Polycyclic aromatic hydrocarbon sorption and bacterial community composition of biodegradable and conventional plastics incubated in coastal sediments

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HIGHLIGHTS

- PS sorbed more PAHs than the other plastic types (PA, CA, PLLA).
- The PAH concentrations were lower in plastics than in the sediment.
- The bacterial community composition on CA differed from that of the other plastic types.

GRAPHICAL ABSTRACT
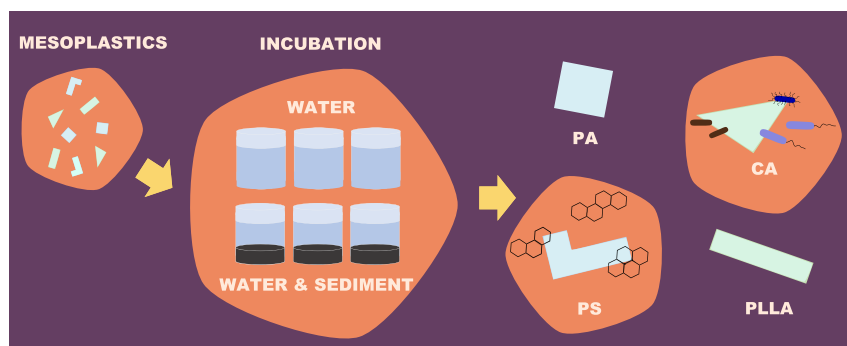
ABSTRACT

Resistant to degradation, plastic litter poses a long-term threat to marine ecosystems. Biodegradable materials have been developed to replace conventional plastics, but little is known of their impacts and degradation in marine environments. A 14-week laboratory experiment was conducted to investigate the sorption of polycyclic aromatic hydrocarbons (PAHs) to conventional (polystyrene PS and polyamide PA) and bio-based, biodegradable plastic films (cellulose acetate CA and poly-L-lactic acid PLLA), and to examine the composition of bacterial communities colonizing these materials. Mesoplastics (1 cm^2) of these materials were incubated in sediment and seawater collected from two sites in the Gulf of Finland, on the coast of the highly urbanized area of Helsinki, Finland. PS sorbed more PAHs than did the other plastic types at both sites, and the concentration of PAHs was consistently and considerably smaller in plastics than in the sediment. In general, the plastic bacterial biofilms resembled those in the surrounding media (water and/or sediment). However, in the sediment incubations, the community composition on CA diverged from that of the other three plastic types and was enriched with Bacteroidia and potentially cellulolytic Spirochaetia at both sites. The results indicate that certain biodegradable plastics, such as CA, may harbour potential bioplastic-degrading communities and that PAH sorption capacity varies between polymer types. Since biodegradable plastics are presented as replacements for conventional plastics in applications with risk of ending up in the marine environment, the results highlight the need to carefully examine the environmental behaviour of each biodegradable plastic type before they are extensively introduced to the market.

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1. Introduction

Marine litter, consisting of a wide range of materials that are artificially produced or modified, is a ubiquitous threat to the marine environment (UNEP 2009). Synthetic polymers, or plastics, represent by far the largest category of marine litter (Galgani et al. 2015). The predominance of plastic materials among marine litter is due to their massive, ever-growing production volumes, wide application in society, poor waste-management practices and resistance to degradation (Andrady 2015; Chen 2015; PlasticsEurope 2019).

Most of the plastic litter probably ends up on the seafloor (Barnes et al. 2009). Plastics denser than seawater readily sink, whereas the more buoyant floating plastics begin to settle when their density increases as a result of biofilm formation (Lobelle and Cunliffe 2011). On the seafloor, the distribution and abundance of plastic litter is patchy, and in coastal areas densities range from 0 to >7700 items per km^2 (Galgani et al. 2015; Maes et al. 2018).

Most plastics are very resistant to biological degradation, especially in the dark, cold and sometimes oxygen-deprived conditions prevailing in deeper parts of the sea (Andrady 2015). Hence, plastics can cause long-lasting harm to benthic ecosystems, e.g. by smothering and entanglement of marine organisms (Kühn et al. 2015), inhibiting gas exchange between the sediment and overlying water (Green et al. 2015) and leaching out harmful substances (Suhrhoff and Scholz-Böttcher 2016).

Plastics also serve as human-introduced substrates for microbial colonization (plastisphere) in marine environments (Carpenter et al. 1972; Zettler et al. 2013). They are rapidly colonized both in the sediment (Harrison et al. 2014) and in the water column (Oberbeckmann et al. 2014; De Tender et al. 2017). The microbial succession on plastics resembles that on any other surface and is divided into three stages: primary colonizing, growth and maturation phases (Lorite et al. 2011; Dang and Lovell 2000; Salta et al. 2013; Harrison et al. 2018). Some studies have observed differences in bacterial communities on plastic surfaces, compared with other biofilms (Kirstein et al. 2018; Ogonowski et al. 2018), whereas others have not (incubations varying from 2 to 6 weeks) (Oberbeckmann et al. 2014, 2016, 2018). Thus, the existence of distinct plastisphere bacterial communities is still under debate (reviewed in Amaral-Zettler et al. 2020).

Most of the studies on plastisphere bacterial communities and environmental impacts of plastics have focused on conventional plastics (e.g. polyolefins). They dominate the production and consumption of plastics globally (PlasticsEurope 2019) and thus also represent the most common plastic types found in marine ecosystems (e.g. Ory et al. 2020). However, bioplastics (i.e. plastics produced from biological source materials) have been developed in response to environmental concerns related to conventional plastics, and although their percentage in the global market is still small (less than 1%), their production is expected to increase almost fivefold over the next 5 years (Verbeek and Uitto 2017). The renewable resources used to produce bioplastics include starch, cellulose, plant oils or bacterially produced polyhydroxyalkanoates (PHAs) (Chen 2010; Iwata 2015). Bioplastics can also be biodegradable; as such, microorganisms can fully degrade them to carbon dioxide and water (Song et al. 2009).

Before rushing to replace conventional plastics with new materials, their potential impacts on the environment should be carefully investigated. For example, knowledge of the actual degradation of biodegradable bioplastics in the marine environment and the community composition of microbial biofilms on them is still scarce (Dussud et al. 2018; Morohoshi et al. 2018) and, hence, there is a need to investigate their fate and effects in marine systems. There are promising results demonstrating that certain bioplastics may be colonized by specialized and more active bacterial communities compared with conventional plastics (Dussud et al. 2018). Certain starch-based biodegradable plastics already show signs of degradation within 2 weeks in the benthic habitat (Eich et al. 2015). However, a study examining putatively

biodegradable plastic bags showed no signs of biodegradation after 98 days of incubation in organic-rich marine sediments, even though the plastic was covered with rich microbial biofilm (Nauendorf et al. 2016).

Plastics on the seafloor may also act as adsorption surfaces for the reservoir of harmful substances deposited and accumulated in the sediments. In the Baltic Sea, especially polycyclic aromatic hydrocarbons (PAHs) are ecologically relevant, due to their wide abundance (e.g. Pikkarainen 2004), persistence, as well as acute and chronic toxicity (carcinogenicity and mutagenicity; e.g. Tobiszewski and Namieśnik 2012). They are continuously emitted into the Baltic Sea from combustion processes (e.g. marine and land traffic, power plants, household wood burning) and land and marine spills of refined oil products (Witt 2002). In this study, PAHs were selected as model substances to study the vector-effect of plastics, since it is known that plastics are able to adsorb PAHs and polychlorinated biphenyls (PCBs) from their surrounding water, and act as their potential vectors to biota (Besseling et al. 2013; Rochman et al. 2013a). Especially those plastics of smaller size, i.e. microplastics (particle size <5 mm), may be efficient vectors, because they have large surface area-to-volume ratios for adsorption. For example, significantly higher concentrations of hydrophobic organic contaminants (HOCs) (PCBs and dichlorodiphenyldichchloroethylene (DDE)) are found in microplastics than in the ambient seawater (Mato et al. 2001). Due to their small size, microplastics can be readily ingested by various organisms on the seafloor (Courtene-Jones et al. 2017; Setälä et al. 2016a; Taylor et al. 2016).

The aim of the present study was to compare selected conventional plastics with biodegradable bioplastics with respect to their proposed vector-effect for PAHs in sediments of the brackish Baltic Sea. In addition, bacterial communities on various plastic polymers were compared to evaluate their potential ability to degrade synthetic polymers.

