the deployments, suggesting that the samplings were quite different among each other. Indeed, they resulted quite evenly distributed in the whole PC space. In order to further quantify the correlation between couples of variables, the Pearson's correlation coefficients and the corresponding *p*-values were also determined. Tables S5 and S6 represent the correlation matrix of the same data used in the PCA, and the one computed on single SPE results, respectively.

The 2-week average SPE concentrations of CAFF and its metabolite PRX (and TFL), as well as several NSAIDs (IBU, NAPR), strongly correlated to the number of people at the base and to each other. This is clearly shown by generally higher average values at the start of the campaign and lower values at the end. These findings are consistent with the positive correlations between caffeine and human-use pharmaceuticals commonly found in aquatic environments (Comeau et al., 2008). On the other hand, KETO showed no correlation to these compounds, as it was measured at the highest concentrations in the middle of the campaign. This is most likely due to the switch of medical prescriptions from NAPR to KETO due to stock depletion at the base.

Generally, the 2-week average SPE concentrations of the analytes were more strongly correlated than the 13 individual spot sample concentrations. For example, $r_{CAFF/PRX\text{-}TFL} = 0.915$ for the 2-week average SPE concentrations and $r_{CAFF/PRX\text{-}TFL} = 0.647$ for the individual spot concentrations. This highlights how the use of single spot samples may not be suitable for general evaluations. Despite being the main metabolite of CAFF (80 % of excretion in humans), PRX was observed at approximately 3 times lower concentrations, suggesting different inputs of CAFF in wastewater (Magkos and Kavouras, 2005) and/or different removal efficiencies compared to a conventional WWTP. Nevertheless, the concentrations of these compounds in WWTP effluents vary depending on the influent composition and the treatment methods, and a higher CAFF concentration is not unusual (Tong et al., 2015).

Considering the correlation matrix for the single SPE's extracts (Table S6), it is worth noticing that a high correlation ($r_{EHMC/OC} = 0.921$, $p < 0.001$) between EHMC and OC was observed, while the other detected UV filter (BP-3) followed a different profile, despite an average concentration similar to the one of OC.

In general, correlations were stronger for 2-week average SPE concentrations than for POCIS, as shown by the correlation matrix reported in Table S5. This could be ascribed to both the differences in sampling and processing: if the spot sampling is performed during "basal levels" of contamination, major differences among compounds due to single "high-pollution events" could be missed by the SPE results. On the other hand, passive samplers integrate these events along time, allowing to better highlight such differences. Still, there are a couple of exceptions for which the opposite happened: ACS and BP-3, as well as PFOA and NAPR resulted significantly correlated only in POCIS extracts ($r = 0.836$ and 0.851, and $p = 0.038$ and 0.032, respectively).

No significant correlations were observed between the concentrations of BPA, PFOS and the number of people present at the research station in either POCIS or SPE, indicating a contamination source independent from the number of residents.

Finally, a good correlation was observed between the results obtained in the sorbent and those in the PES for BP-3 and TCS ($r_{HLB\text{-}PES} = 0.868$ and 0.856, respectively). BP-3, TCS and OC were quantified in all PES membranes and showed moderate correlations ($r_{SPE\text{-}PES}$ in the 0.620–0.804 range) to the 2-week averaged spot sample concentrations (Table S5). These results suggest a good agreement between the sampling techniques employed as the higher the concentration observed in the PES membranes of a specific sampling period, the higher the concentration found in the corresponding spot samples (SPE) or POCIS sorbent.

3.1.4. Grab vs passive sampling

To estimate in situ Rs, compounds must be detected both by POCIS and by spot sampling and follow a good agreement. In particular, concentrations found by SPEs must present a low variability during the entire passive sampler deployment time (Vrana et al., 2021). Moreover, estimating the average concentration should be preferably performed by collecting a relatively high number of spot samples, in order to increase the probability of catching possible sudden fluctuations.

