TURUN YLIOPISTO

Seasonal variation of microplastics in sediment traps in the non-tidal estuary of the Northern Baltic Sea

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Increased use of plastic products has led to pollution of marine environments and accumulation of microplastics (1 µm to 5 mm). The accumulation of microplastics and the factors associated with their deposition are not fully understood. Therefore, it is essential to study the deposition of microplastics as part of sedimentation processes and the influence of seasonal and spatial variations in deposition conditions on the quality and quantity of microplastics.

In this master's thesis sedimentation and microplastic accumulation rates were studied using sediment trap monitoring in Halikonlahti Estuary and around the Haverö and Seili Islands, located in the southwestern coast of Finland at the Archipelago Sea, in the Baltic Sea. Microplastic samples were treated with heavy liquid and enzyme purification treatment followed by the identification of microplastics performed with Fourier transform infrared spectroscopy (FTIR) and with siMPle software.

The sediment accumulation rates decrease from upper estuary towards the open sea. Despite the clear trend in the research area, variation in sedimentation rates in different locations are due to changes in riverine sediment transport and resuspension which channel narrowness and shallowness promote. During winter seasons snow cover determine the character of the sediment: mild winters with low snow cover result to high minerogenic, organic and overall sediment accumulation whereas snow cover, frozen soil and ice cover result respectively lower rates.

Microplastic accumulation (9,0–1656,0 MPs m^{-2} day^{-1}) follow the similar trend as sediment fluxes even though the amount of microplastic accumulation seems to be more related to the anthropogenic activities and location of the plastic sources such as urban areas, major roads, and cultivated lands than sediment accumulation rates. The high concentrations of microplastics in the research area imply that estuarine systems could work as a sink for microplastics.

Key words: Baltic Sea, Enzyme purification, Estuary, FTIR, Marine geology, Microplastic, Sediment trap

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Muovituotteiden lisääntynyt käyttö on johtanut meriympäristöjen pilaantumiseen ja mikromuovien (1 µm–5 mm) kertymiseen luontoon. Mikromuovien kulkeutumiseen ja kerrostumiseen liittyviä tekijöitä ei täysin tunneta. On keskeistä tutkia ja ymmärtää mikromuovien kerrostumista osana kiintoaineksen sedimentaatioprosesseja ja kerrostumisolosuhteiden kausittaisten ja alueellisten vaihteluiden vaikutusta mikromuovien määrään ja laatuun.

Tässä tutkimuksessa selvitettiin sedimentin ja mikromuovin kerrostumisnopeuksia sedimenttikeräimien avulla Halikonlahden estuaarissa sekä Haverö- ja Seili-saarien ympäristöissä, jotka sijaitsevat lounaisrannikolla Saaristomerellä. Mikromuovinäytteet käsiteltiin raskasneste- ja entsyymikäsittelyllä, ja mikromuovien tunnistaminen tehtiin FTIR-spektroskopialla ja siMPle-ohjelmistolla.

Tulokset osoittavat, että sedimentaationopeus hidastuu estuaarin yläosasta avointa merta kohti. Tutkimusalueella vallitsevasta trendistä huolimatta sedimentaationopeudet vaihtelivat eri paikoissa. Vaihtelu johtuu vuodenaikojen välisistä eroavaisuuksista joen sedimenttikuormassa sekä sedimentin uudelleen kerrostumisessa, jota edistävät virtauskanavan kapeus ja mataluus. virtauskanavan kapeudessa tai mataluudessa, jotka edistävät sedimentin uudelleen kerrostumista. Talvikaudella lumipeite vaikuttaa sedimentin ominaisuuksiin: leudot talvet ja vähäluminen lumipeite johtavat suureen minerogeenisen sekä orgaanisen aineksen kerrostumiseen. Sedimentaationopeus on myös korkeampi näinä talvina verrattuna kylmiin talviin, jolloin lumi- ja jääkerros sekä routa pienentävät sedimentaationopeuksia.

Mikromuovin kerrostumisnopeudet (9,0–1656,0 MPs m^{-2} day^{-1}) noudattavat samankaltaista trendiä kuin sedimentaationopeudet. Tästä huolimatta mikromuovien kertyminen näyttäisi olevan enemmän kytköksissä ihmistoimintaan kuin sedimentaationopeuteen. Muovien kertymiseen vaikuttavat muovilähteiden sijainnit, kuten kaupunkialueet, päätiet ja viljelymaat. Mikromuovien korkeat pitoisuudet tutkimusalueella viittaavat siihen, että estuaarit voivat olla merkittäviä mikromuovikeskittymiä.

Avainsanat: entsyymipuuhdistus, estuaari, FTIR, Itämeri, merigeologia, mikromuovi, sedimenttikeräin

Content

1. Introduction

Increased use of plastic products has led to a pollution of marine environment and expanded to a global problem (Hartmann *et al.* 2019). Plastic products are inexpensive and easy to produce and thus widely used in everyday life (Geyer *et al.* 2017). As the plastic debris are degraded and weathered into smaller pieces in the environment by sunlight, oxidants, and physical stress, but not decomposed, the plastic materials can be considered durable, leading to accumulation of plastic waste (Ritchie *et al.* 2023). Microplastics (particles size from 1 µm to 5 mm) are shown to be deposited in marine environments (Thompson *et al.* 2004; Andrady 2011; Kallenbach 2022) and can cause severe health issues to human and animal life (Gewert *et al.* 2015; Wang *et al.* 2020). The effects of microplastics to human health are still unclear but are known to cause oxidative stress, cancer, and dysfunctions in organs (Wang *et al.* 2020).

Estuaries receive microplastics and terrigenous sediment loads through rivers and, as the sediment sinks in coastal areas (Jokinen *et al.* 2015), the microplastics can aggregate to the suspended particles and accumulate or sink as a consequence of biofouling or on their own due to the density of plastics, particle sizes and flow velocity (Dame 2008; Kaiser *et al.* 2017). In addition, estuaries potentially act as microplastic filters partly preventing microplastics entering the oceans (Kaiser *et al.* 2017). Therefore, studying accumulation of microplastics is essential to understand processes affecting the sedimentation of microplastics in an estuary system.

In this work, sediment and microplastic fluxes and sediment composition with seasonal resolution using 11 sediment traps in a non-tidal estuary, Halikonlahti Estuary were monitored. Plastic materials and particle sizes and shapes were identified using Fourier transform infrared spectroscopy (FTIR). Microplastic concentrations, fluxes and material types were compared to the sediment flux data to evaluate the response of different plastic materials to changes in sedimentation patterns.

This master's thesis is a part of *Baltic Sea Monitoring on Microplastic sedimentation processes* project of the University of Turku and Helsinki, where the deposition of microplastics and their seasonal variation in the Halikonlahti Estuary were studied. The main purpose of this master's thesis is to understand the deposition of microplastics as a part of solids sedimentation processes. It is important to study the effect of seasonal variation of deposition conditions and spatial differences on the quality and quantity of microplastics.

2. Background

2.1 Microplastics

Production of plastics begun by production of natural rubber in 1800 century and the first mass produced polymer chain was Bakelite (phenol-formaldehyde resin) developed in 1909 (Lambert and Wagner 2018). At first plastics were used principally in military use but widespread development and usage increased after 1950 (Geyer *et al.* 2017). Due the benefits of plastic products such as their lightweight, durability, corrosion-resistant properties, and inexpensiveness, they were favorable target for mass production (Napper and Thompson 2020). Production of plastics have increased from 1,7 million tons to 300 million tons per year during 1950-2012 meaning 8,7 % growth per year (Gourmelon 2015). Geyer *et al.* (2017) estimate that 8300 Mt of plastic materials have been produced to date and 30 % of that (2500 Mt) are currently in use. Approximately 10 % (600 Mt) is recycled, 12 % are incinerated (800 Mt) and 60 % (4900 Mt) are accumulated in environment (Geyer *et al.* 2017; Kallenbach 2022).

Regardless marine environment being the largest deposit of microplastics, majority of microplastic pollution result of terrestrial runoff from anthropogenic sources such as urban drainage, insufficient water management, industrial discharges, and landfills (Kallenbach 2022). Other plastic sources according to Kallenbach (2022) are plastic materials used in agriculture (plasticulture), biosolid applications, microencapsulated products, and litter. Approximately 18 % of marine plastic debris located in the oceans are attributed to the fishing industry such as Polyehtylene, Polypropylene and nylon fishing nets and gear (Andrady 2011).

The first mentions of microscale particles in scientific publications were made in 1970 century at numerous locations (Carpenter and Smith 1972; Colton *et al.* 1974; Gregory 1977). However, the term ‘microplastic’ was first mentioned in 2004 and the definition of microplastics was introduced in 2009 (Thompson *et al.* 2004; Arthur *et al.* 2009). The consequences of accumulation of plastic litter have evoked conversation among scientific communities and in society level as well (Geyer *et al.* 2017; Napper and Thompson 2020).

2.1.1 Physical and chemical properties

Plastics in general are synthetic or semi-synthetic polymer chains mostly made of ethylene and propylene which are processed from fossil hydrocarbons (Fjäder 2016; Geyer *et al.* 2017). In semi-synthetic plastics cellulose or starch is used as a part of a composition and, in fully synthetic plastics only oil-based substances are used in polymer chains (Setälä *et al.* 2017). Different polymer chains

and additives have distinct properties and thus their usage and behavior in environment varies depending on the polymer type (Gewert *et al.* 2015; Fjäder 2016). Some additives such as bisphenol A and phthalates are designed to stabilize the polymer and make it more durable (Gewert *et al.* 2015). However, according to Gewert *et al.* (2015) these additives are not usually covalently bonded to the polymer and thus are leachable from the plastic as it degrades in environment.

Bioplastics are made entirely or in part from sugarcane, corn or other renewable biomass sources (Ashter 2016). However, bioplastics are not biodegradable whereas plastics that can be decomposed by the action of microbes, in optimal pH and temperature are considered biodegradable plastics (Setälä *et al.* 2017). None of the most produced and used plastic types in Europe, such as polyethene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), polyethylene terephthalate (PET) and polyurethane (PU) are biodegradable plastics (Gewert *et al.* 2015; Geyer *et al.* 2017). Plastic particles are categorized as fibres, fragments, film pieces and quasi-spherical particles (Brandon *et al.* 2019) and densities of different plastics varies from 0,91 to 1,41 depending on the plastic type (Table 1).

Table 1. Density differences between common plastics. Density values taken from Lambert and Wagner (2018).