2. Material and methods

2.1. Preparation of plastic pieces

Films of transparent plastics were purchased from Goodfellow Cambridge Ltd. (Huntingdon, Cambridgeshire, UK). We selected two conventional plastic films (ST311050 polystyrene (PS) film; AM301051 polyamide (PA) - nylon 6 film) and two biodegradable plastic films (AC311051 cellulose acetate (CA) film; ME331050 poly-L-lactic acid (PLLA) film) with a similar thickness (0.06 mm for PA, 0.05 mm for other types). Their selection was based on their negative buoyancy in Baltic Sea water and wide usage in society. PS is one of the most common plastic polymers used, e.g. in food packaging, PA is extensively used in fishing lines and nets, while cigarette filters are made of CA and polylactides are commonly used in packaging (Gross and Bhanu 2002; Andrady 2015; PlasticsEurope 2019). Plastic films were placed over blotting paper and cut to same-sized pieces (surface area of 1 cm^2), but into different shapes to allow their distinction. When applicable, the equipment was precleaned with 70% ethanol, and nitrile gloves were used to prevent microbial contamination. The plastic pieces were placed in glass vials (20 ml), covered with aluminium foil and weighed (Mettler Toledo AX205, Greifensee, Switzerland); 20 pieces of each plastic type were produced for each experimental unit. On average, the total weight of the 80 plastic pieces per cylinder was 495 mg, consisting on average of 104.0 ± 2.1 mg (standard deviation sd) of PS, 129.9 ± 4.5 mg of PA, 130.0 ± 3.8 mg of PLLA and 131.5 ± 1.6 mg of CA. The difference in weights of the plastic types was dependent on their specific densities and possible cutting errors.

2.2. Sample collection

Sediment and water for the experiment were collected as a part of the City of Helsinki Urban Environment Division's routine monitoring in autumn 2017. The sampling sites were located in the Helsinki (capital of Finland) area and selected, based on the different expected PAH sources in the surface sediment deposits. The first site, West Harbour

(WH; 60.15904° N, 24.93003° E, depth 8.8 m), is a passenger and cargo harbour in Helsinki that was Europe's second most active passenger harbour in 2016. The second site, Vanhankaupunginlahti Bay (VKL; 60.19587° N, 24.99375° E, depth 2.5 m) was a recipient area of treated municipal waste waters until the 1980s. The Vantaanjoki River, meandering across densely populated regions (more than one million people in its catchment area), also flows into the bay. Currently, the bay is a nature reserve belonging to the European Union's Natura 2000 programme and is also classified as a BirdLife International's Important Bird Area (Fig. 1).

Sediment samples were taken with a GEMAX gravity corer (Oy Kart Ab, Somero, Finland), which consists of two parallel core barrels. From WH, four sediment cores (two GEMAX lifts) were taken at one time, and the topmost 10 cm of each sediment core were stored in clean glass jars. One core from each GEMAX lift was mixed together to produce two pooled samples. These pooled samples were homogenized, and one sample was used for PAH analyses and another for the laboratory incubation. From VKL, the sediment for the PAH analyses and for the laboratory incubation was collected on different sampling occasions, but each sample also consisted of two 10-cm sediment cores (one GEMAX lift) that were homogenized. In addition to sediment sampling, 20 l of seawater (salinity 3–5) were collected with a custom-made Ruttner-type water sampler (sampler volume: 2.8 l) into glass bottles right above the seafloor at both sampling sites. The sediment and water samples were placed in coolers and transported to a temperature-controlled room (8 °C, dark) immediately after sampling.

2.3. Experimental setup

The experiment was conducted in a temperature-controlled room (8 °C, dark) at Tvärminne Zoological Station, University of Helsinki during autumn and winter 2017–2018. Nitrile gloves were used when processing the samples, and all equipment was cleaned with 70% ethanol prior to use. Plastic material was avoided; instead, equipment made of glass and steel was prioritised.

The sediment was carefully mixed, and the macrofauna (the bivalve *Limecola balthica*) were removed. Homogenized sediment, 400 ml per

Fig. 1. Map of the Baltic Sea and an insert of the Helsinki metropolitan coastal sea area with the two sampling stations (West Harbour = WH, Vanhankaupunginlahti Bay = VKL).

sampling site, was added into each of three experimental units (glass cylinders: height 21 cm, diameter 16.5 cm). Due to the varying water content of the sediment, this volume corresponded to approximately 191.5 g of dry sediment in each WH unit and approximately 90.4 g of dry sediment in each VKL unit. Then, 600 ml of unfiltered seawater collected from the same location were added into each cylinder on top of the sediment, as well as into three empty cylinders acting as control units. All six units were placed in a water bath with a 10-cm layer of precooled water (8 °C) to buffer temperature changes. The units were left overnight to settle.

On the next day, 80 plastic pieces (20 of each plastic type) were added to each experimental unit. Every piece was individually placed with tweezers to ensure they did not overlap. The pieces placed on the sediment surface were gently buried a few millimetres below the surface, and the unit was carefully shaken to cover the plastics with loose sediment. In the control units, the plastic pieces were placed on the bottom of the unit. Water was then gently added to all units to reach a total volume of 2.5 l. Air pumps were used to constantly aerate the units, and lids were placed on top of them to prevent evaporation. The temperature and oxygen concentration were measured weekly from the units (YSI Environmental ProODO™, YSI Inc., Yellow Springs, OH, USA).

The plastics were incubated in the units for 14 weeks, after which the experiment was terminated. During the experiment, the average temperature was 9.5 ± 1.4 °C (sd), and the oxygen concentration 10.9 ± 0.7 mg/l. At the end of the experiment, 0.5 l of water were taken from each unit and filtered onto sterile 0.22-μm membrane filters (Ø 47 mm; Whatman GE Healthcare, Little Chalfont, Buckinghamshire, UK), and a sample from the sediment was pipetted for microbial community analysis. The filters and samples were frozen immediately at −80 °C. To collect the incubated plastic pieces, the contents of each unit (water and sediment) were poured through a metal sieve with a mesh size of 4 mm. Ten plastic pieces of each type were packed into glass vials and stored at −20 °C for further PAH analysis, and the remaining pieces were put into plastic tubes for microbial analysis. No apparent degradation of any of the plastic types was observed in visual inspection after the incubations.

2.4. Sample analysis

2.4.1. PAH analyses

Analyses of PAHs in the sediment and plastic samples were conducted in laboratories specialized in environmental samples and accredited by the Finnish Accreditation Service (FINAS). The sediment samples, which were part of the City of Helsinki Environment Service's routine monitoring campaign, were analysed by their partner MetropoliLab Oy (Helsinki, Finland). However, since MetropoliLab does not offer PAH analyses from plastics, they had to be ordered from the Laboratory Centre of the Finnish Environment Institute (Helsinki, Finland). For the sediment PAHs, the limit of quantification (LOQ) was 20–100 μg/kg depending on the congener, whereas for PAHs analysed from plastics, the LOQ was 0.5 μg/kg. For concentrations falling below these limits, the concentrations were assumed to be at the LOQ. Hence, the reported concentrations represent maximum estimates of PAH concentrations in the sediments and on plastics.

The PAHs were extracted and analysed from the sediment samples (one pooled sample from each site) according to SFS-ISO 18287: 2007. Briefly, NaCl, a mixture of internal standards (acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, naphthalene-d8) and extraction solvents (methanol, acetone, hexane, water) were added to the weighed sample. The sample was mixed briefly by hand, then on a shaker for 30 min. After shaking, the sample was centrifuged for 5 min (Eppendorf Centrifuge 5810 R, Eppendorf, Hamburg, Germany). An extract was taken from the surface of the sample into a test tube, Na2SO4 and Al2O3 were added and vortexed briefly (Heidolph Reax Top, Heidolph Instruments, Schwabach, Germany). The purified extract
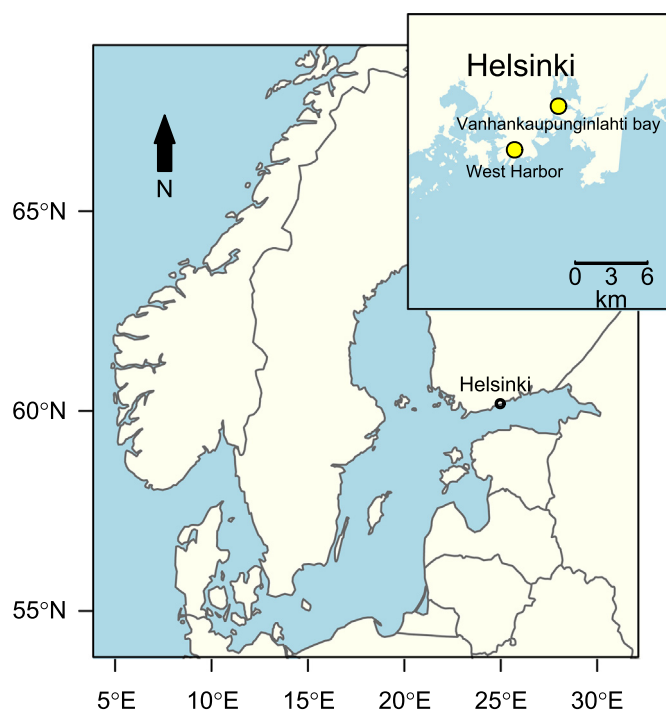
was taken up in a new test tube, where the extract was concentrated to a small volume (0.5 ml) with a stream of nitrogen gas and analysed, using gas chromatography–mass spectrometry (Agilent 6890 GC (Agilent Technologies, Beijing, China) - 5973 N MSD (Agilent Technologies, Santa Clara, CA, USA); analytical column Agilent HP5-MSUI, 30 m × 0.25 mm × 0.25 um; Agilent Technologies, Santa Clara, CA, USA). The concentrations were normalized, using a Dutch standard of 10% organic matter. The concentrations were expressed as μg/kg sediment dry weight (dw).