The occurrence pattern of the POCIS concentrations of DCF ($r = 0.928$), IBU ($r = 0.910$), TCS ($r = 0.889$) and NAPR ($r = 0.997$) were in

Table 2
POCIS wastewater treatment plant TWA concentrations (see Table S6 for sampling periods) using the Rs calculated in Table 3.

POCIS sampling period	CAFF	KETO	NAP	IBU	DCF	BPA	PFOS	PFOA	E1
	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
1	13 ± 4	16 ± 2	15 ± 1	0.90 ± 0.05	0.62 ± 0.12	0.234 ± 0.004	35 ± 2	15 ± 2	<LOD
2	14.6 ± 0.3	10.7 ± 0.2	12 ± 0.3	0.81 ± 0.06	0.263 ± 0.008	0.22 ± 0.03	<LOQ	19.7 ± 0.3	<LOD
3	8 ± 5	22 ± 4	2.2 ± 0.3	0.61 ± 0.02	0.19 ± 0.01	0.201 ± 0.008	70 ± 2	<LOQ	<LOD
4	16 ± 2	16 ± 2	3.1 ± 0.4	0.85 ± 0.05	0.59 ± 0.07	0.31 ± 0.02	36 ± 5	<LOQ	<LOD
5	8 ± 2	10 ± 1	2.6 ± 0.6	0.19 ± 0.03	0.36 ± 0.05	0.31 ± 0.02	39 ± 5	<LOQ	<LOD
6	17 ± 2	9 ± 1	2.7 ± 0.3	0.33 ± 0.04	0.26 ± 0.05	0.21 ± 0.03	50 ± 8	<LOD	52.4 ± 0.6

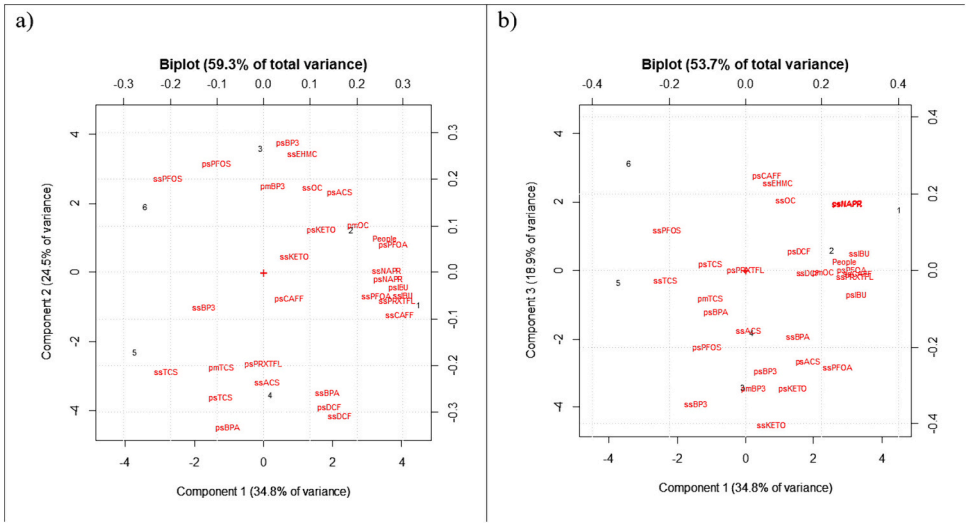

Fig. 3. Biplots of the PCA built on 2-week average SPE (ss = spot sampling) and passive sampling concentrations (ps = POCIS sorbent, pm = POCIS membrane). a) PC1 vs PC2 and b) PC1 vs PC3.

good agreement with the concentrations estimated by spot samples, making it theoretically possible to estimate in-situ Rs. The concentrations of KETO, PFOA and BPA correlated less strongly ($0.5 < r < 0.8$), while CAFF, PFOS, BP-3 showed no or very little correlation ($r < 0.4$). This high variability in the spot sample results during POCIS deployments makes the estimation of Rs less reliable. The lack of positive correlation between POCIS and SPE results could be related to an insufficient number of spot samples; a larger number of spot samples are required to better estimate the average water concentration of ECs with highly fluctuating concentrations and reasonably compare it to the TWA from passive sampling for the same period.