Polymer type	**Abbverbiation**	**Density (g/cm^3)**
Polyehtylene-low density	LDPE	0,91–0,93
Polyehtylene-high density	HDPE	0,94–0,97
Polypropylene	PP	0,85–0,94
Polystyrene	PS	0,96–1,05
Polyamide	PA	1,12–1,14
Polycarbonate	PC	1,20
Cellulose acetate	CA	1,28
Polyvinyl chloride	PVC	1,38
Polylactic acid	PLA	1,21–1,43
Polyethylene terephthalate	PET	1,34–1,39
Polyoxymethylene	POM	1,41

Density of seawater is approximately 1,03 g/cm^3 which means that some of plastics float on the water surface. However, biofouling, the successive buildup of organic material and organisms on a microplastic particle, in marine and estuary environment can increase the density of plastic particles and increase their sinking velocity (Kaiser *et al.* 2017).

2.1.2 Primary and secondary microplastics and degradation of plastics

Not all microplastics are degraded in environment. Some of them are made initially small for example pre-production plastic pellets and commercial used microbeads are called primary microplastics

whereas secondary particles are degraded from primary or other plastic particles and products (Cole *et al.* 2011). As briefly mentioned in *2.1.1 Physical and chemical properties* polymer chain type determines how durable different plastic types are and how they behave in environment. Degradation of microplastics is initiated thermally, hydrolytically or by UV-light exposing polymer surface to chemical or enzymatic attacks leading to high surface to volume ratio of microplastic and thus proceeds faster than degradation of macroplastics (Gewert *et al.* 2015).

Especially polymers with a carbon backbone such as PE, PP, PS and PVC are easily exposed to photo-initiated oxidative degradation in marine environment which leads to a decrease in the molecular weight (Gewert *et al.* 2015). According to Gewert *et al.* (2015) polymers with lower molecular weight result in chain scission which accelerate and enable the biodegradation of microplastics. Polymer chains with heteroatoms attached to them such as PET and PU are usually degraded by hydrolysis, photo-oxidation and biodegradation (Gewert *et al.* 2015).

2.1.3 The amount of microplastic in the environment

Microplastics degrade rather than decompose via abiotic or biotic pathways in environment leading to accumulation in landfills or natural environments (Gewert *et al.* 2015; Geyer *et al.* 2017). Erosion, catchment dynamics and transport processes have an influence on microplastics ending up in marine environments (Kallenbach 2022). For example, 4 to 12 Mt of plastic debris has been estimated to enter marine environment from land in 2010 alone (Geyer *et al.* 2017).

There are only few mentions of measured microplastic fluxes in marine environment (Brandon *et al.* 2019; Enders *et al.* 2019; Reineccius and Waniek 2022) and freshwater environment (Turner *et al.* 2019; Saarni *et al.* 2021; 2023). However, microplastic concentrations are widely studied especially in marine environment (Claessens *et al.* 2011; Stolte *et al.* 2015; Frère *et al.* 2017; Constant *et al.* 2019). Measuring microplastic flux rates are essential for examining the accumulation of microplastics in various environments and for comprehending the changes in microplastic concentrations in various timescales (Saarni *et al.* 2021).

2.1.4 Impacts on the environment of microplastic pollution

The degraded plastic litter can fragment into microplastics and even smaller nanoplastics (< 1 µm) and can cause severe health issues to human and animal life (Gewert *et al.* 2015; Wang *et al.* 2020). Microplastic debris is contained in marine environment by over 690 marine species from different trophic levels and have reported to cause reduced growth, cell death, feeding behavior and hormonal

regulation to name a few (Carbery 2018). For instance, microplastics and plastic leach are known to cause physiological and metabolic changes but also decreasing photosynthesis and primary production (Amaneesh *et al.* 2023). Estuarine ecosystems such as Halikonlahti Estuary, provide ecologically diverse environment for various plant and animal life in consequence of dilution of seawater by freshwater (Dame 2008). According to Dame (2008) estuary systems have a poor resilience to ecological changes and are particularly vulnerable to anthropogenic influence such as plastic littering. The effects of microplastics and nanoplastics to human health are still unclear but are known to cause oxidative stress, cancer, and dysfunctions in organs (Wang *et al.* 2020).

3. Regional setting

3.1 Study site

This master's thesis study was performed mainly in the Halikonlahti Estuary but also around the Haverö and Seili Islands which are located in the southwestern coast of Finland at the Archipelago Sea, in the northeast corner of the Baltic Sea (Fig. 1). Halikonlahti forms an enclosed estuary for the Uskelanjoki and Halikonjoki Rivers running through the town of Salo with ca. 51 000 inhabitants (City of Salo 2020). Estuaries are semi-enclosed coastal areas, and they typically receive freshwater input from land drainage which is mixed with saline seawater (Dame *et al.* 2008). The mean annual discharge of Uskelanjoki and Halikonjoki Rivers are 4,9 m^3/s and 2,8 m^3/s, according to Salmela *et al.* (2020; 2022). The Halikonlahti Estuary is approximately 45 km long with two openings to the Archipelago Sea separated by Kemiönsaari Island with steep banks and gently sloping fields surrounding the channels (Salmela *et al.* 2020; 2022). Sea level fluctuations in Archipelago Sea are predominantly forced by passing low air pressure systems (Salmela *et al.* 2022). The depth of the Halikonlahti Estuary varies from 3 to over 20 meters in both channels (Salmela *et al.* 2020; 2022). The shallowest parts of the estuary are located around the town of Salo, and the deepest parts are at both sides of the Angelniemi Peninsula and at the Rungonsalmi Strait. However, the southern channel has a shallow threshold which restrain water exchange between the open sea and the Halikonlahti Estuary (Salmela *et al.* 2020). Salinity varies between 0–6 PSU in Halikonlahti Estuary and weak or no stratification occur during winter and summer seasons in the study location due the shallowness of the estuary (Salmela *et al.* 2020; 2022). Average temperature during the research period was 8,3 °C, the coldest month was February in 2021 (-6,8 °C) and the warmest month was July in 2018 (20,6 °C). The length of snow covered period which briefly reflects the ice cover duration in the research site was on average 53,4 days ranging from 11 to 95 days. The soil type in the research area is mostly post-glacial clay dominated with some bedrock outcrops around the estuary (Salmela *et al.* 2022).

3.2 Anthropogenic activities around Halikonlahti Estuary

Urban environments and urban drainage systems are considered as pathways to microplastic waste to the freshwater and marine environments via urban runoff, wastewater management, industrial areas, but also by traffic and agriculture (Kallenbach 2022). Urban runoff is concentrated to the town of Salo and are leached to Halikonjoki and Uskelanjoki Rivers. Local snow dump and wastewater treatment plant are located at the entrance of the Uskelanjoki River and both leach and flush to the Halikonlahti Estuary. Industrial area around Uskelanjoki River consist mainly of construction, car, industrial kitchen and food production companies and corporations. Traffic is concentrated to the town center but villages, major roads, and bridges in and around the Kemiönsaari Island are active especially at summertime due the vacation season. Summer cottages are located throughout the Kemiönsaari Island apart from the farmlands. The environmental protection act concerning the treatment of wastewater initiated in 2017 which meant that areas in dispersed settlement or apartments near waterbodies had to treat their wastewaters properly by 2019 (Kangas 2017). In addition, 36 % of the catchment of Halikonjoki and Uskelanjoki Rivers are cultivated (Salmela *et al.* 2022).

3.3 Sample sites

In this master's thesis, total of 11 sediment traps were placed 1 meter above seafloor around the Kemiönsaari Island (Sediment trap sites 1-4, 6 and 8-11), Haverö and Seili Islands (sediment traps 13 and 14) (Fig. 1). The sediment traps in the basins near the Haverö and Seili Islands were designed for control purposes reflecting background microplastic fluxes in the open sea area while the estuarine sediment traps are expected to reflect flux gradient from town activities to open water.

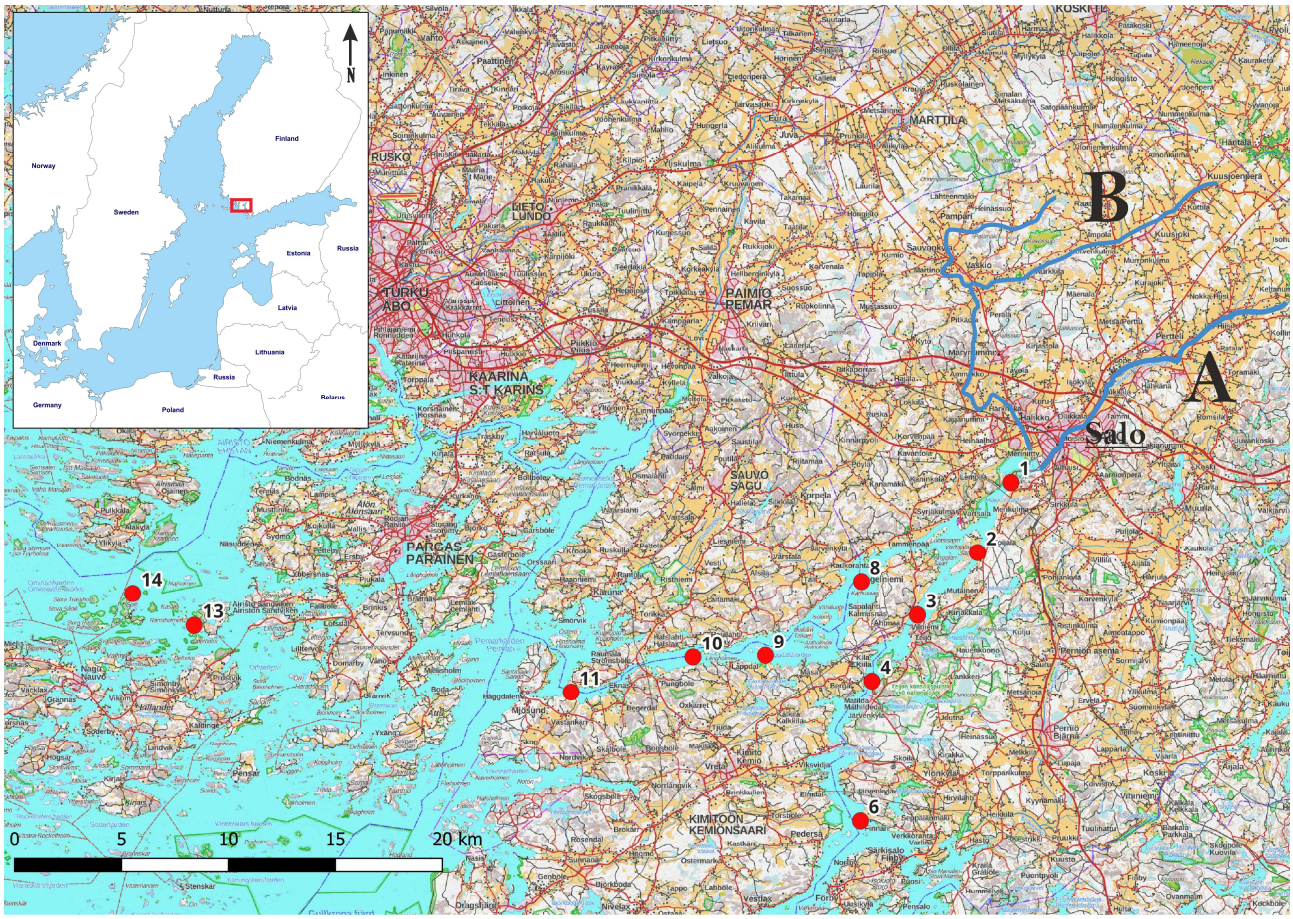

Figure 1. Research area around the Halikonlahti Estuary and Haverö and Seili Islands. Red square indicate the location in the index map and red dots mark the location of sediment traps. Town of Salo, Uskelanjoki (A) and Halikonjoki (B) Rivers are highlighted (D-maps.com 2023; National Land Survey of Finland 2023).