Plastic pieces of the same polymer type in each experimental unit were pooled into one sample. This resulted in three replicates of each plastic type incubated in the sediment and three replicates incubated in water at both sites. The samples were mixed with internal standards (fluorinated PAHs: 1-fluoronaphthalene, 4-fluorobiphenyl, 3-fluorophenanthrene, 1-fluoropyrene, 3-fluorochrysene, 9-fluorobenzo(k)fluoranthene), and the PAHs were extracted from all samples without pretreatment by shaking them twice for 1 h in 5 ml of n-hexane. The extract was concentrated to a smaller volume, using nitrogen gas, and 100 μl of isooctane (solvent keeper) were added. After concentration, the final volume of each plastic sample extract was 100 μl. The PAHs extracted from the plastics were identified and quantified by gas chromatography–tandem mass spectrometry (Trace 1310 GC Ultra gas chromatograph (Thermo Fisher Scientific, San Jose, CA, USA); TSQ Quantum XLS ultra mass spectrometer (Thermo Fisher Scientific); TriPlus RSH autosampler (Thermo Fisher Scientific, Rodano, Milan, Italy).

A total of 25 PAH congeners were analysed (24 from the sediments and 21 from the plastics, of which 20 were analysed from both matrices). These congeners were naphthalene (NP), 2-methylnaphthalene (2-MNP), 1-methylnaphthalene (1-MNP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP). In addition to these, biphenyl (BP), 2,6-dimethylnaphthalene (2,6-DMN), 2,3,5-trimethylnaphthalene (2,3,5-TMN) and 1-methylphenanthrene (1-MPH) were analysed from the sediments and triphenylene (TRI) from the plastics.

2.4.2. Bacterial community analyses

DNA was extracted with a DNeasy PowerSoil kit (Qiagen, Hilden, Germany) and stored at −80 °C for further processing. Negative controls without samples were also extracted to control possible contamination.

For sequencing, the 16S ribosomal RNA gene region V3-V4 was amplified with a two-step polymerase chain reaction (PCR), using the universal bacterial primers 341F and 785R (Klindworth et al. 2013). PCR and Illumina MiSeq (Illumina Inc., San Diego, CA, USA) paired-end multiplex sequencing were performed at the Institute of Biotechnology, University of Helsinki, Finland (Aho et al. 2019).

In total, 9.9 million paired raw reads were obtained with the Illumina MiSeq platform. Primer removal was done with Cutadapt (settings -m 1 —O 15 -e 0.2, V 1.10 with Python 2.7.3; Martin 2011). The reads were merged and processed according to the DADA2 pipeline (DADA2 v. 1.4.0, Rcpp v. 0.12.19; Callahan et al. 2016) with filterAndTrim maxEE = 3. After filtering and trimming, a total of 6.2 million sequences remained, of which 4.9 million were merged and 4.2 million were nonchimeric and used for further analyses. Taxonomic classification of the amplicon sequence variants (ASVs) was done with DADA2 default parameters (minBoot = 50), using Silva for DADA2 (v. 123; Quast et al. 2013, Callahan 2018). Before the statistical analyses, chloroplast and mitochondria sequences were removed, ending up with 7357 ASVs. The raw reads were deposited into the Sequence Read Archive of the National Centre for Biotechnology Information, under BioProject accession number PRJNA646885.

2.5. Statistics and data analysis

Diagnostic ratios of the PAH isomers present in the sediments were calculated to indicate whether they were of petrogenic or pyrogenic origin. The following concentration-based diagnostic ratios were calculated: low-molecular-weight (LMW) PAHs (2–3 aromatic rings)/high-molecular-weight (HMW) PAHs (4–6 aromatic rings) (LMW/HMW), ANT/(ANT+PHE), FLA/(FLA + PYR), BaA/(BaA + CHR), IcdP/(IcdP +BghiP) and HMW/PAHsum.

Statistical analyses were performed with R (v. 3.6.1; R Core Team 2019), using the car package (v. 3.0–8; Fox and Weisberg 2019). One-way analysis of variance (ANOVA) with Tukey's test was used to compare the concentrations of the PAHs on different plastic types, and the *t*-test for independent samples was used to compare the PAH concentrations on plastics incubated in different matrices (sediment/water). In some cases, the data were log-transformed to achieve normality. Levene's test was used to verify the homogeneity of variance, and occasional unequal variances were corrected with Welsh modification. The nonparametric Kruskal-Wallis test was used for plastic-type comparison when the transformation did not correct the normality, and Dunn's test with Bonferroni adjustment was used for pairwise comparisons of the PAHs in different plastic types. The nonparametric Mann-Whitney *U* test was used for comparison between matrices when issues with normality could not be corrected with transformations. A significance level of 0.05 was used, and the results were given as the average (± sd). Figs. 2 and 3 were drawn with R (v. 3.6.1; R Core Team 2019), using the ggplot2 package (v. 3.3.2; Wickham 2016) and edited with Inkscape (v. 1.0).

Pairwise comparison between PA (conventional plastic) and CA (bioplastic) was performed to explore the differences between bacterial community composition on conventional and biodegradable plastics. DESeq2 (v. 1.28.1; Love et al. 2014) with default parameters was used to analyse the differential abundant taxa between bacterial communities on PA and CA, using an adjusted *p*-value of 0.05 as a cutoff. The figures were drawn with R (Fig. 4 and Fig. 6 with v. 3.5.2, and Fig. 5 with v. 4.0.0; R Core Team 2018); Fig. 5 with ggplot2 (v. 3.3.1; Wickham 2016) and Fig. 4 and Fig. 6 (Bray-Curtis dissimilarity) with phyloseq (v. 1.26.1; McMurdie and Holmes (2013)).

3. Results and discussion

3.1. PAHs in sediments

Of the 24 targeted PAH congeners 12 exceeded their LOQs in WH and 7 in VKL. The highest concentrations were quantified for PHE, FLA, PYR, BaA and CHR, but the congener profile and PAHsum in WH and VKL differed (Table S1). In WH, the sum of PAHs exceeding their LOQs was 1570 μg/kg dw (maximum concentration based on LOQs: 2670 μg/kg dw) and in VKL 1670 μg/kg dw (maximum concentration based on LOQs: 2930 μg/kg dw). These values were higher than the total PAH concentrations earlier measured from the sediments of the Gulf of Finland (611–847 μg/kg dw) (Pikkarainen 2004). However, based on routine monitoring of the study area (32 sampling stations) in 2017, the average (± sd) total PAH concentration in sediments in the coastal areas outside Helsinki was 996 (± 1630) μg/kg dw, with a maximum observation of 8400 μg/kg dw (Vahtera et al. 2018). In other parts of the Baltic Sea, such as in the Arkona Basin and Mecklenburg Bight in the southern Baltic, the total PAH concentrations were more similar to those in the present study, varying between 800 and 1900 μg/kg dw (Witt 1995).

For most of the PAH compounds, the concentrations were below the environmental risk limits given in the Finnish national guidelines for dumping of dredged sediments at sea (Ympäristöministeriö 2015) with a few exceptions: the concentration of BaA (810 μg/kg dw) and CHR (720 μg/kg dw) in VKL and BaA (210 μg/kg dw) and FLA (310 μg/kg dw) in the WH exceeded the 1B lower environmental risk limit
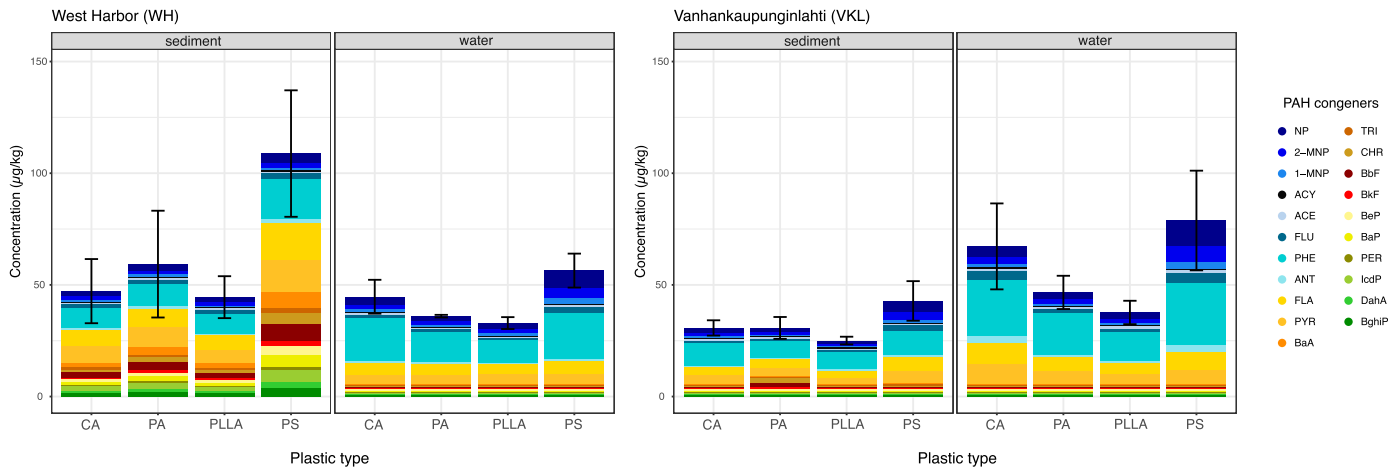
Fig. 2. Average sum of polycyclic aromatic hydrocarbon (PAH) congeners and total PAHs (mean and sd, $n = 3$) in the plastic types examined (CA = cellulose acetate, PLLA = poly-L-lactic acid, PA = polyamide, PS = polystyrene) incubated in West Harbour (WH) and Vanhankaupunginlahti Bay (VKL) sediments and water.