In previous studies comparing both spot and passive sampling, the number of spot samples collected varied considerably (Allinson et al., 2023): for example, while Vallejo et al. only collected spot samples during POCIS deployment and removal (Vallejo et al., 2013), Baz-Lomba et al. collected several composite samples every day (Baz-Lomba et al., 2017).

Due to the high uncertainty on the 2-week average spot sample concentration for most detected compounds, in-situ Rs were not used for TWA estimation. Higher frequency spot sampling, including replicates, would improve the consistency between both methods, allowing to estimate more in situ Rs (Shi et al., 2014).

In order to verify the agreement among passive sampling and spot sampling results, TWA obtained by POCIS were calculated by using median sampling rates from the literature. An exception is represented by TCS. For this compound, no reliable Rs were found in the literature. Indeed, the evaluations on POCIS uptake are generally performed by measuring the TCS water loss, without proper verification of the accumulation onto the HLB phase (MacKeown et al., 2022). The in situ Rs calculated for TCS in this study is of 0.022 ± 0.006 L d^{-1}.

Using median literature Rs values, the POCIS-derived TWA concentrations of CAFF, NAPR, KETO, DCF, PFOA, PFOS, IBU, BPA and E1 (for the last period) were highly comparable to mean concentrations derived from grab samples that were collected over the same deployment time: the TWAs calculated for these compounds were all within a factor of 4 from the 2-week average spot sample concentration (Fig. 4 and Table S11). Moreover, 75 % of the individual Cw measured for these 9 compounds were within a factor of 2. Similar findings are reported in the literature (≈50–80 %) (Criquet et al., 2017; Vrana et al., 2021). Ratios for NAPR and BPA, in particular, were all between 0.71 and 0.97.

It therefore implies that, for these 9 ECs, (i) the literature estimated Rs values in this study were within reasonable limits of the real in situ Rs and thus appropriate for determination of TWA concentrations and (ii) a

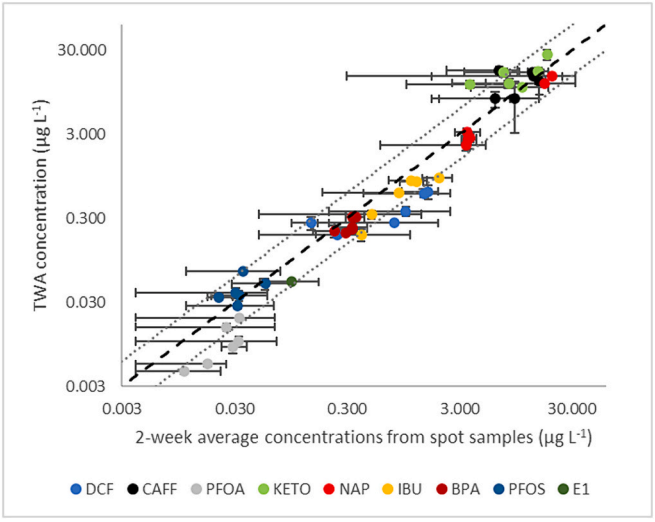

Fig. 4. Comparison of TWA concentrations (calculated from literature Rs) and two-week average spot sample concentrations. Horizontal error bars: minimum and maximum spot water concentrations. Vertical error bars: measurement uncertainty from duplicate co-deployed POCIS. Diagonal dashed line: $TWA_{POCIS} = Cw_{spot}$. Area between the parallel dotted lines: range where both compared values differ by less than a factor of 2.

frequency of one spot sample per week was sufficient for a general characterization of the WWTP effluent. If using only 2 spot samples per exposure period (at the deployment and during recovery of the sampler), the agreement is noticeably poorer for several compounds, KETO, PFOA and PFOS (data not presented).