Bathymetry and the channel width of the Halikonlahti Estuary differ locally which affect the sedimentation intensity (Salmela *et al.* 2022) (Table 2). Sediment traps 1 and 2 located at the shallow shelf of the estuary where channel width is narrow. Sediment traps 3, 4 and 8 located at the deepest parts of the estuary whereas sediment trap 6 was the nearest to the open sea in the southern channel. Channel width in southern channel was throughout narrower compared to northern channel. Sediment traps 9, 10 and 11 located at the shallow part of the Halikonlahti Estuary. Channel width at sediment traps 9 and 10 were significantly wider than at sediment trap 11. In addition, occasional high near-bottom flow events occurred at sediment traps 9 and 10 whereas at sediment trap 11 high flow events occurred throughout the year (Salmela *et al.* 2022). Sediment trap 11 was also closest to shoreline compared to sediment traps 8, 9 and 10. Sediment traps 13 and 14 were located at Archipelago between islands.

Table 2. Water depth (m) and location of the sediment traps.

Sediment trap	Water depth (m)	Coordinates (WGS84)	
1	3	N60°21,67’	E23°04,38’
2	3	N60°19,23’	E23°02,13’
3	24	N60°16,35’	E22°57,43
4	22	N60°13,75’	E22°54,28’
6	19	N60°08,45’	E22°54,07’
8	22	N60°17,46’	E22°53,03’
9	16	N60°14,47’	E22°46,09’
10	13	N60°14,23’	E22°40,60’
11	12	N60°12,60’	E22°31,54’
13	20	N60°14,11’	E22°02,64’
14	20	N60°15,11’	E21°57,80’

4. Material and methods

4.1 Sampling and subsampling of sediments

All research in this master’s thesis was based on sediment trap monitoring which was validated research method to determine and calculate microplastic fluxes (Saarni *et al.* 2021). Sediment trapping had been continuous since 2018 in the study area and years 2018-2021 were used in this master’s thesis, which was a total of three winter and four growing seasons. The sediment traps were picked up every spring and autumn to collect the data of the growing and winter seasons, separately.

A sediment trap consisted of different parts: bottom weight, rope, floats in the metal body of the sediment trap, directing wing, collector tubes, flotation buoy and signal buoy (Saarni *et al.* 2021; Fig. 2). Bottom weight kept the sediment trap in place, rope connected the bottom weight to the sediment trap body and floats and directing wing kept the sediment trap aligned for potential currents that occurred in the estuary. The data were collected by 2 collector tubes which were attached in sediment trap body: one for the sediment (tube a) and the other for the microplastic (tube b) flux research. The collector tubes were made of polymethyl methacrylate (PMMA), and the bottom was made of stainless steel (Saarni *et al.* 2021). The collector tube height was 405 mm and the inner diameter 62 mm (Salmela *et al.* 2022). Flotation buoy was to keep the sediment trap aligned and signal buoy was to notice the marine traffic.

Sediment traps 1-4, 6, 13 and 14 were collected with R/V Aurelia owned by Archipelago Research Institute (University of Turku). These traps were buoyed and relatively easy to reach from the deck of the research vessel. Sediment traps 8-11 were mooring near the bottom of the estuary without a signal buoy. Therefore, these sediment traps were collected using dragging method with MAAGEO buster owned by department of Geography and Geology (University of Turku). In dragging method, the buster was driven to the GPS point of the sediment trap and a 100 m long line with hooks attached to it was gradually set to the water. The buster was driving around the sediment trap coordinates in order that the hooks attached to the line could stick to the sediment trap. After a couple of rounds with the boat, the sediment trap was carefully lifted.

As the sediment traps were carefully lifted from the bottom and the tubes were released from the sediment trap body, the sediment content from each collector tube was poured to containers with the help of deionized distilled water. The containers were closed, marked, and stored in the fridge +5˚C degrees.

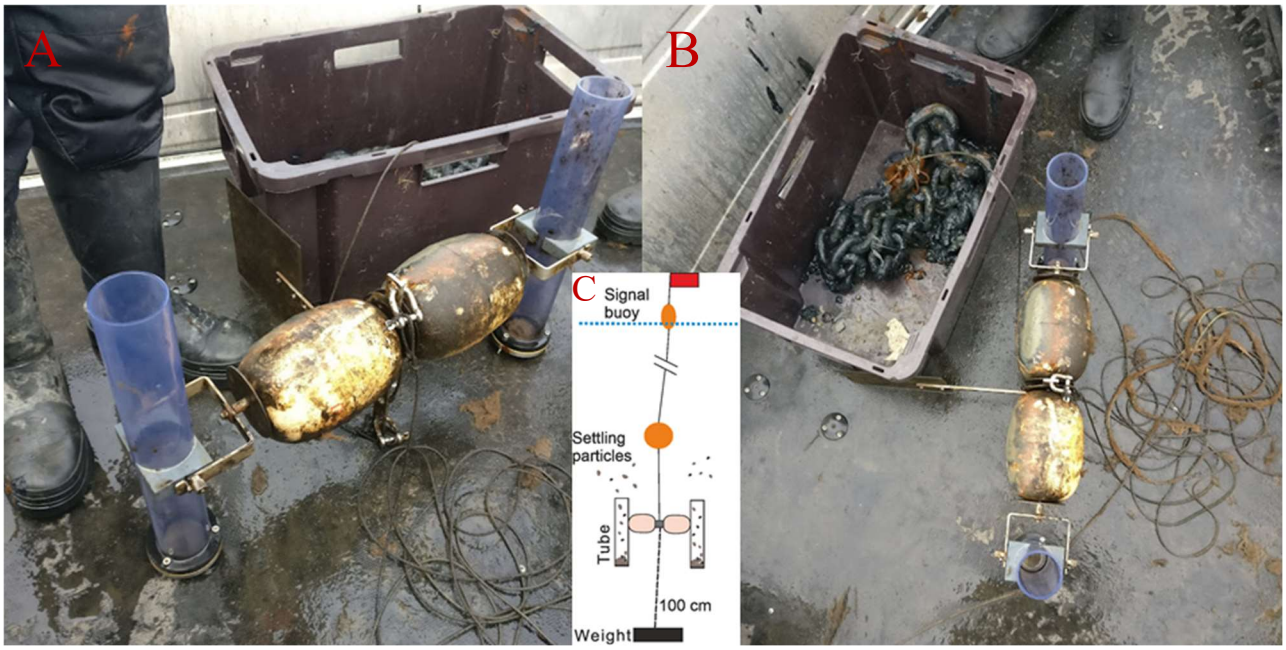

Figure 2. A: Picture in front of sediment trap. B: Picture above the sediment trap with the weight in the container. Weight kept the sediment trap in place. Two whitish floats and the directing wing stabilized and aligned the sediment trap. C: Simplified sketch of the sediment trap. In sediment traps 8-11 no signal buoys were used.

In the laboratory, the containers were allowed to rest couple of days to let the suspended sediment to sink to the bottom of the container before the subsampling. The seawater was ejected with a 60 ml syringe carefully not to let the sediment to suspend. In addition, the excess organic matter such as seaweeds, crustaceans and polyps were cautiously removed out of the sample. This same procedure

was used for both sediment and microplastic analysis, however microplastic samples from tube b were treated in the clean laboratory.

After removing the seawater out of the containers, the sediment was collected and rinsed to crucibles and weighted for wet weight. The samples were dried in an oven over night in 40 ˚C to remove the excess water, then frozen and freeze dried in main drying phase (44 h, -25 ˚C, 0,63 mbar) and in final drying phase (4h, -50 ˚C, 0,040 mbar) in Christ Alpha 1-4 LDplus and weighted afterwards to record the sample dry weight. The dry samples from tube a were grinded and homogenized in mortar and shared in sub samples for magnetic susceptibility and loss on ignition (LOI) measurements. The dried samples from tube b were put in 50 ml centrifuge tubes for density separation.

4.2 Magnetic susceptibility

Low field magnetic susceptibility was used to provide information about the magnetic properties of the sediment trap samples (Dearing 1999). Magnetic susceptibility is efficient way to identify Fe-bearing minerals within the samples and the processes of their formation and transport (Dearing 1999).

Low field magnetic susceptibility was measured using Bartington MS2 meter with a MS2B sensor in SI-form through the transparent polystyrene sampling boxes (external dimensions 2.2 × 2.2 × 1.8 cm, volume 6.2 cm^3). According to Dearing Handbook (1999), MS2B sensors are capable to detect fine ferromagnetic minerals, described as superparamagnetic minerals which provide essential information about mineral characteristics of the sample. A calibration sample was used before the first sample and air reading was measured before and after every sample to monitor the possible drift. The average air reading was subtracted from the initial magnetic susceptibility measurement to obtain corrected magnetic susceptibility.

4.3 Organic matter content

Loss on ignition (LOI) is common Quaternary geology research method to estimate organic and carbonate content in sediments (Heiri *et al.* 2001). Grinded sediment samples were weighted first obtaining dry weight and then heated in order to burn organic matter away in 550 ˚C for 4 hours. After heating, the samples were cooled down in desiccator and weighted again. Heiri *et al.* (2001) equation was used to calculate LOI-percentage:

$$\mathrm{LOI}_{550} = ((\mathrm{DW}_{105} - \mathrm{DW}_{550})/\mathrm{DW}_{105}) * 100$$

The sediments were not expected to include carbonate minerals, and hence burning in 950 ˚C was omitted.

4.4 Microplastic analysis

Heavy liquid separation and enzymatic purification were used to separate microplastics from the sediment (Löder *et al.* 2017; Fig. 3). After density separation and enzymatic treatments, the samples were ready for FTIR analyses in SIB Laboratory at the University of Eastern Finland. FTIR spectroscopy images and quantifies the quality and the amount of microplastics in samples (Löder *et al.* 2017). The final microplastic flux data is obtained from the FTIR analyses according to Löder *et al.* (2017).

4.4.1 Density separation

The principle behind the heavy liquid separation are density differences between plastics, minerogenic matter and the liquid (Löder *et al.* 2017). According to Löder *et al.* (2017), the purpose of density separation is to reduce the subsample volume and remove mineral matter from samples leaving only organic matter and microplastics within the solution.