(100 μg/kg dw for BaA, 200 μg/kg dw for FLA, 300 μg/kg dw for CHR). Despite being above the limit, these concentrations are still considered to represent normal intrinsic background concentrations and thus are unlikely to cause harm to aquatic organisms (Ympäristöministeriö 2015).

In most cases, the PAH diagnostic ratios at both sites indicated pyrogenic rather than petrogenic sources. The LMW/HMW ratio was <1 at both sites (WH 0.24, VKL 0.06), signalling a pyrogenic source (Zhang et al. 2008), and other examined diagnostic ratios further support this: an ANT/(ANT+PHE) ratio > 0.1 (WH 0.125, VKL 0.5) indicates the predominance of pyrogenic sources, and an FLA/(FLA + PYR) ratio > 0.5 (WH 0.65, VKL 0.5) indicates grass, wood and coal combustion. The BaA/(BaA + CHR) ratios were 0.6 and 0.53 for WH and VKL, respectively, and thus over the 0.35 threshold value, indicating coal combustion (Tobiszewski and Namieśnik 2012 and references therein). The HMW/PAHsum ratio was >0.5 at both locations (WH 0.8, VKL 0.94), indicating petroleum burning, coal combustion and softwood combustion (Biache et al. 2014 and references therein). Our results correspond to the estimations that most PAHs in the environment are released from combustion processes, such as energy production and industrial processes (Zhang and Tao 2009). The predominance of these sources was predictable, since large coal- and wood-fired power plants are located near both sampling sites (Hanasaari and Salmisaari power plants). However, the sites differed in their IcdP/(IcdP+BghiP) ratio. In WH,

the value of 0.31 signalled petroleum combustion (Yunker et al. 2002), which is not surprising: WH is an active harbour, where a likely source of PAHs is maritime traffic. In VKL the IcdP/(IcdP+BghiP) ratio of 0.5 indicated grass, wood and coal combustion (Yunker et al. 2002).

3.2. Sorption of PAHs on plastics

3.2.1. Differences between plastic types

At both sites and matrices examined the PAHsum differed between plastic types, as determined by one-way ANOVA; WH sediment (F $(3,8) = 5.891$, $p = 0.020$), WH water (F$(3,8) = 10.82$, $p = 0.003$), VKL sediment (F$(3,8) = 7.045$, $p = 0.034$), VKL water (F$(3,8) = 4.465$, $p = 0.040$). PS consistently sorbed greater concentrations of PAHs than did CA, PLLA and PA (Fig. 2), which is in line with previous studies comparing the sorption capacities of different plastic types (Lee et al. 2014; Rochman et al. 2013b). In WH sediments, the PAHsum was significantly higher in PS (mean 108.8 ± 28.3 μg/kg) than in CA (47.2 ± 14.4 μg/kg) ($p = 0.032$) and PLLA (44.5 ± 9.4 μg/kg) ($p = 0.024$). In WH water, the PAHsum was higher in PS (56.4 ± 7.6 μg/kg) than in PA (36.0 ± 0.6 μg/kg) ($p = 0.009$) and PLLA (32.9 ± 2.7 μg/kg) ($p = 0.004$). In VKL sediment, the PAHsum was higher in PS (42.8 ± 8.8 μg/kg) than in PLLA (25.1 ± 1.7 μg/kg) ($p = 0.008$). Similarly, PS (78.8 ± 22.3 μg/kg) having a higher concentration than PLLA (37.6 ± 5.2 μg/kg), was also observed in VKL water ($p = 0.046$). The
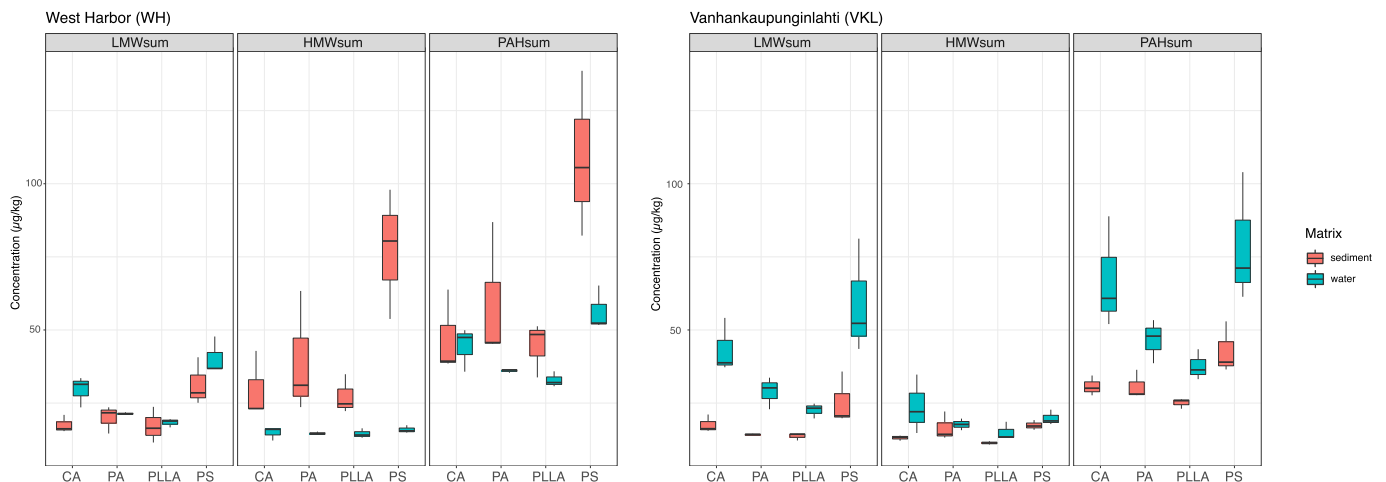