In general, passive sampler derived data tended to be below grab sample concentrations for PFOA (6/6 sampling periods), BPA (6/6), IBU (6/6), NAPR (6/6) DCF (5/6). While ratios were only slightly below 1 for NAPR and BPA, TWA concentrations estimated for DCF and PFOA were generally significantly lower than 2-week average spot sample concentrations, with ratios below 0.5 for 4/6 deployment periods.

A final remark can be done, regarding a cost comparison between traditional spot sampling and passive samplers. As widely discussed, the use of passive samplers as a complementary method can improve assessment quality when a large temporal variation or fluctuation of contaminant sources are expected. Considering the temporal variation

of the concentrations of the ECs observed in the MZS WW effluent, the use of SPE to determine average environmental concentrations involves the processing of a minimum of 3 cartridges, while one single POCIS can be used in alternative. A POCIS device costs approximately the double of an SPE cartridge and the solvent consumption for POCIS processing is 1/3 compared to 3 SPEs (see Materials and methods for details). In addition, the time required for processing, as well as the time, energy and solvent consumption of instrumental analysis must be considered. It follows that passive samplers are strongly recommended as a greener, cost-effective and advantageous option, outweighing the benefits of a

Table 3
Reported spot sample concentrations in Antarctica wastewater for the studied ECs.

Compounds	Period of sampling	Detection frequency	Concentration range (μg L^{-1})	Area of study	Reference
BPA	2009	1/1	0.03	McMurdo	Emnet et al. (2015)
	2009	1/1	0.03	Scott Base	Emnet et al. (2015)
	2012–2013	13/13	0.0047–0.986	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Esteban et al. (2016)
	2017, 2019	0/2	nd	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.150–0.450	Mario Zucchelli	This study
BP-3	2009	1/1	0.080	McMurdo	Emnet et al. (2015)
	2009	1/1	0.12	Scott Base	Emnet et al. (2015)
	2012–2013	13/13	0.0167–0.195	Scott Base	Emnet et al. (2015)
	2012–2013	1/1	0.02	Esperanza	Domínguez-Morueco et al. (2021)
	2019	0/1	nd	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.19–2.0	Mario Zucchelli	This study
CAFF	2012–2013	1/1	71	Esperanza	González-Alonso et al. (2017)
	2019	1/1	3.3	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	1.7–25	Mario Zucchelli	This study
CBZ	2012–2013	1/1	nd or <LOQ	Esperanza	González-Alonso et al. (2017)
	2017, 2019	1/2	nd - 0.0088	Arctowski	Szopińska et al. (2022)
	2021–2022	0/13	nd	Mario Zucchelli	This study
DCF	2012–2013	1/1	15	Esperanza	González-Alonso et al. (2017)
	2017, 2019	2/2	0.074–0.747	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.095–2.5	Mario Zucchelli	This study
E1	2009	0/1	nd	McMurdo	Emnet et al. (2015)
	2009	1/1	0.09	Scott Base	Emnet et al. (2015)
	2012–2013	11/13	0.0031–0.331	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Esteban et al., (2016)
	2017, 2019	1/2	nd - 0.0799	Arctowski	Szopińska et al. (2022)
	2021–2022	1/13	nd - 0.169	Mario Zucchelli	This study
E2	2009	0/1	nd	McMurdo	Emnet et al. (2015)
	2009	0/1	nd	Scott Base	Emnet et al. (2015)
	2012–2013	0/13	nd	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Esteban et al. (2016)
	2017, 2019	0/2	nd	Arctowski	Szopińska et al. (2022)
	2021–2022	0/13	nd	Mario Zucchelli	This study
EE2	2009	0/1	nd	McMurdo	Emnet et al. (2015)
	2009	0/1	nd	Scott Base	Emnet et al. (2015)
	2012–2013	7/13	0.0115–0.0778	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Esteban et al. (2016)
	2017, 2019	0/2	nd	Arctowski	Szopińska et al. (2022)
	2021–2022	0/13	nd	Mario Zucchelli	This study
EHMC	2009	0/1	nd	McMurdo	Emnet et al. (2015)
	2009	0/1	nd	Scott Base	Emnet et al. (2015)
	2012–2013	0/13	nd	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Domínguez-Morueco et al. (2021)
	2021–2022	8/13	nd - 0.79	Mario Zucchelli	This study
IBU	2012–2013	1/1	10	Esperanza	González-Alonso et al. (2017)
	2019	1/1	0.48	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.050–2.6	Mario Zucchelli	This study
KETO	2012–2013	1/1	nd or <LOQ	Esperanza	González-Alonso et al. (2017)
	2019	1/1	0.015	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	1.0–19	Mario Zucchelli	This study
NAPR	2012–2013	1/1	0.10	Esperanza	González-Alonso et al. (2017)
	2017, 2019	2/2	0.662–2.653	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.30–32	Mario Zucchelli	This study
PFOA	2012–2013	1/1	0.53	Esperanza	Domínguez-Morueco et al. (2021)
	2021–2022	7/13	nd - 0.061	Mario Zucchelli	This study
PFOS	2012–2013	0/1	nd	Esperanza	Domínguez-Morueco et al. (2021)
	2021–2022	12/13	nd - 0.095	Mario Zucchelli	this study
OC	2012–2013	0/1	nd	Esperanza	Domínguez-Morueco et al. (2021)
	2021–2022	13/13	0.45–4.9	Mario Zucchelli	This study
OD-PABA	2012–2013	0/1	nd	Esperanza	Domínguez-Morueco et al. (2021)
	2021–2022	0/13	nd	Mario Zucchelli	this study
TCS	2009	0/1	nd	McMurdo	Emnet et al. (2015)
	2009	1/1	0.24	Scott Base	Emnet et al. (2015)
	2012–2013	13/13	0.0752–0.807	Scott Base	Emnet et al. (2015)
	2012–2013	0/1	nd	Esperanza	Esteban et al. (2016)
	2019	0/1	nd	Arctowski	Szopińska et al. (2022)
	2021–2022	13/13	0.040–0.180	Mario Zucchelli	This study