Heavy liquid used in density separation was lithium heteropolytungstate (LST) density of 2,85 g/ml at 25°C (Central Chemical Consulting 2018). The needed density of 2,0 g/ml was obtained adding water to the LST using LST calculator provided by Central Chemical Consulting. The density was ensured with hydrometer and the LST was filtered before the use in separation process.

5-10 ml of sediment trap sample and 15 ml heavy liquid were subsampled to the prewashed centrifuge tubes. The sediment was suspended by shaking the tubes and put in centrifuge for 10 minutes (4000 rpm 6 acc. 5 dec. and 3655 bucket) allowing organic and plastic material to float in the heavy liquid. After the centrifuge run the float, which included the plastic and organic material, were poured to another pre-washed tube avoiding any mineral matter to leak in. Another portion of heavy liquid was poured on the centrifuge tube with residual, which included sediment and were suspended and centrifuged again. This procedure was repeated at least three times to ensure high recovery of the microplastics.

After all three centrifuge runs the heavy liquid was filtered through stainless steel filters (20 µm) in a bottle top filtration device. The centrifuge tubes edges were rinsed carefully with deionized distilled water to collect potential plastic particles attached on the edges. However, some samples rich in clays had a loose residual after centrifuge runs complicating the filtration process. Therefore, small portion (10 ml) of deionized distilled water was added to such tubes and centrifuged. The solution density decreased, and residual depressed allowing the heavy liquid flow effortlessly through the filter.

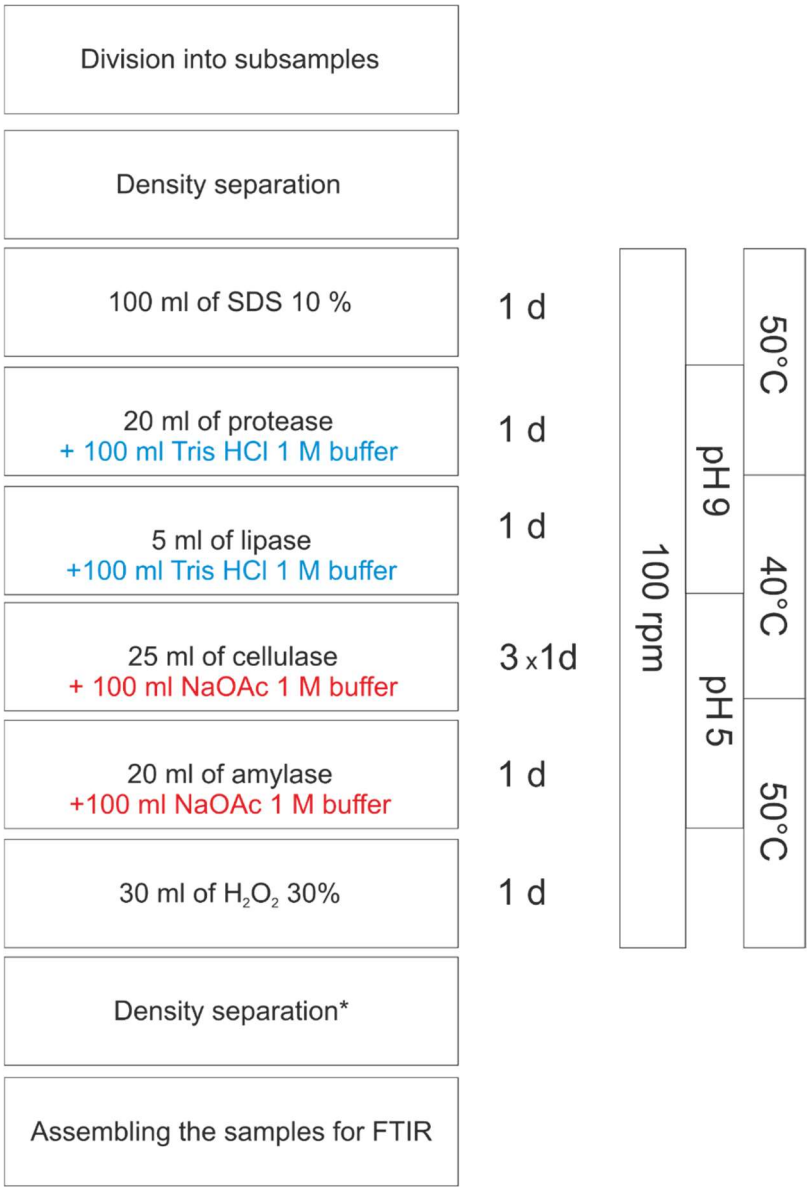

Figure 3. Microplastic analysis protocol modified from Löder *et al*. (2017) used in this research. Buffer solutions are marked as blue (Tris) and red (NaOAc) for clarify the process and * stand for optional density separation if sample contained mineral matter.

4.4.2 Organic matter enzyme digestion

Multiphase enzymatic purification of microplastics following the workflow with minor modifications by Löder *et al.* (2017) was conducted after heavy liquid separation (Fig. 3). This is a relatively new studying method and has not been widely used in microplastic research (Claessens *et al.* 2013; Nuelle *et al.* 2014; Löder *et al.* 2017). The purpose of enzymatic purification was to reduce the sample matrix for reliable FTIR analysis and to conserve the composition of microplastics (Löder *et al.* 2017).

In enzymatic purification processes, samples were filtered through stainless steel filters in a bottle top filtration device in laminar flow cabinet. Enzymes and chemical solutions were used to remove targeted biological substrates (Löder *et al.* 2017). Between filtering, samples were put in a shaking incubator in incubation bottles for respective time and temperature to accelerate the purification processes (Löder *et al.* 2017). In addition, specific pH was obtained with buffer solutions to attain optimum reaction activity (Löder *et al.* 2017).

4.4.2.1 Sodium Dodecyl Sulfate treatment

Sodium dodecyl sulfate (SDS) is an anionic surfactant, which macerates planktonic organisms, plant residue, and increases contact surface for the following enzymatic purification treatments (Löder *et al.* 2017). After filtration of heavy liquid, the bottle top filtration device was rinsed with deionized distilled water. The bottle top filtration device was opened, and the top part was placed on the top of incubation bottle with a funnel. To avoid losing any microplastics, the top part, gasket and used instruments were cautiously rinsed with 10 % SDS. Finally, the filter was placed within the incubation bottle and bottle was topped up to 100 ml of 10 % SDS. Bottle top was rinsed with deionized distilled water and placed lightly on top of the bottle avoiding pressure to rise inside the bottle. Incubation bottle with the filter inside was placed in incubator with following settings: 24 h, 100 rpm and 50 ˚C.

4.4.2.2 Protease enzyme treatment

The first enzymatic purification step was conducted with protease, which catalyzes the decomposition of protein chains into easily dissolving form (Löder *et al.* 2017). In addition, according to Löder *et al.* (2017) protease treatment disperses peptides, macerates planktonic organisms, and cell residues. Tris(hydroxymethyl)-aminomethane (TRIS HCl 1 M) buffer solution was used with protease enzyme to obtain the optimal pH of 9 for the digestion of protein chains.

After 24 h incubation in SDS, the bottle was taken out of incubator and the filter inside was rinsed on the funnel to the same bottle and then placed on the bottle top filtration device. The content inside the

incubator bottle was poured through the filter and the bottle was respectively rinsed with deionized distilled water and 70 % ethanol to remove SDS remnants.

The following work procedure was the same as in SDS treatment and in further treatment steps involving the rinse of bottle top filtration device and other used instruments into the incubation bottle. However, different buffer solutions and substrates were used in distinct treatment stages. In protease treatment, TRIS HCl 1 M buffer solution was used for the rinse. Filter was placed to incubation bottle which was topped up to 100 ml of TRIS HCl 1 M-buffer solution and 20 ml of protease enzyme was added in the incubation bottle. Finally, the bottles were placed in incubator for 24 h, 100 rpm and 50 ˚C.

4.4.2.3 Lipase enzyme treatment

According to Löder *et al.* (2017), lipase enzyme was applied after protease treatment to treat lipids or polysaccharides e.g., biota and tissues released during digestion process. The same laboratory filtration procedure described earlier, was performed to change protease enzyme to lipase bath. In total 100 ml of TRIS HCl 1 M-buffer solution to attain pH 9 and 5 ml of lipase enzyme were measured in incubation bottles and placed to incubator for 24 h, 100 rpm and 40 ˚C.

4.4.2.4 Cellulase enzyme treatment

According to Löder *et al.* (2017), cellulase enzyme was used to macerate phytoplankton cell walls and other plant residue in the sample. Cellulase enzyme attain its optimum reaction activity at pH 5 therefore, sodium acetate buffer (NaOAc 1 M) was used (Löder *et al.* 2017). Filtration procedure was similar as lipase and protease treatments however, cellulase step was repeated 3 times. In total 100 ml of NaOAc 1 M buffer and 25 ml of cellulase enzyme was measured in incubation bottles and put in incubator for 24 h, 100 rpm and 40 ˚C. Sodium hydroxide (NaOH 2 M) was added in the bottle just before the filtration to redissolve flocs formed during the treatment. Based on experience in laboratory work, NaOH catalyzes the solvation of cellulase precipitate, leading to a clear solution, which accelerates the filtration process significantly.

4.4.2.5 Amylase enzyme treatment

Amylase enzyme was applied after three repeated cellulase treatments to further accelerate the digestion of e.g., phytoplankton cell walls (Löder *et al.* 2017). The previously described filtering procedure was performed. In total, 100 ml of NaOAc 1 M buffer was added to attain pH 5 and 20 ml of amylase was measured to incubation bottles and placed in incubator for 24 h, 100 rpm and 50 ˚C. Sodium hydroxide (NaOH 2 M) was used to dissolve flocculate prior the filtration.

4.4.2.6 Hydrogen peroxide treatment and density separation

Exoskeletons of crustaceans contains protective coating of proteins and calcium carbonate, which makes them rigid and difficult to digest (Löder *et al.* 2017). Hydrogen peroxide facilitated the efficient digestion of partly dissolved organic matter. The filtration procedure was similar to earlier enzyme treatment steps. However, no buffer was required, and rinsing was performed with H_2O_2 (30%). In total, 30 ml of H_2O_2 was measured in incubation bottles and placed in incubator for 24 h, 100 rpm and 50 ˚C. Before the final step sediment sample treatment, density separation was repeated for samples which contained some mineral mater.

4.4.2.7 Assembling the samples for FTIR analysis

Assembling the microplastic samples was the final step of sample purification process. After final treatments, bottle top filtration device was rinsed carefully with deionized distilled water and 70 % ethanol into a new prewashed test tube. Filter was rinsed above a centrifuge tube in a funnel with tiny amount of deionized distilled water to detach material which was attached to the filters. In addition, filter was rinsed with 70 % ethanol to remove any microplastics which were attached to the filters. After rinsing the filters and used laboratory equipment above the centrifuge tubes, samples were labelled and stored in 70 % ethanol within the test tubes and send to the University of Eastern Finland in SIB laboratory. After the treatment, stainless steel filters were cleaned in ultrasonic bath and reused.