Fig. 3. Concentrations of low-molecular-weight (LMW) and high-molecular-weight (HMW) polycyclic aromatic hydrocarbons (PAHs) and PAHsums in plastics (CA = cellulose acetate, PLLA = poly-L-lactic acid, PA = polyamide, PS = polystyrene) incubated in West Harbour (WH) and Vanhankaupunginlahti Bay (VKL) sediments and water.
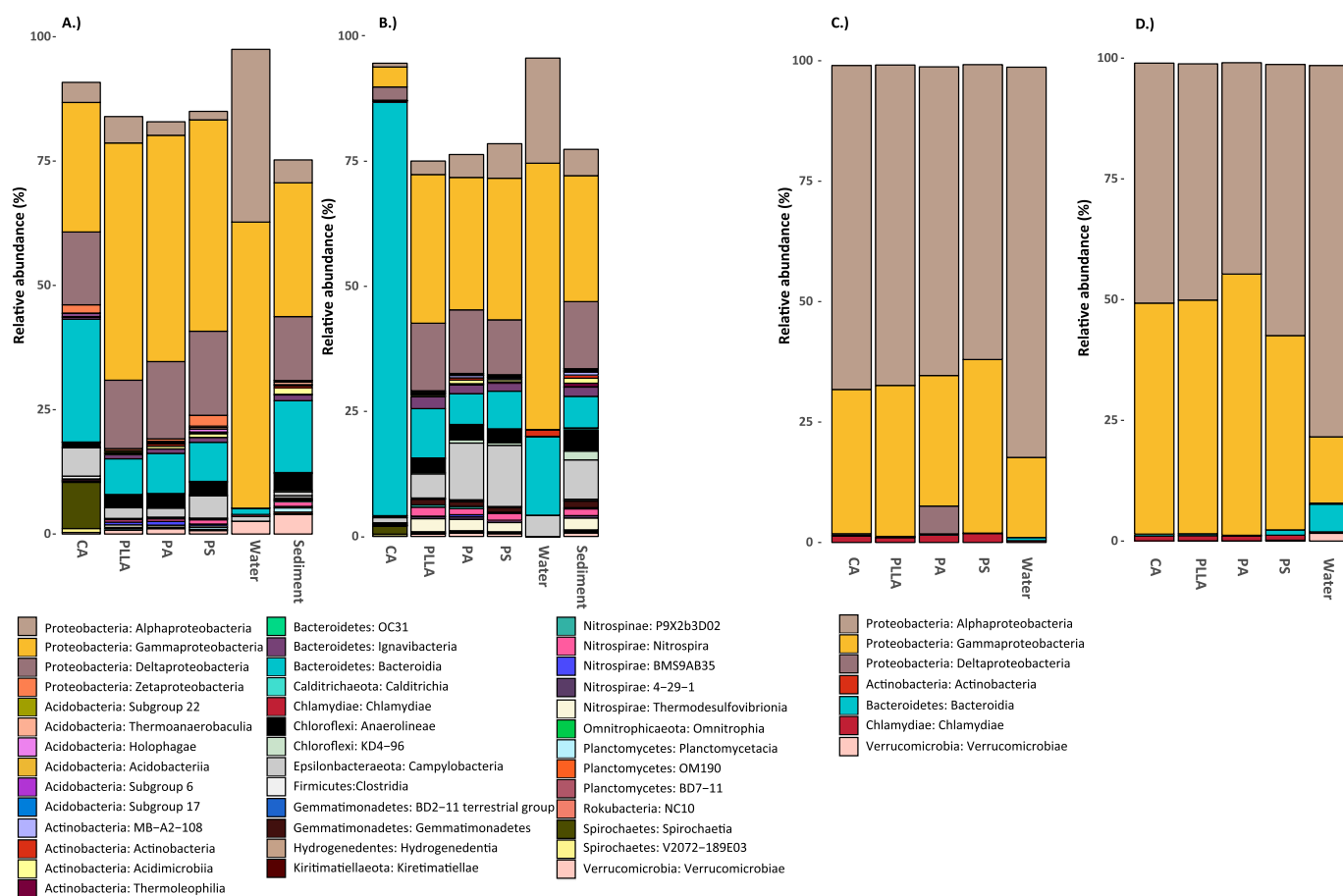
Fig. 4. Class-level bacterial diversity of 16S ribosomal RNA (rRNA) gene sequences (~450 base pairs bp) representing >0.1% of all amplicon sequence variants (ASVs) on different plastic types (CA = cellulose acetate, PLLA = poly-L-lactic acid, PA = polyamide, PS = polystyrene) and in sediment and water in West Harbour (WH) (a, c) and in Vanhankaupunginlahti Bay (VKL) (b, d).

concentrations of individual PAH congeners in plastic replicates are presented in Table S2.

Various polymers show different ratios of amorphous and crystalline contents (Müller et al. 2018). Since sorption occurs predominantly in amorphous domains (Teuten et al. 2009), these ratios are likely to impact the sorption capacities of the plastic types examined. The relatively high sorption capacity of PS probably stems from the amorphous structure of the PS molecule (Rochman et al. 2013b). Each of the styrene monomers contains aromatic rings that are randomly distributed on both sides of the polymer chain, creating a space between adjacent polymer chains where chemicals can diffuse (Pascall et al. 2005). Hydrophobic PAHs can also be effectively adsorbed onto hydrophobic PS, due to noncovalent π–π interactions between the aromatic groups (e.g. Claessens and Stoddart 1997). According to the manufacturer, CA is defined as an amorphous and PA as a semicrystalline polymer, whereas PLLA has high crystallinity (60–70%). In accordance with its high crystallinity, the concentrations of PAHs measured from PLLA were lower, albeit not significantly, than in other plastic types. PLLA is also highly hydrophobic (e.g. Neumann et al. 2017), but is devoid of aromatic groups and harbours oxygen heteroatoms, explaining PLLA's tendency as a less active adsorbent for PAHs. The PA type used in the present study was nylon-6 (polycaprolactam), a hydrophobic plastic with five unsubstituted alkyl carbons in each monomer unit and expected to have relatively good PAH absorptivity. PA is less hydrophobic than PS (e.g. Min et al. 2020), but does not provide any π–π-type adsorption. The hydrophobicity of CA is dependent on its degree of hydroxyl-by-acetyl substitution per hexose unit. Here, we are unaware of the acetyl substitution degree of the CA type used. The quite similar

PAH adsorption affinity onto CA (Fig. 2) compared with PLLA and PA suggests a high degree of CA acetylation.

In the 14-week incubation, the higher PAH concentration on PS may reflect its capability for reaching equilibrium between the plastic and the surrounding media faster than the other plastic types examined. Since the sorption kinetics were not followed, it is not possible to know whether the equilibrium was achieved. In previous studies investigating the sorption behaviour of PAHs to high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) plastics, PAHs with lower molecular weight (MW) and lower octanol/water partition coefficient (log K_{ow}) achieved saturation faster than PAHs with higher MW and log K_{ow} (Rochman et al. 2013a). In contrast, when a similar study was conducted with PS, no obvious differences in sorption patterns were observed, and the sorption equilibrium was achieved quickly after deployment (Rochman et al. 2013b). Hence, this suggests that the rate in which the equilibrium is achieved is dependent not only on the MW of PAHs, but also on the plastic type. This agrees with the previous study (Rochman et al. 2013b), in which the sorbed concentrations of PAHs in PS, HDPE and LDPE were similar after 6 months of incubation, but PS reached its predicted equilibrium faster.

Ultimately, our results show that during the 3-month burial in PAH-containing sediments, both conventional and biodegradable plastics sorbed PAHs. The sorption to various plastics is affected by the macroscopic material properties (e.g. surface area, three-dimensional shape), degree of crystallinity plus hydrophobic and noncovalent interactions. The biofilms on plastic may also play a role in PAH sorption; in this study, the plastics were analysed with their associated biofilms,
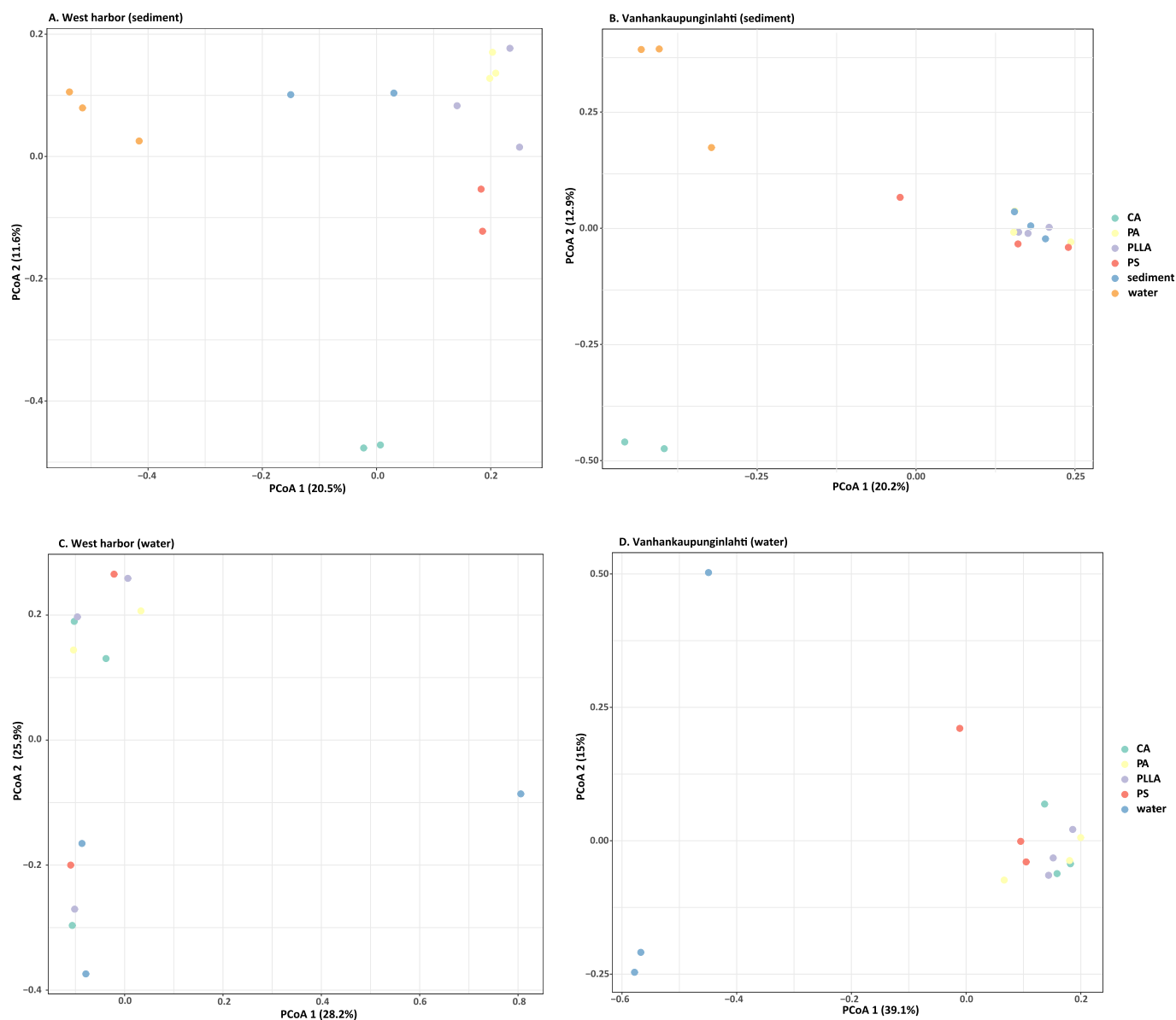
Fig. 5. Principal coordinate analysis (PCoA) plots showing bacterial community dynamics on different plastic types CA = cellulose acetate, PLLA = poly-L-lactic acid, PA = polyamide, PS = polystyrene and in sediment and water in West Harbour (A, C) and in Vanhankaupunginlahti Bay (B, D).

representing environmentally relevant circumstances for animals ingesting plastics.