larger number of traditional spot samples when single spot sampling is not suitable to provide sufficient information. Finally, the use of the integrative passive sampling in polar regions, characterized by harsh environmental conditions, is of paramount importance for monitoring purposes. In fact, this sampling strategy, avoiding frequent samplings, limits the effort of the scientific staff and the cost of the transport to the sites under investigation, but at the same time provides a complete portrait of the human impacts on the studied areas.

3.2. Discussion on other wastewaters in Antarctica

The results obtained by spot sampling in the wastewater effluent at MZS were compared with those reported in others scientific stations in Antarctica for the same ECs (Table 3). Including our results, 28 samples were taken from the Ross Sea and 2 or 3 from the Antarctic Peninsula.

In 3 of the research stations, some sort of treatment took place before release in the environment, but at Arctowski and Esperanza stations, no treatment took place at the time of sampling (Esteban et al., 2016; Szopińska et al., 2022).

Only in this study and previously at Scott Base were >2 samples collected. In Scott Base, only one sample was collected in 2009 after aerated fixed thin film beds and UV treatment. The UV system was then changed to an ozonation system, but it was mostly out of operation during the two large campaigns – daily for one week and monthly for 6 months – in 2012–2013 at the same station. At McMurdo, one single sample was collected after extended aeration and UV irradiation.

Regarding UV filters, BP-3 was the most frequently detected analyte, quantified in all analyzed samples from 4 research stations, with the sole exception of the Arctowski sample. The highest concentration of BP-3 was observed in MZS, at least one order of magnitude higher than those reported at Scott Base. EHMC on the other hand was only detected in this study, despite its extensive investigation at Scott Base. In the same samples at Scott Base, high concentrations were also found for 4-methylbenzylidene camphor and benzophenone-1 (0.32–11.7 and 0.024–6.8 μg L^{-1}, respectively). Finally, data on OC and OD-PABA is severely lacking, with only one previous investigation on a single sample collected at Esperanza Base. There, OC was only detected in the sample of suspended particulate matter. The current study is the first to report a constant presence of OC in Antarctic treated wastewater, thanks to the simultaneous use of spot and passive sampling.