4.4.3 Identification of microplastics with imaging FTIR

Identification of microplastics was performed in University of Eastern Finland in SIB laboratory using Fourier transform infrared spectroscopy (FTIR) analyses. FTIR spectroscopy is widely used along Raman spectroscopy to determine chemical composition of particles (Uurasjärvi 2021).

According to Uurasjärvi (2021) dissertation, the principle of FTIR spectroscopy is to observe interactions between electromagnetic radiation and the material. FTIR spectroscopy measures the amount and which wavelengths of infrared radiation the given sample absorbs (Uurasjärvi 2021). FTIR spectrometer equipment composes from source, which emits infrared radiation and a detector, which measures the intensity of infrared light reflected or transmitted from the examined sample (Uurasjärvi 2021). The spectrometer produces an interferogram which is converted to an actual spectrum using Fourier transform (Uurasjärvi 2021). According to Uurasjärvi (2021), molecular bonds excite higher vibrational energy levels from the ground state when molecules absorb infrared light. The wavelength of the absorbed infrared light correlates to the energy difference between the

energy levels, which depends on the features of the chemical bonds (Uurasjärvi 2021). According to Uurasjärvi (2021), the chemical bonds in the sample molecule produce peaks in the FTIR spectrum identifying the molecule spectrum.

Before imaging, the samples were filtered in a bottle top filtration device through a silver membrane filter which diameter of analyzed area was 12 mm and particle retention was 5.0 µm. The device was rinsed with deionized distilled water and the silver membrane filter was put on preparation glass. Calibration and background tests were performed before the FTIR analysis. Equipment used in the FTIR analysis were Agilent Cary 670 spectrometer and Cary 620 microscope incorporated with focal plane array (128×128 FPA) detector. Absorbance mode was used to conduct the measurements with a pixel size of 5.5 µm, a spectral resolution of 8 cm^{-1}, and a spectral range of 3800-750 cm^{-1}. Liquid nitrogen was poured into the infrared source before the calibration to maintain the optimal temperature for imaging.

4.4.4 Data processing and statistics

For the spectral interpretation siMPle software developed by Primpke *et al*. (2020) was used to process the data obtained from FTIR-analyses. After FTIR measurements the data was converted to .hdr files which were necessary for siMPle software. The raw data (.dmd files) was converted to siMPle file format (.spe) and reference spectral library (.txt) was also loaded. The siMPle file format (.spe) was analyzed for spectra fit with spectral library (.txt) which contained spectra of the most common plastics and fabrics such as PA, PVC, PET, HDPE, PS, ABS, PU, PP, PMMA, polyacryl fibre, wool, cotton, silk, viscose and linen. The software calculated Pearson's correlation coefficient between sample and the reference spectra and, if the correlation was above specified level, a particle was recognized (Primpke *et al*. 2020). The spectra of the matched particles were then verified and checked for identification errors. For instance, PS and ABS spectra were remarkably similar and easily mixed to each other. The verified data was saved in .csv file and used in Excel for raw data sorting and calculating microplastic fluxes and concentrations.

Sorted microplastic data from Excel (.csv) was imported to SAS Enterprise Guide software where it was used for statistical analysis such as normality test and correlation analysis. Shapiro-Wilk normality test was performed for microplastic flux, sediment flux, low field magnetic susceptibility and organic content to test normality of the data. Spearman correlation was chosen based on the normality test results and it was performed to identify potential connections between factors.

The standard deviation and central tendencies such as median and average were calculated to observe the dataset. The standard deviation is a measure of the amount of variation or dispersion of a set of values. Standard deviation (σ) is calculated by following equation:

$$\sigma = \sqrt{\frac{\Sigma(x_i - \bar{x}^2)}{n-1}}$$

Where x_i is number of observations, $\bar{x}$ is mean and n is sample size.

4.5 Sediment and microplastic calculations

Sediment flux i.e., sediment accumulation rate (SAR) was calculated using following equation:

$$SAR = \frac{m_{dry}}{At}$$

Where m_{dry} stands for sediment dry weight, A for the collector tube surface area and t for time (number of days in research period).

Microplastic fluxes were calculated using following equation:

$$Microplastic\ flux = \frac{MP}{At}$$

Where MP is number of microplastics in sample, A is the surface area of the collector tube and t is time (number of days in research period).

Microplastic concentrations were calculated using following equation:

$$Microplastic\ concentration = \frac{MP}{m_{dry}}$$

Where MP is number of microplastics in sample and m_{dry} is sediment dry weight.

4.6 Quality control

Three blank samples (B1-B3) and three recovery samples (R1-R3) were used for identifying the contamination levels and microplastic loss during the treatment. The blank samples were empty

centrifuge tubes, and they went through all microplastic analysis steps, FTIR-imagining and data processing.

The recovery samples were prepared by picking 100 pieces of red PET fragments (density 1,3-1,4 g/m, particle size 250-500 µm) and 100 white HDPE fragments (density <1 g/ml, particle size 250 µm) to each of three centrifuge tubes (Saarni *et al.* 2021). The plastic pieces were mixed with the Palojärvi Lake sediment, which was assumed to be free of microplastics, with deionized distilled water in centrifuge tubes before microplastic analysis treatment. The recovery samples were poured to a filter after enzymatic purification and the plastic pieces were counted and recovery rate, which was average of all three recovery results, were calculated in Excel.

5. Results

5.1 Low field magnetic susceptibility

Median low field magnetic susceptibility (hereafter susceptibility) was $78*10^{-6}$ and average was $76*10^{-6}$. The lowest measured susceptibility ($21*10^{-6}$) was in the sample from sediment trap 8 in growing season 2019 (GS19). The sites showed relatively low susceptibility values throughout the growing seasons apart from GS21. The highest susceptibility values of the dataset were recorded during GS21 and the highest value ($134 *10^{-6}$) was recorded from the sediment trap 9 (Fig. 4).

In GS18 the lowest measured value was $39 *10^{-6}$ in the sediment trap 8 and the highest value was $78 *10^{-6}$ from the sediment trap 1. In the winter season 2018-2019 (WS18-19) the lowest susceptibility was $29 *10^{-6}$ in sediment trap 10 and the highest was $81,5 *10^{-6}$ in sediment trap 9. In GS19 the lowest susceptibility was $21 *10^{-6}$ in sediment trap 8 and the highest $71 *10^{-6}$ in sediment trap 3. The lowest susceptibility value in WS19-20 was $81 *10^{-6}$ in sediment trap 10 and the highest was $98,5 *10^{-6}$ in sediment trap 9. In GS20 the lowest value was $38,5 *10^{-6}$ in sediment trap 8 and the highest was $99 *10^{-6}$ in sediment trap 9. In WS20-21 the lowest susceptibility value was $59,5 *10^{-6}$ in sediment trap 6 and the highest was $96,5 *10^{-6}$ in sediment trap 8. In GS21 the lowest susceptibility value was $44,5 *10^{-6}$ in sediment trap 13 and the highest was $134 *10^{-6}$ in the sediment trap 9.

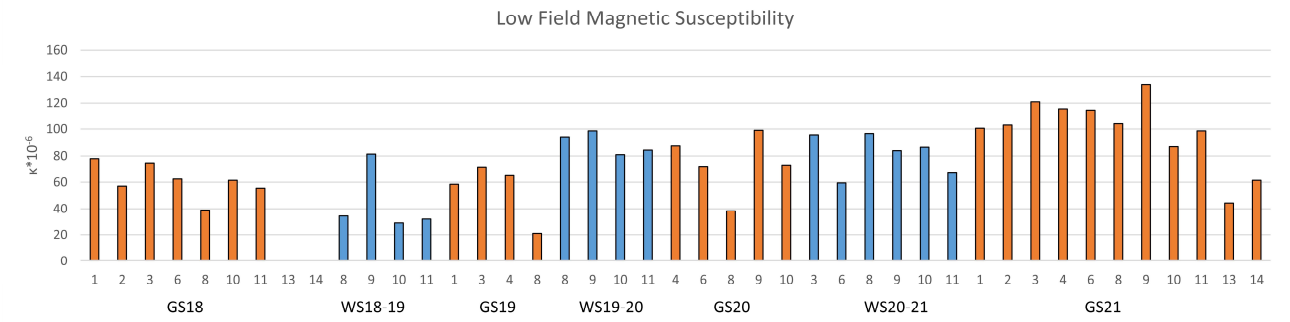

Figure 4. Low field magnetic susceptibility values in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively. Median susceptibility was $78*10^{-6}$ and average was $76*10^{-6}$. The lowest measured susceptibility ($21*10^{-6}$) was in sediment trap 8 in GS19 and the highest value ($134*10^{-6}$) was in sediment trap 9 in GS21.

5.2 Organic content

Organic content was obtained from LOI calculations. Median organic content was 12,5 % and average was 12,6 %. The organic content varied from 10,4 % in GS21 in sediment trap 6 to 15,6 % in in GS21 in sediment trap 8 in dataset (Fig. 5).

In GS18 the lowest measured organic content 10,4 % was in sediment trap 1 and the highest 14,6 % was in sediment trap 8. In WS18-19 the lowest organic content was 13,9 % in sediment trap 11 and the highest was 14,6 % in sediment trap 8. In GS19 the lowest organic content was 10,5 % in sediment trap 1 and the highest was 15,1 % in sediment trap 8. In WS19-20 the lowest organic content was 10,4 % in sediment trap 11 and the highest organic content was 12,8 % in sediment trap 8. In GS20 the lowest organic content was 11,3 % in sediment trap 6 and the highest was 14,7 % in sediment trap 8. In WS20-21 the lowest organic content was 10,6 % in sediment trap 6 and the highest organic content was 12,8 % in sediment trap 8. In GS21 the lowest organic content was 10,4 % in sediment trap 6 and the highest was 15,6 % in sediment trap 8.

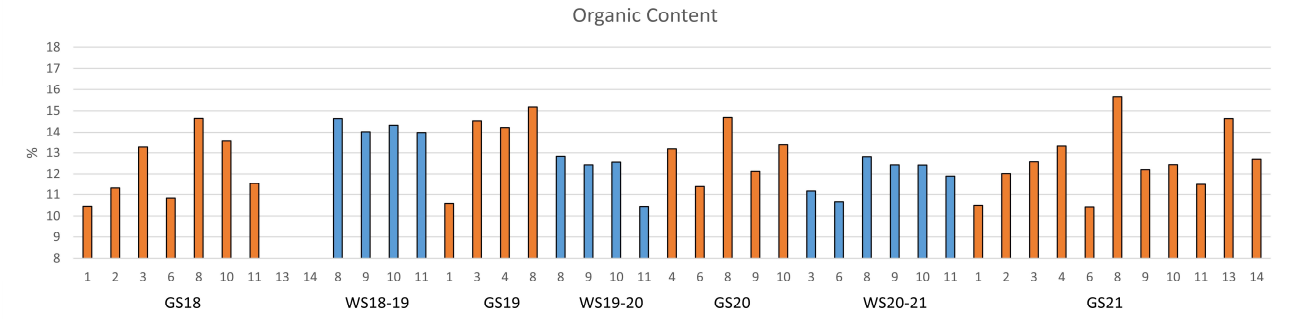

Figure 5. Organic content in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively. Median organic content was 12,5 % and average was 12,6 %. The lowest organic content (10,4 %) was in sediment trap 6 in GS21 and the highest (15,6 %) was in sediment trap 8 in GS21.