3.2.2. Differences between sites and matrices

When plastics incubated in sediment and water were compared, the matrix affected the total concentrations of PAHs measured from the plastics. In WH, the PAHsum was higher in the PS incubated in the sediment (mean + sd) (108.8 ± 23.3 μg/kg), than in the PS incubated in the water (56.4 ± 7.6 μg/kg) (t-test: t(4) = 3.0948, p = 0.036), but no significant differences were found in the other plastic types ($p > 0.05$). The matrix-related difference observed in PS in WH may reflect the supposedly higher PAH concentration of the sediment matrix, but this remains speculative, because the data on PAH concentration in the water are lacking. However, the PAH profiles of plastics and sediments were similar: the same congeners were detected both in the sediment and in the plastics incubated in sediments (Table 1). It is also noteworthy that the concentrations of all the examined PAH congeners in plastics were considerably lower than the initial concentrations in the WH sediments. In VKL, similar comparisons between the initial PAH concentrations in sediment and the sorbed concentrations on plastics could not be done,

because at the VKL site the samples for sediment analysis and for the incubation experiment were taken on different days. Similar to the WH site, in VKL more PAHs were sorbed to plastics from water than from sediment in the case of CA (water 67.2 ± 19.2 μg/kg, sediment 30.7 ± 3.4 μg/kg (t-test: t(4) = −3.2352, p = 0.032), PA (water 46.6 ± 7.4 μg/kg, sediment 30.7 ± 4.9 μg/kg (t-test: t(4) = −3.0903, p = 0.036); PLLA (water 37.6 ± 5.2 μg/kg, sediment 25.1 ± 1.7 μg/kg(t-test: t(4) = −3.9524, p = 0.017). No differences were observed for PS ($p >$ 0.05). The cause of this contradictory pattern between sites in unclear, but these differences in total PAH concentrations may reflect the initial concentrations of PAHs present in the various matrices and the qualities of the matrices (e.g. amount of organic matter, clay content; see Table S1).

In addition to the PAHsum, the type of congener adsorbed onto plastics from different matrices can also be examined. PAHs are hydrophobic and have inverse relationships between solubility and MW; hence, in water they tend to associate with settling particles and their dissolved concentrations are low (Lamichhane et al. 2016; Lima et al. 2005; Witt 1995). In Baltic Sea water, LMW PAHs such as NP, ACE and PHE predominate in the water phase, whereas the concentrations of HMW PAHs
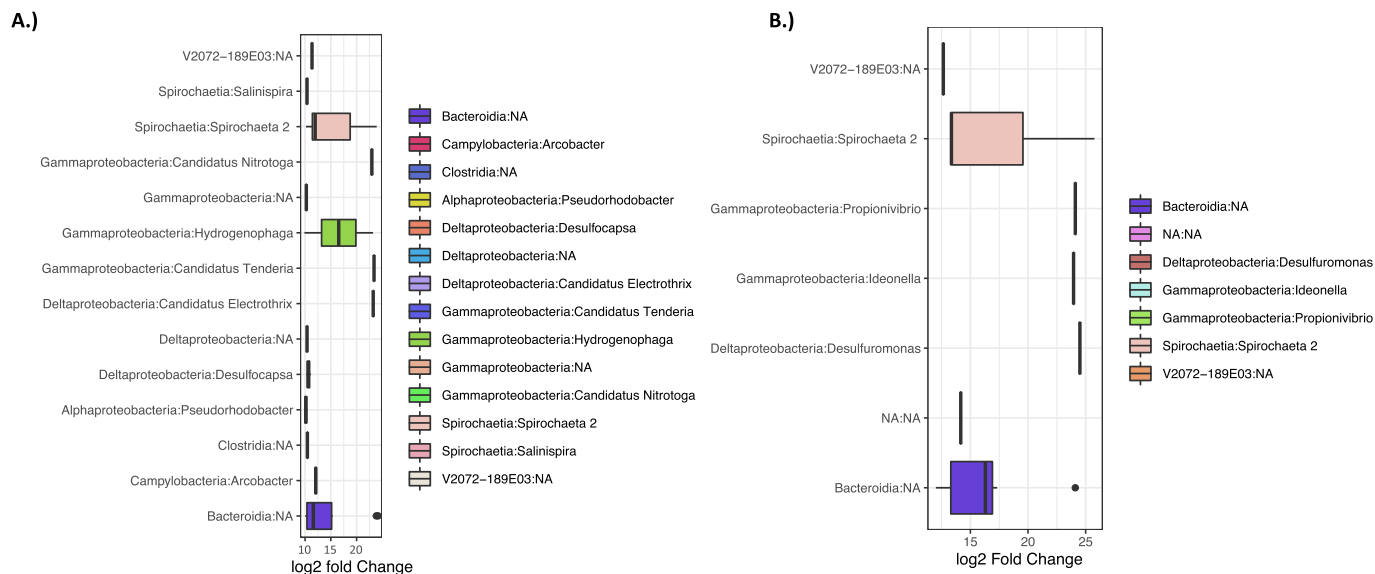
Fig. 6. Bacterial genera enriched on cellulose acetate A) in West Harbour (WH) and B) in Vanhankaupunginlahti Bay (VKL).

remain small (Witt 1995). In contrast to water, in sediments HMW PAHs predominate (Witt 1995). Even though the initial PAH concentrations in water were not quantified in the present study, in general the concentrations on plastics seem to reflect this pattern at the WH site. More HMW PAHs were sorbed to plastics from the WH sediments than from the WH water in the case of PA (sediment 39.4 ± 21.1 µg/kg, water 14.6 ± 0.6 µg/kg (t-test: t(4) = 3.0573, p = 0.037), PLLA (sediment 27.3 ± 6.7 µg/kg, water 14.5 ± 1.7 µg/kg (t-test: t(4) = 4.1011, p = 0.015) and PS (sediment 77.4 ± 22.2 µg/kg, water 15.9 ± 1.3 µg/kg (t-test: t(4) = 4.7747, p = 0.009). CA also seemed to follow

the same pattern, but the difference was not significant (p > 0.05). In the case of LMW PAHs, slightly more of them adsorbed onto plastics from water than from the sediment, but these differences were not significant.

In VKL, the LMW PAHs dominated the PAH profile of plastics incubated in both matrices, and their concentrations were higher in plastics incubated in water than in plastics incubated in sediments (Fig. 3). Significantly more LMW PAHs were sorbed onto CA, PA and PLLA from water than from sediment (CA (water 43.4 ± 9.3 µg/kg, sediment 17.6 ± 3.0 µg/kg (t-test: t(4) = −4.547, p = 0.010), PA (water 28.9 ± 5.5

Table 1
Concentrations of polycyclic aromatic hydrocarbons (PAHs) (maximum concentration based on limits of quantification LOQs) in West Harbour (WH) sediment (single analysis of a pooled sample), and average concentrations of PAHs measured in plastics (CA = cellulose acetate, PLLA = poly-L-lactic acid, PA = polyamide, PS = polystyrene) after the experiment (n = 3).