The four studied NSAIDs and CAFF were detected in all samples but were only searched for in 2 or 3 non-treated samples outside of this study; thus, concentration levels are not easily comparable. Still, among the considered NSAIDs, only KETO concentrations were always significantly higher in our study than in the two other studies (Table 3), maybe suggesting different prescriptions of these pharmaceuticals in the different bases.

BPA and TCS were in the same range of concentrations in MZS and at Scott Base. There, a wide range of concentrations was observed, while values varied much less at MZS (especially for BPA).

3.3. Road Bay

A summarizing table of the detected compounds at this site is reported in the Supplementary Material (Table S12). In such a remote area, it is plausible that no other source of contamination could be significant rather than the research stations themselves. The huge dilution factor due to the water volume of the bay requires extremely sensitive methods; the exploitation of the high preconcentration factors obtained by passive samplers' deployment could therefore be useful in such cases.

The analysis of the POCIS sorbent extracts allowed to detect PFOA, PFOS, NAPR (in the same period as the peak of concentration detected in the WWTP), DCF and EHMC, all always under the LOQ. On the other hand, only BP-3 (which was never observed in the sorbent extracts) was detected in POCIS's PES membranes, during the second deployment, when the ice pack had melted. Regarding the 6 spot samples, 6 compounds were detected: PFOA, NAPR and IBU were detected only once and under LOQ while OC, BP-3 and GEM were at concentrations up to 38, 37 and 4.8 ng L^{-1} for, respectively. The detection of GEM was definitely unexpected, since this hypolipidemic drug was never found within the WWTP.

4. Risk assessment

Since the 2-week averaged WWTP spot sample concentrations for each compound did not significantly differ from TWA concentrations (when available), the highest individual spot sample concentration was used as the MEC for each compound.

Marine PNECs were used not only for the risk assessment at the sampling site in Road Bay, but also at the WWTP effluent discharge point. CAFF, PRX, and BPA presented the highest PNEC values among the studied ECs. The lowest PNECs were for PFOS, E1, E2 and EE2.

Overall, the highest risk for wastewater samples was attributed to IBU, followed by DCF and NAPR (Table 4). These three substances were always detected above their respective PNECs and IBU displayed the highest maximum HQ (2336) of all the detected compounds. IBU and DCF were also identified as part of the ECs presenting the highest risk at the wastewater discharge of the permanent base Esperanza, in Hope Bay (Olalla et al., 2020). Among compounds with a PNEC >1, only CAFF concentrations exceeded the PNEC with a max HQ of 2.8. Regarding PRX-TFL concentrations, the HQ was calculated considering in turn a total concentration of PRX or TFL. In the case of PRX a low risk was expected (HQ = 2.4), while TFL presented no significant risk (maximum HQ below 1). The low WW effluent volume mixes with the seawater at ever increasing dilution factors as the distance increases from the output. Still using marine PNECs, a rough estimation of problematic compounds for marine life in close proximity of the discharge point can be established. Considering the important dilution of the effluent in the bay, the actual risk in the marine environment should be lower.

Further away from the WWTP outlet, the much lower concentrations detected present a much lower risk. Although detected in one of the POCIS, NAPR and DCF were not detected in the SPEs and their PNEC > LOD. On the other hand, traces of IBU (<LOQ) were detected, slightly above its PNEC, demonstrating that IBU may still be problematic.

While EHMC, E1, PFOS, E2, and EE2 were not detected, their low PNECs were below detection limits, thus no reliable risk assessment was possible for these compounds.

5. Conclusions

This study represents the first passive sampling campaign in Antarctica for both semi polar and apolar compounds through accumulation in POCIS (both HLB phase and PES membranes). It also represents one of the more intensive spot sampling campaigns in Antarctica WW effluent waters.