5.3 Sediment fluxes

Sediment fluxes varied significantly locally and seasonally throughout the dataset. Median sediment flux was 37,6 g m^{-2} day^{-1} and average was 37,2 g m^{-2} day^{-1}. Sediment fluxes in Halikonlahti Estuary varied from 7,0 g m^{-2} day^{-1} (WS18-19, sediment trap 10) to 119 g m^{-2} day^{-1} (GS21, Sediment trap 11) (Fig. 6).

In GS18 the lowest sediment flux was 12,1 g m^{-2} day^{-1} in sediment trap 10 and the highest sediment flux was 77, 4 g m^{-2} day^{-1} in sediment trap 14. In WS18-19 the lowest sediment flux was 7,0 g m^{-2} day^{-1} in sediment trap 10 and the highest was 15,1 g m^{-2} day^{-1} in sediment trap 9. In GS19 the lowest sediment flux was 10,9 g m^{-2} day^{-1} in sediment trap 8 and the highest was 63,8 g m^{-2} day^{-1} in sediment trap 1. In WS19-20 the lowest sediment flux was 14,6 g m^{-2} day^{-1} in sediment trap 10 and the highest was 44,9 g m^{-2} day^{-1} in sediment trap 11. In GS20 the lowest sediment flux was 13,1 g m^{-2} day^{-1} in sediment trap 8 and the highest is 62,8 g m^{-2} day^{-1} in sediment trap 4. In WS20-21 the lowest sediment flux was 12,0 g m^{-2} day^{-1} in sediment trap 10 and the highest was 57,3 g m^{-2} day^{-1} in sediment trap 3. In GS21 the lowest sediment flux was 12,7 g m^{-2} day^{-1} in sediment trap 13 and the highest 119,8 g m^{-2} day^{-1} was in sediment trap 11.

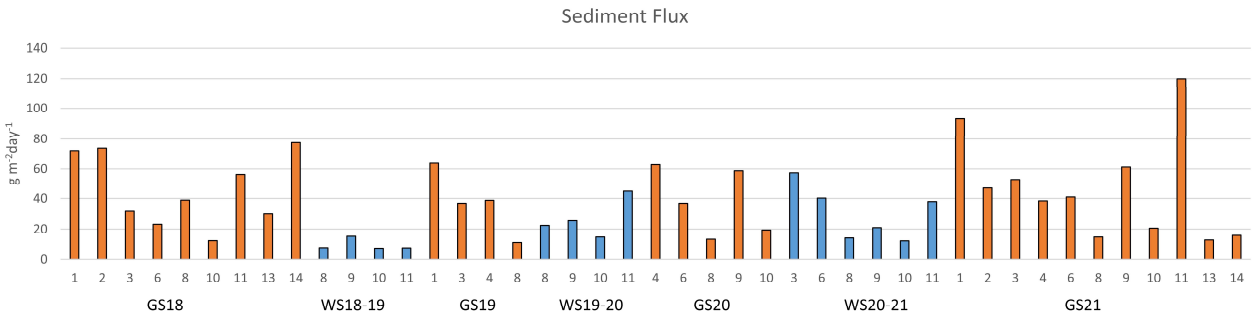

Figure 6. Sediment flux in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively. Median sediment flux was 37,6 g m^{-2} day^{-1} and average was 37,2 g m^{-2} day^{-1}. The lowest sediment flux (7,0 g m^{-2} day^{-1}) was in sediment trap 10 in WS18-19 and the highest (119 g m^{-2} day^{-1}) was in sediment trap 11 in GS21.

5.4 Microplastic analysis

5.4.1 Material types and quality control

The average recovery rate was 63 % for PET and 77 % for PE. Great amount of PE (B1:0, B2:0, B:875 plastic particles/sample) and PP (B1:86, B2:173, B3:875 plastic particles/sample) plastics were found in all blank samples. Therefore, PE and PP were removed from all plastic data for maintaining reliability of the results and minimizing the effect of possible contamination. Separation of PE and

PP materials left only few particles in blank samples (B1: 2 PS, 1 PA; B2: 2 PS, 1 PA; B3: 1 PA plastic particles/sample). After removing the PP and PE from dataset, the majority of the plastic types in the sediment traps were polystyrene (PS) with 143 particles, polyethylene terephthalate (PET) with 35 particles and polyamide (PA) with 25 particles (Table 3; Fig. 7).

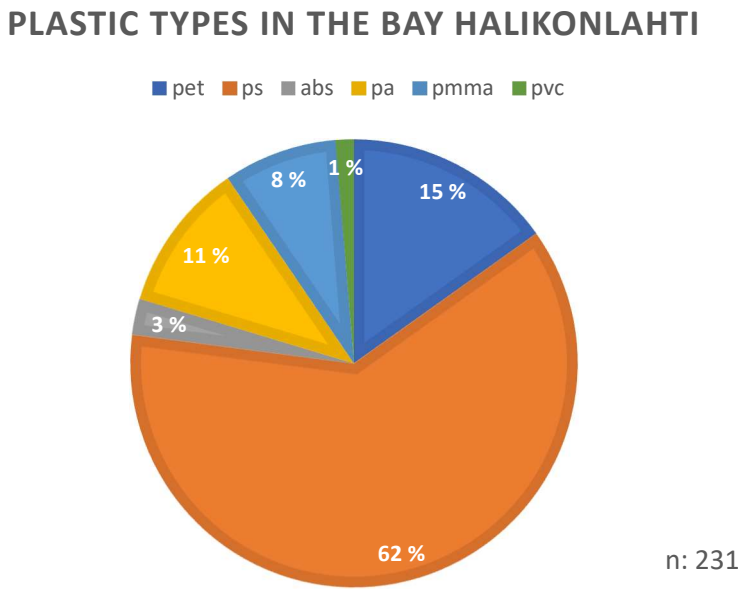

Figure 7. Plastic types in the Halikonlahti Estuary including sediment traps 13 and 14. After removing the PP and PE, most of the plastic types in the sediment traps were PS (143 particles), PET (35 particles) and PA (25 particles).

Other plastic types were poly(methyl methacrylate) (PMMA), acrylonitrile butadiene styrene (ABS) and polyvinyl chloride (PVC) (Table 3). Total of 231 different plastic particles were discovered in the sediment traps. Fibers were total of 14 particles and fragments 217 particles. Average particle size was 88 µm and standard deviation was 80 % among all the data. The largest particle was 543 µm and smallest was 13. General factors are described in more detail in table 3.

Table 3. Details of microplastics in the Halikonlahti Estuary.

Season	Trap	ps	pet	pa	pmma	abs	pvc	Fiber	Fragment	Average	SD	Largest	Smallest	n
GS18	1	32	1	4	4	0	0	4	37	92	88	485	30	41
	2	3	1	0	0	0	0	0	4	62	15	81	39	4
	3	2	0	1	0	0	0	1	2	128	65	218	68	3
	6	0	0	1	0	0	0	0	1	93	0	93	93	1
	8	0	1	0	0	0	0	0	1	40	0	40	40	1
	10	0	1	0	0	0	0	0	1	45	0	45	45	1
	13	2	0	1	0	0	0	1	2	128	65	218	68	3
	14	1	0	0	0	0	1	0	2	85	5	90	80	2
WS18-19	8	0	0	0	0	0	2	0	2	72	23	95	49	2
	9	1	0	0	0	0	0	1	0	65	0	65	65	1
	10	2	1	1	0	0	0	1	3	75	44	151	45	4
	11	1	1	0	0	0	0	0	2	44	9	53	35	2
GS19	1	29	1	0	2	1	0	0	33	107	109	543	18	33
	3	3	1	0	1	0	0	0	5	105	91	270	39	5
	8	1	1	1	0	0	0	0	3	50	13	67	35	3
WS19-20	9	1	1	0	1	1	0	0	4	60	29	90	30	4
	10	1	1	0	0	0	0	0	2	41	11	51	30	2
GS20	4	3	0	0	0	0	0	0	3	156	56	207	78	3
	8	0	0	0	0	1	0	0	1	65	0	65	65	1
	9	1	2	0	0	0	0	0	3	50	11	66	39	3
	10	0	1	4	0	0	0	0	5	51	14	71	35	5
WS20-21	3	4	3	0	1	0	0	1	7	78	49	171	25	8
	8	2	4	1	0	1	0	0	8	63	26	111	29	8
	9	2	3	0	0	0	0	0	5	136	140	409	33	5
	11	1	0	0	0	1	0	0	2	99	53	152	45	2
GS21	1	38	1	1	1	0	0	2	39	97	79	505	28	41
	2	5	2	1	0	1	0	0	9	92	96	357	18	9
	3	0	1	2	0	0	0	1	2	81	68	177	30	3
	4	2	1	0	0	0	0	0	3	93	35	122	44	3
	6	3	2	5	8	0	0	1	17	53	21	94	21	18
	8	2	0	0	0	0	0	0	2	91	45	136	46	2
	9	0	2	0	1	0	0	1	2	103	103	248	18	3
	10	0	0	2	0	0	0	0	2	23	10	33	13	2
	11	0	1	0	0	0	0	0	1	42	0	42	42	1
	14	1	1	0	0	0	0	0	2	117	7	124	110	2
TOTAL		143	35	25	19	6	3	14	217	88	80	543	13	231

5.4.2 Microplastic Flux

The spatial microplastic flux variation was large between sediment traps. Seasonal variation occurred with major change between GS18, GS19 and GS21. Median microplastic flux was 31,6 MPs m^{-2} day^{-1} and average was 139 MPs m^{-2} day^{-1}. The measured microplastic fluxes varied from 9,0 MPs m^{-2} day^{-1} (WS18-19, sediment trap 11) to 1656,0 MPs m^{-2} day^{-1} (GS19, sediment trap 1) (Fig. 8).

In GS18 the lowest microplastic flux was 0 MPs m^{-2} day^{-1} in sediment trap 11 but the lowest measured microplastic flux was 10,6 MPs m^{-2} day^{-1} in sediment trap 8. The highest microplastic flux was 511,7 MPs m^{-2} day^{-1} in sediment trap 1. In W18-19 the lowest microplastic flux was 9,0 MPs m^{-2} day^{-1} in sediment trap 11 and the highest was 26,4 MPs m^{-2} day^{-1} in sediment trap 10.