		Abbr.	Sediment	Plastics in sediment				Plastics in water			
				CA	PA	PLLA	PS	CA	PA	PLLA	PS
			µg/kg			µg/kg				µg/kg	
LMW PAHs	Napthalene	NP	30	2.5	3.0	2.1	4.2	3.3	2.5	2.6	7.7
	2-Methylnapthalene	2-MNP	< 100	1.5	1.7	1.7	2.2	2.1	1.6	1.8	4.8
	1-Methylnapthalene	1-MNP	< 100	0.9	1.1	0.9	1.3	1.3	0.9	1.3	2.6
	Asenapthylene	ACY	< 100	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Asenaphtene	ACE	< 100	0.6	0.7	0.6	0.8	0.6	0.6	0.6	0.7
	Fluorene	FLU	< 100	1.6	1.8	1.6	2.3	1.7	1.1	1.0	3.0
	Phenanthrene	PHE	210	9.2	10.2	9.3	17.9	19.0	13.5	9.9	20.3
	Anthracene	ANT	30	0.8	1.0	0.5	2.2	1.1	0.7	< 0.5	0.9
HMW PAHs	Fluoranthene	FLA	310	7.3	8.5	6.5	16.3	5.4	5.2	4.6	6.2
	Pyrene	PYR	170	7.6	8.6	6.1	14.5	3.9	4.0	4.4	4.2
	Benz[a]anthracene	BaA	210	1.8	3.5	2.1	7.0	< 0.5	< 0.5	< 0.5	< 0.5
	Chrysene	CHR	140	1.1	2.0	1.4	4.8	0.5	< 0.5	< 0.5	0.6
	Benzo[b]fluoranthene	BbF	110	2.4	3.6	2.2	7.6	< 0.5	< 0.5	< 0.5	< 0.5
	Benzo[k]fluoranthene	BkF		0.8	1.1	0.8	2.2	< 0.5	< 0.5	< 0.5	< 0.5
	Benzo[e]pyrene	BeP	130	1.2	1.7	1.3	4.0	< 0.5	< 0.5	< 0.5	< 0.5
	Benzo[a]pyrene	BaP	100	1.6	2.3	1.3	5.8	< 0.5	< 0.5	< 0.5	< 0.5
	Perylene	PER	< 100	< 0.5	0.6	0.5	1.4	< 0.5	< 0.5	< 0.5	< 0.5
	Indeno[1,2,3-cd]pyrene	IcdP	40	1.9	2.9	1.8	5.4	< 0.5	< 0.5	< 0.5	< 0.5
	Dibenz[a,h]anthracene	DahA	< 100	0.6	1.1	0.9	2.2	< 0.5	< 0.5	< 0.5	< 0.5
	Benzo[g,h,i]perylene	BghiP	90	1.5	2.1	1.5	3.9	< 0.5	< 0.5	< 0.5	< 0.5
	PAH sum (20 congeners)		2270	45.9	58.0	43.6	106.7	43.9	35.5	32.4	55.9
Not analysed from both	Biphenyl	BP	< 100	NA	NA	NA	NA	NA	NA	NA	NA
	2,6-Dimethylnapthalene	2,6-DMN	< 100	NA	NA	NA	NA	NA	NA	NA	NA
	2,3,5-Trimethylnapthalene	2,3,5-TMN	< 100	NA	NA	NA	NA	NA	NA	NA	NA
	1-Methylphenanthrene	1-MPH	< 100	NA	NA	NA	NA	NA	NA	NA	NA
	Triphenylene	TRI	NA	1.0	1.3	0.9	2.1	< 0.5	< 0.5	< 0.5	< 0.5
	PAH sum (all analysed congeners)		2670	46.9	59.3	44.5	108.8	44.4	36.0	32.9	56.4

μg/kg, sediment 14.2 ± 0.4 μg/kg (t-test: t(4) = −4.6324, p = 0.010) and PLLA (water 22.6 ± 2.6 μg/kg, sediment 13.7 ± 1.3 μg/kg (t-test: t (4) = −5.3593, p = 0.006), but not to PS (p > 0.05). However, no significant differences were found in the sorption of HMW PAHs onto plastics in the various matrices in VKL (p > 0.05) (Fig. 3). One apparent explanation for the small concentrations of HMW PAHs in plastics incubated in the VKL sediment is the high water content of the sediment. Although the concentration of HMW PAHs by gram of sediment was similar at both sites, the higher water content in the VKL sediment likely resulted in considerably lower total amounts of HMW PAHs in each experimental unit than in the WH sediment unit. In addition to the sediment mass, the sediment quality may also have played a role in HMW PAH adsorption. PAHs are sorbed especially onto the particulate organic matter in the sediment (Wang et al. 2001), which is mainly due to the significant aromatic fraction of the organic matter (Chiou et al. 1998). In the VKL sediment, the amount of organic matter from which the PAHs could partition onto plastic was lower, possibly further limiting the amount of HMW PAHs available for sorption. Moreover, the seawater collected from the VKL site also contained more solids (clay particles) than did the WH water. The VKL site is shallow (2.5 m deep) and located in an area where the Vantaanjoki River flows into the sea. The clay particles present in the water collected from this site may have originated from the Vantaanjoki River or been resuspended in the water column at this sampling site. These particles may have carried more PAHs to the water units and could explain the high concentrations of PAHs in plastics incubated in the VKL water.

3.3. Bacterial community composition and potential plastic-degrading bacteria

The bacterial communities in the sediment and on plastics were distinct from those in the water column (Fig. 5 A and B), similar to those in previous studies (Zettler et al. 2013; Amaral-Zettler et al. 2015; De Tender et al. 2015, 2017; Oberbeckmann et al. 2014, 2016; Dussud et al. 2018; Kirstein et al. 2018). In the water incubations, Gammaproteobacteria and Alphaproteobacteria predominated in both the plastic and water bacterial communities, whereas in the sediment incubations the classes Gammaproteobacteria, Deltaproteobacteria and Bacteroidia predominated in the communities, both on plastic and in the sediment (Fig. 4). Interestingly, the class Bacteroidia was more abundant in the water samples in VKL than in WH (Fig. 4), likely due to the higher clay particle content in the water column.

In the sediment incubations, the bacterial community on CA was distinct from that of the other plastic types (Fig. 5 A and B), whereas in the water incubations all the plastic types clustered together or were mixed (Fig. 5 C and D). In the sediment incubations, the class Bacteroidia predominated on CA in both areas (Fig. 4, Fig. S1). However, Candidatus *Tenderia* (Gammaproteobacteria), *Arcobacter* (Campylobacteria) and *Spirochaeta* 2 (Spirochaetia) were the most abundant genera in WH, whereas *Sphaerotilus* (Gammaproteobacteria), Candidatus *Tenderia* and *Arcobacter* predominated in VKL (Fig. S1 A and C). Pairwise comparison between CA and PA was done to investigate the differences in bacterial community composition between bio- and conventional plastics, respectively. Significant differences in certain genera (DESeQ2, adjusted p < 0.05) were observed between CA and PA at both sampling sites (Fig. 6, Table S3); however, most of them were observed only in the sediment incubations. Certain taxa such as the classes Bacteroidia and Spirochaetia were enriched significantly compared with conventional PA (Fig. 6). Bacteroidia, which are potential degraders of complex carbon substrates including cellulose (Kirchman 2002), were the most abundant on CA at both sites. The same classes were also detected on plastic biofilms in previous studies (Oberbeckmann et al. 2014, 2016, 2018; De Tender et al. 2017; Dussud et al. 2018; Kirstein et al. 2018). In addition to Bacteroidia, *Spirochaeta*, which are potentially cellulolytic bacteria capable of growing on cellobiose (Breznak and Warnecke 2008) and potentially have beta-galactosidase genes (Chen et al.

2019), as well as potentially cellulolytic Clostridia (Pohlschroeder et al. 1994) were significantly enriched on CA in the sediment incubations at both sites (Fig. 6). Also, *Pseudorhodobacter* (Alphaproteobacteria), which are also potentially beta-galactosidase-active bacteria (Li et al. 2016), were enriched on CA in WH (Fig. 6A). The enrichment of potentially cellulolytic bacteria indicates that the CA bacterial community may have been selected due to their capability for degrading CA. However, also interactions between non-cellulolytic and cellulolytic bacteria may enhance the breakdown of cellulose (Pohlschroeder et al. 1994). There is recent evidence that PHA-based bioplastics host bacterial communities that are different and more active than on conventional plastics, thus indicating potential degradation of PHA in marine environments (Dussud et al. 2018; Pinnell and Turner 2019). However, PHA is a bacterially produced bioplastic and the most common bacterial carbon and energy storage substance (Sudesh et al. 2000). Thus, there is a variety of bacteria capable of PHA degradation in comparison to cellulose-degrading bacteria (Sudesh et al. 2000). There were also several PHA-producing strains enriched on our plastic biofilms, such as *Hydrogenophaga* and *Sphaerotilus* (Fig. 6 and Fig. S1; Povolo et al. 2013, Kämpfer and Spring 2015), indicating that there is also a potential for PHA degradation in Baltic Sea sediments. However, since we did not study PHA degradation, this is purely speculation. In all, our results suggest that Baltic Sea sediment bacterial communities are potentially able to degrade biodegradable CA. However, since we did not measure bacterial activity or transcription of cellulolytic enzymes or observe visual signs of plastic degradation, the result should be interpreted with caution.

Similar to previous studies, plastic biofilms were enriched with hydrocarbonoclastic bacteria, i.e. those capable of degrading hydrocarbons, such as *Arcobacter* and taxa specialized in complex carbon substrates, e.g. class Bacteroidia (Fig. 6 and Fig. S1; Harrison et al. 2014, Dussud et al. 2018 Oberbeckmann et al. 2016, Bryant et al. 2016, Debroas et al. 2017), indicating potential capacity of the bacterial community for degrading plastics.