The hypothesized usefulness of passive sampling was confirmed in particular in the small WWTP of the research base, since more concentration fluctuations were expected compared to classic urban WWTPs. In fact, spot sample concentrations were highly variable, leading to a very high uncertainty on the calculated average concentrations. Thus, the lower correlation among average grab sample results and passive sampling results for some analytes may be due to an insufficient number of spot samples to correctly represent the contamination situation. Passive sampling, on the other hand, helped in reliably estimating TWA concentrations over a time period, reducing the need for intensive and costly grab sampling monitoring to take into account variability in the WW contamination, especially in such a remote region.

The ECs detected at the highest concentrations and in every sample included CAFF and four NSAIDs. Considering literature data on the presence of organic ECs in the wastewater of research stations in Antarctica, only KETO showed a significant higher concentration in MZS. Despite those high levels, the treated volume is lower compared to

Table 4
Risk assessment. na "not assessed" due to signal suppression, ND not detected; a: LOD < PNEC < LOQ, b: PNEC < LOD.

Compound	Highest measured concentration [$\mu g\ L^{-1}$]		Lowest PNEC [$\mu g\ L^{-1}$]	Frequency of detection [%]		Frequency of PNEC exceedance [%]		Hazard quotient	
	WWTP effluent	Road Bay	Marine water	WWTP (N = 13)	Road Bay (N = 6)	WWTP (N = 13)	Road Bay (N = 6)	WWTP	Road Bay
OC	4.88	0.038	23	100	50	100	33	0	0
BPA	0.45	ND	16	100	0	0	0	0	–
CAFF	24.69	na	8.7	100	na	62	na	2.8	na
TFL[a]	5.03	na	10	100	na	0	na	0.5	na
PRX[a]	5.03	na	2.14	100	na	62	na	2.4	na
KETO	18.57	ND	0.21	100	0	100	0	88	–
CBZ	nd	na	0.2	0	na	0	na	–	na
NAPR	32.05	ND	0.17	100	0	100	0	189	–
BP-3	1.99	0.037	0.067	100	50	100	50	30	0.6
GEM	nd	0.0048	0.05	0	33	0	17	–	0.1
OD-PABA	nd	ND	0.03	0	0	0	0	–	–
PFOA	0.07	<LOQ	0.018	54	17	54	<17a	4	−a
TCS	0.18	ND	0.0069	100	0	100	0	26	–
DCF	2.47	ND	0.005	100	17	100	0	494	–
EHMC	0.79	ND	0.0027	62	0	62b	0b	291	−b
IBU	2.57	<LOQ	0.0011	100	17	100	17	2336	−b
E1	0.17	ND	0.00036	15	0	15b	0	469	−b
PFOS	0.09	ND	0.0002	92	0	92	0b	474	−b
E2	ND	ND	0.00004	0	0	0b	0b	−b	−b
EE2	ND	ND	0.0000037	0	0	0b	0b	−b	−b

[a] The HQ was calculated considering in turn a total concentration of PRX or TFL, since dividing the contributions of the two analytes was not possible.

a standard WWTP, being thus subjected to huge dilution in the near bay. Indeed, a preliminary risk assessment did not highlight especially critical situations on single compounds in Road Bay.

Given the advantages of passive sampling to investigate contamination of polar regions, caused by the research activities, future research may involve the deployment of such devices in other international stations. A comparison of the impacts may serve for a more diffused risk assessment in different Antarctic regions. If critical situations should be observed, a push towards upgrading the treatment plants could be necessary.

CRediT authorship contribution statement

Henry MacKeown: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Chiara Scapuzzi:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Matteo Baglietto:** Writing – review & editing, Methodology, Investigation, Data curation. **Barbara Benedetti:** Writing – review & editing, Supervision, Methodology. **Marina Di Carro:** Writing – review & editing, Supervision. **Emanuele Magi:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.171755.

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