In GS19 the lowest microplastic flux was 14,8 MPs m^{-2} day^{-1} in sediment trap 8 and the highest was 1656,0 MPs m^{-2} day^{-1} in sediment trap 1. In WS19-20 the lowest microplastic flux 0 MPs m^{-2} day^{-1} was in sediment traps 8 and 11, but the lowest measured microplastic flux was 12,1 MPs m^{-2} day^{-1} in sediment trap 9 and the highest was 14,2 MPs m^{-2} day^{-1} in sediment trap 10.

In GS20 the lowest microplastic flux was 0 MPs m^{-2} day^{-1} in sediment trap 6, but the lowest measured sediment flux was 23,0 MPs m^{-2} day^{-1} in sediment trap 8. The highest microplastic flux was 86,2 MPs m^{-2} day^{-1} in sediment trap 9. In WS20-21 the lowest microplastic flux 0 MPs m^{-2} day^{-1} were in sediment traps 6 and 10, but the lowest measured microplastic flux was 9,3 MPs m^{-2} day^{-1} in sediment trap 11 and the highest flux was 46,1 MPs m^{-2} day^{-1} in sediment trap 8.

In GS21 the lowest microplastic flux 0 MPs m^{-2} day^{-1} was in sediment trap 13, but the lowest measured microplastic flux was 19,8 MPs m^{-2} day^{-1} in sediment trap 8 and the highest flux was 1508,0 MPs m^{-2} day^{-1} sediment trap 1. The sediment trap 6 was clearly highlighted with microplastic flux of 552,0 MPs m^{-2} day^{-1}.

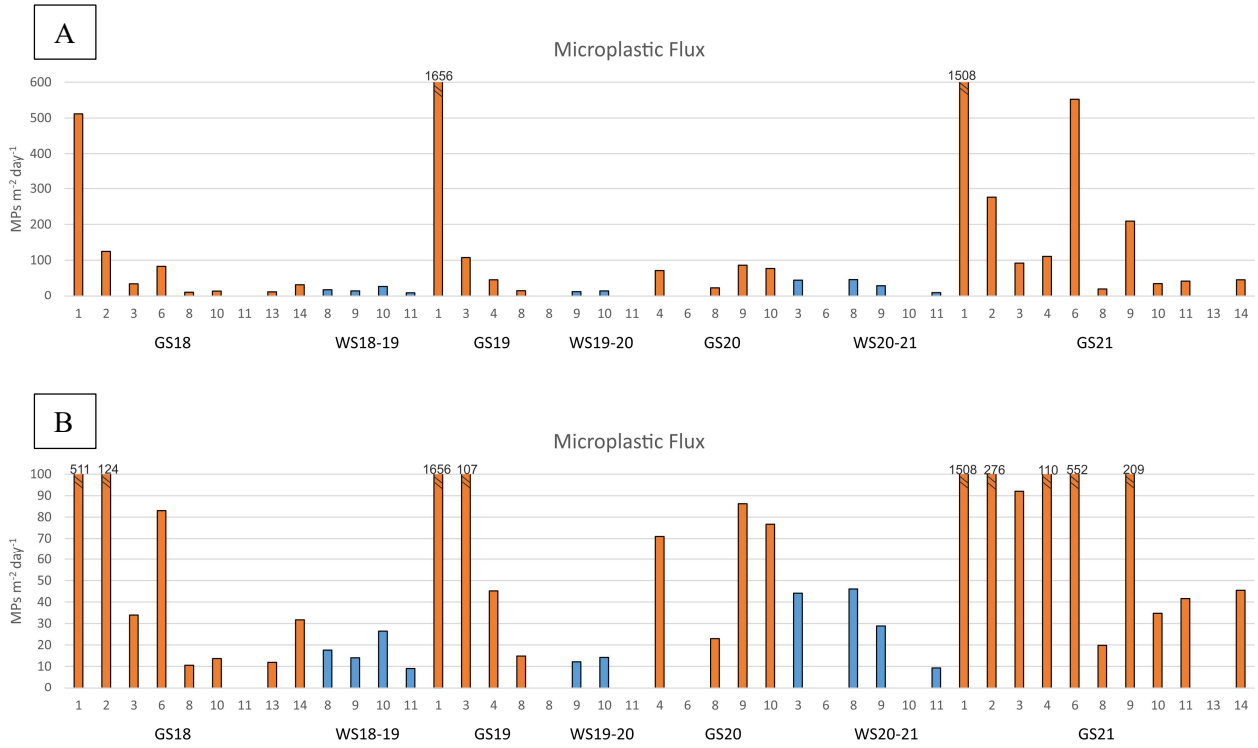

Figure 8. A: Microplastic flux in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively. B: Microplastic flux in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively but in more precise scale. Median microplastic flux was 31,6 MPs m^{-2} day^{-1} and average was 139 MPs m^{-2} day^{-1}. The lowest measured microplastic flux (9,0 MPs m^{-2} day^{-1}) in sediment trap 11 in WS18-19 and the highest (1656,0 MPs m^{-2} day^{-1}) was in sediment trap 1 in GS19.

5.4.3 Microplastic concentration

The local microplastic concentrations was large in sediment traps 1 in GS18, GS19 and GS21 but also seasonal variation occurred. Median microplastic concentration was 1,3 MPs/g and average was 2,8 MPs/g. The measured microplastic concentrations varied from 0,2 MPs/g (WS20-21, sediment trap 11) to 25,9 MPs/g (GS19, sediment trap 1) (Fig. 9).

In GS18 the lowest microplastic concentration was 0 MPs/g in sediment trap 11 but the lowest measured microplastic concentration 0,2 MPs/g was in sediment trap 8. The highest microplastic concentration was 7,1 MPs/g in sediment trap 1. In WS18-19 the lowest microplastic concentration was 0,9 MPs/g in sediment trap 9 and the highest was 3,7 MPs/g in sediment trap 10.

In GS19 the lowest microplastic concentration was 1,1 MPs/g in sediment trap 4 and the highest was 25,9 MPs/g in sediment trap 1. In WS19-20 the lowest microplastic concentration was 0 MPs/g in sediment traps 8 and 11 but the lowest measured microplastic concentration was 0,4 MPs/g in sediment trap 9 and the highest 0,9 MPs/g in sediment trap 10.

In GS20 the lowest microplastic concentration was 0 MPs/g in sediment trap 6, but the lowest measured microplastic concentration was 1,1 MPs/g in sediment trap 4. The highest microplastic concentration was 3,9 in sediment trap 10. In WS20-21 the lowest microplastic concentration was 0 MPs/g in sediment trap 6 and 10, but the lowest measured microplastic concentration was 0,2 MPs/g in sediment trap 11 and the highest was 3,2 MPs/g in sediment trap 8.

In GS21 the lowest microplastic concentration was 0 MPs/g in sediment trap 13, but the lowest measured microplastic concentration was 0,3 MPs/g in sediment trap 11 and the highest was 16,1 MPs/g in sediment trap 1.

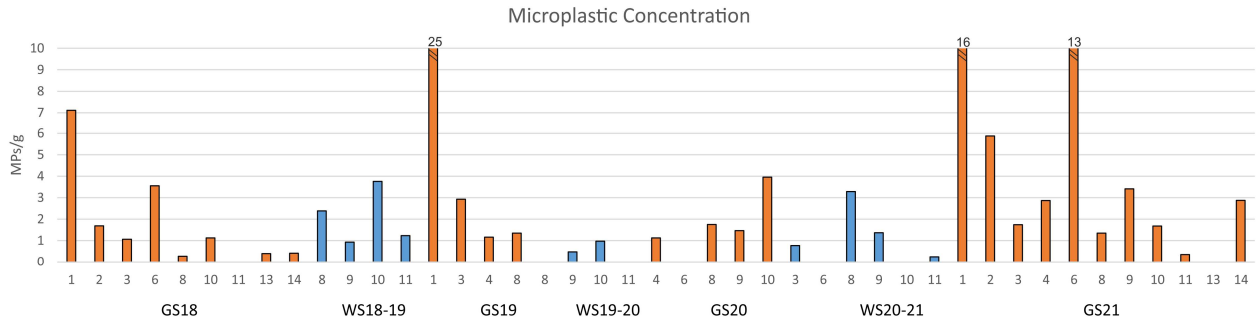

Figure 9. Microplastic concentration in sediment traps during growing seasons (GS) and winter seasons (WS) colored in orange and blue respectively. Median microplastic concentration was 1,3 MPs/g and average was 2,8 MPs/g. The lowest microplastic concentration (0,2 MPs/g) was in sediment trap 11 in WS20-21 and the highest (25,9 MPs/g) was in sediment trap 1 in GS19.

5.5 Statistical analyses

Shapiro-Wilk normality test was performed to selected factors which indicated that the majority of factors were not normally distributed except susceptibility and organic content (Table 4). Therefore, Spearman was used instead of Pearson correlation to identify potential connections between factors.

Table 4. Shapiro-Wilk normality test results.

Factors	**W-value**	**p-value**
Microplastic flux	0,420959	<0,0001
Sediment flux	0,905511	0,0018
Susceptibility	0,985011	0,8561
Organic content	0,95753	0,1288

Correlations were statistically accurate throughout the factors except between microplastic flux and organic content. Positive correlation was identified between sediment flux and microplastic flux, sediment flux and susceptibility, microplastic flux and susceptibility and negative between sediment flux and organic content and susceptibility and organic content (Table 5; Fig. 10).

Table 5. Spearman correlations of the microplastics in the Halikonlahti Estuary.