Interestingly, most of the biofilms were covered with a rust-coloured crust (Fig. S2), possibly due to the activity of a variety of potentially iron-oxidizing bacteria, such as *Sideroxydans* (Gammaproteobacteria), *Gallionella* (Gammaproteobacteria) and *Mariprofundus* (Zetaproteobacteria, Fig. S1 A and C; Hedrich et al. 2011). Potential PAH-degrading bacterial genera, such as *Sphingomonas* and *Sphingobium* (Alphaproteobacteria; Ghosal et al. 2016) were also detected on plastics. However, based on our data we cannot conclude whether bacterial degradation of PAHs occurred in our experiment.

In conclusion, plastic bacterial biofilms were largely composed of the same taxa as in the surrounding media (water and/or sediment); however, certain taxa were enriched on plastics. The result is in line with a previous study in which the bacterial communities resembled those in the particle-size fraction of water and glass biofilms, with only a few discriminant taxa potentially related to plastics (Oberbeckmann et al. 2016). Certain bioplastic types such as PHA (Dussud et al. 2018, Pinnell and Turner 2019) and CA (this study) seemingly are potentially better at recruiting plastic-degrading bacterial communities and thus may have higher potential for bacterial degradation in marine environments than other bioplastics such as PLLA (this study). It should also be noted that biogeography, environmental conditions and the season may affect the potential community composition and thus also degradation potential (Amaral-Zettler et al. 2015; Oberbeckmann et al. 2014, 2016). Since potential plastic-degrading communities were present on CA only in the sediments, it is noteworthy to consider where plastic litter in the marine environment accumulates to be able to assess their persistence and degradation potential. However, since visible degradation of CA was not observed and bacterial production/activity was not measured, further investigations are needed to confirm the potential degradation of CA in marine environments. In addition, the requirements for biodegradation, i.e. complete degradation of the plastic to CO_2, H_2O and biomass (aerobic conditions) or CO_2, CH_4 and biomass

(anaerobic conditions), in a reasonable time frame (Amaral-Zettler et al. 2020) should be verified.

3.4. Ecological implications

Microplastics and other plastic litter in the marine environment may serve as additional sorptive surfaces for newly emitted PAHs in the water and participate in their downward flux, similar to sinking phytoplankton and faecal pellets of copepods that may be important vectors of PAHs to the seafloor (Prahl and Carpenter 1979; Witt 2002). Currently, the microplastic concentrations in the surface waters are relatively low; e.g. in the offshore areas of the Gulf of Finland, the concentration of all >330 μm microlitter is less than 10 particles per m^3 (Setälä et al. 2016b). However, their concentrations are inversely related to size, and on the coast of the Gulf of Finland 22–200 particles per m^3 (20–100 μm) have been found (Railo et al. 2018). Since the concentrations of microplastics in the oceans have been globally estimated to increase (Law and Thompson 2014), their importance as future vectors for PAHs and other HOCs to the seafloor may increase, especially in coastal areas representing multipollution hotspots for both microplastics and chemical pollutants.

Since the sorption capacity and residence time in the water column are influenced by the polymer type and its specific gravity, the polymer type determines how much PAHs can be carried to the seafloor and how far from the source they can be distributed. Our results suggest that in comparison to the other plastic types examined, PS has the potential for efficient transport of higher concentrations of PAHs to the benthic compartment. Rochman et al. (2013b) also proposed that PS may pose a greater risk for the marine environment, not only due to its high sorption capacity, but also because of its harmful styrene monomer (Lithner et al. 2011). PS is often detected in the marine environment in its expanded form (EPS), which floats on the water due to a very low specific gravity (< 0.05 g/cm^3; Hidalgo-Ruz et al. 2012) and thus more probably washes to shore rather than sinks to the seafloor. However, the denser form of PS (specific gravity (~1.05 g/cm^3) is still commonly used, e.g. in food packaging (Andrady 2015). The focus should be on PS and other polymer types that may pose an elevated risk to the environment.

The results suggest that the concentrations of PAHs on the seafloor are considerably lower in plastics than in the sediment, in contrast to field observations in seawater, where the PAH concentrations in plastics may considerably exceed the concentrations in the water (Mato et al. 2001). However, these results must be viewed with respect to the length of the incubation, the limited knowledge on the different factors affecting the results (e.g. PAH concentration and organic matter content of water) and the various sensitivities of PAH analyses in plastic and sediment In the WH sediment, the maximum PAH concentration based on LOQs was 2670 μg/kg, whereas in plastics the average varied between 45 and 109 μg/kg, depending on the plastic type. Even the highest PAH concentration in one PS replicate (139 μg/kg) fell far behind the sediment concentrations. In the sediment, the plastics seemingly acted merely as passive samplers, sorbing PAHs freely dissolved in the sediment pore water, and therefore comprised only a fraction of the bulk sediment concentration. The concentrations on passive samplers represent the bioavailable concentration of HOCs in the sediment better than the bulk sediment concentrations (Maruya et al. 2009; Beckingham and Ghosh 2013). Hence, it could be argued that plastics acting as passive samplers may reduce the bioavailable fraction of PAHs present in the sediments. In the Baltic Sea, the mean macrolitter abundance on the seafloor is relatively low: 5.07 items per km^2 (of which 66% are plastics; Kammann et al. 2018), making the effect on PAH bioavailability negligible. However, the litter is usually unevenly distributed on the seafloor, due to hydrodynamics, geomorphology and human influence (Pham et al. 2014; Galgani et al. 2015). It is still unclear whether large aggregations of plastics may affect PAH bioavailability when focusing on their impacts on a smaller scale.

Seafloor sediments also contain microplastics; e.g. the microplastic (> 20 μm) abundance on the northern coasts of the Baltic Sea can reach over 20,000 pieces per kg dw (Tirroniemi 2019), supporting the theory of seafloors acting as sinks for microplastics (e.g. Eriksen et al. 2014; Woodall et al. 2014; Näkki et al. 2019). Similar to macroplastics, microplastics in the sediment are also likely to sorb PAHs from the pore water, but unlike most of the larger plastics, they can be ingested by benthic fauna. The vector-effect of microplastics has been under considerable focus and debate, and in general their importance as HOC carriers to fauna is suspected to be rather low at current exposure levels compared with other pathways of HOC exposure (Gouin et al. 2011; Bakir et al. 2016; Koelmans et al. 2016). However, they may become an important source especially for plastic-bound chemicals (e.g. additives) in cases where animals prefer plastic particles over sediment particles, as observed by Graham and Thompson (2009), or when the animals are unable to distinguish their natural food source from plastics. Since the biofilms on plastics resembled the taxa present in the sediment, organisms using chemosensory cues in foraging may be deluded into ingesting these plastics. This occurs in the pelagic environment, where biofouling of microplastics promoted their ingestion by marine copepods (Vroom et al. 2017). Biofilm can occasionally also carry pathogenic bacteria; e.g. potentially pathogenic *Vibrio parahaemolyticus* was detected "hitchhiking" on floating microplastics in the Baltic Sea (Kirstein et al. 2016). In our study, however, no potentially pathogenic bacteria were found.

Although our results suggest that Baltic Sea sediment bacterial communities have the potential to degrade biodegradable CA, the results also indicate that there are differences between potential degradation of bioplastics (CA vs PLLA), i.e. certain materials are more susceptible to degradation, whereas others are as inert as conventional plastics. In addition to sorbing HOCs and serving as substrates for microbial colonization, a recent study by Seeley et al. (2020) indicates that microplastics may also alter nitrogen-cycling processes in marine sediments. The effects varied, depending on the polymer type, including biodegradable PLA (Seeley et al. 2020). Little is known of the complex interaction of plastics and sediments, and thus further research and consideration are needed in choosing materials to replace conventional plastics in applications with the risk of ending up in the marine environment.

4. Conclusions

The present study revealed differences in the bacterial community composition and in the PAH sorption between plastic types (CA, PA, PLLA, PS). The consistently highest PAH concentrations were quantified on PS, making it potentially a more effective vector for HOCs. However, the overall vector-effect of plastics in PAH-containing sediments is likely to be low, since the PAH concentrations sorbed to plastics were considerably lower than the PAH concentrations in the sediment. The vector-effect may be more profound in water, and sinking plastics may contribute to the PAH flux down to the seafloor. In general, the bacterial communities on plastics resembled those in their surrounding matrices, but the study was also able to pinpoint differences in the bacterial community composition on the plastic surfaces. The bacterial community composition on CA in sediment diverged from that of the other three plastic types and was enriched with potentially cellulolytic bacteria, indicating that CA may be degraded better in the Baltic Sea sediment than the other biodegradable plastic type tested, PLLA. When these two properties were examined, the results suggest that certain biodegradable plastics may have shorter lifespans and smaller environmental impacts than conventional plastics. These results emphasize the need for further study of the properties, effects and fate of plastic materials in the marine environment to better assess their potential risks to ecosystems.

CRediT authorship contribution statement

Pinja Näkki: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Writing - review &

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143088.

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