Spearman Correlation					
		Sediment flux	**Microplastic flux**	**Susceptibility**	**Org%**
Sediment flux	Correlation (r_s) p-value total (n)	1.00000 43	0.48305 0.0010 43	0.43114 0.0049 41	-0.67787 <.0001 41
Microplastic flux	Correlation (r_s) p-value total (n)	0.48305 0.0010 43	1.00000 43	0.39839 0.0099 41	-0.26808 0.0901 41
Susceptibility	Correlation (r_s) p-value total (n)	0.43114 0.0049 41	0.39839 0.0099 41	1.00000 41	-0.34106 0.0291 41
Org%	Correlation (r_s) p-value total (n)	-0.67787 <.0001 41	-0.26808 0.0901 41	-0.34106 0.0291 41	1.00000 41

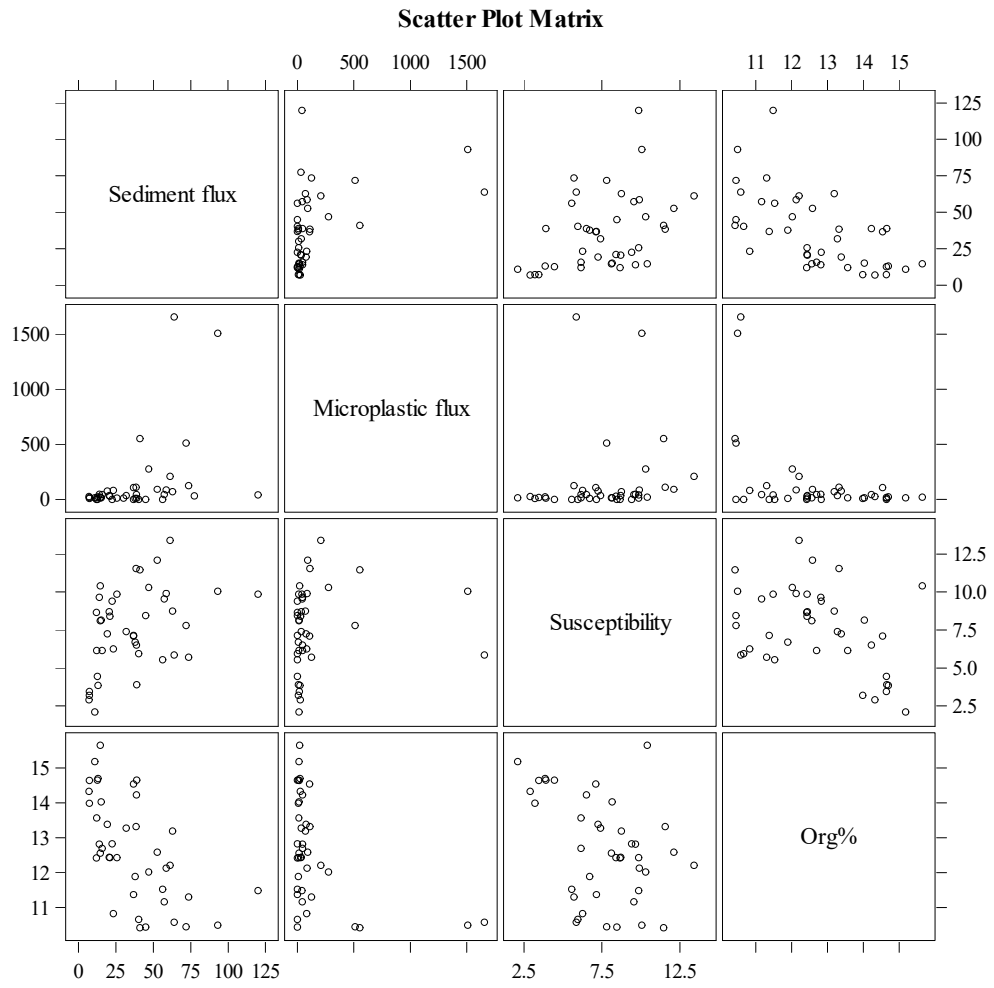

Figure 10. Scatter plot matrix of Spearman correlations.

5.6 Weather conditions

Weather data was obtained from Finnish meteorological institute (Fig. 11). The weather data used in this thesis is from weather station Kemiönsaari, Kemiö (WGS84: 60°10'16.4"N 22°45'27.7"E).

GS18 was the warmest season in all the dataset with an average temperature of 16,5 C°. Precipitation average was 1,5 mm in GS18 which was the driest growing season in the dataset. WS18-19 was the coldest season in the dataset with the average of 2,2 C°. Snow coverage was respectively the thickest in WS18-19 with the average of 8,2 cm. Precipitation average in WS18-19 was 1,5 mm which was the driest winter season in the dataset.

GS19 average temperature was 16,1 C° and precipitation average 2,3 mm. In WS19-20 the average temperature was 3,8 C° and precipitation average 3,0 mm which was the rainiest season in all dataset. The lowest snow coverage average 0,2 cm was in WS19-20.

In GS20 the average temperature was 14,5 C° and average precipitation was 2,0 mm. WS20-21 was the most temperate of all winter seasons with average of 4,2 C°. Precipitation average was 1,7 mm and snow coverage average 3,6 cm in WS20-21. In GS21 the average temperature was 15,2 C° and the average precipitation was 2,7 mm which was the rainiest summer season of the dataset.

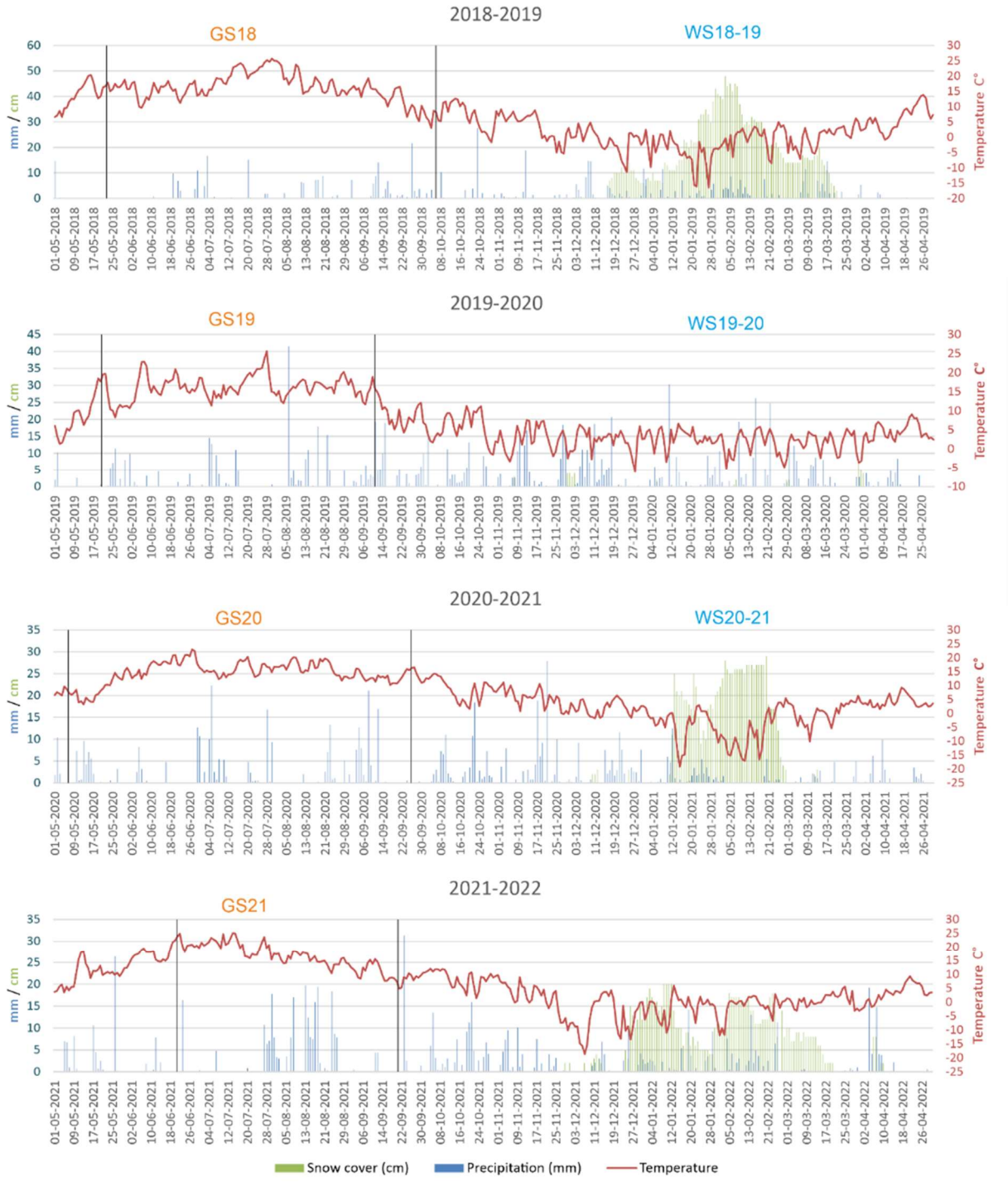

Figure 11. Weather conditions during research period (GS18 to GS21) in the Kemiönsaari Island which represents the prevailing conditions in the research area. The warmest growing season was GS18 (avg. 16,5 C°) and the coldest was GS20 (avg. 14,5 C°). The most temperate winter season was WS20-21 (avg. 4,2 C°) and the coldest was WS18-19 (avg. 2,2 C°). The rainiest growing season was GS21 (avg. 2,7 mm) and the driest was GS18 (avg. 1,5 mm). The rainiest winter season was WS19-20 (avg. 1,5 mm) and the driest was WS18-19 (avg. 1,5 mm). The thickest snow coverage was in WS18-19 (avg. 8,2 cm) and the thinnest in WS19-20 (avg. 0,2 cm).

6. Discussion

6.1 Sedimentological conditions

Susceptibility in sediment describes the amount of inorganic material in the basin (Thompson *et al.* 1975) and the LOI describes the organic content respectively (Heiri *et al.* 2001). Most of the organic matter in marine sediments are derived from biosynthesized marine organisms at surface waters (Meyers and Ishiwatari 1993; Wakeham and Lee 1993) but in Halikonlahti Estuary much of the organic matter is transported via rivers and terrigenous sources (Salmela *et al.* 2022). Minerogenic material is washed from surrounding soils of the drainage basin (Thompson *et al.* 1975). However, sediment transport from rivers to the Baltic Sea are usually small compared to resuspension in basins and erosion of coastal areas (Gingele and Leipe 1997; Jokinen *et al.* 2015). For instance, frequent low pressures and precipitation mainly increases the erosion on the catchment and resuspension in the Halikonlahti Estuary (Salmela *et al.* 2022).

High flow velocity events in the Halikonlahti Estuary caused by sea level changes and river discharge peaks increase the sediment accumulation rates (Salmela *et al.* 2022). In addition, shoreline and bottom resuspension is important factor increasing the sedimentation especially in shallow areas which are common in the Halikonlahti Estuary (Jokinen *et al.* 2015; Salmela *et al.* 2022). Another factor affecting flow velocities which increase the sediment accumulation rate in the Halikonlahti Estuary is the channel narrowness where flow velocities become higher at smaller cross-sectional sites (Salmela *et al.* 2022). Due to the glacio-isostasic uplift post-glacial clays become vulnerable to the sediment resuspension in the coastal areas (Jokinen *et al.* 2015).

Varying winter conditions affects the sedimentation during winter seasons (Salmela *et al.* 2020; 2022). Sediment flux was significantly lower during cold winter (WS18-19) compared to winters with prevailing open water conditions (WS19-20 and WS20-21). This is due to the increased precipitation, river discharge and frequent storm events during these seasons (Salmela *et al.* 2022). The organic content during winter seasons decreases towards open sea due to the terrigenous organic matter transport by rivers (Meyers and Ishiwatari 1993; Salmela *et al.* 2022). The lack of ice and snow cover and frozen soil with frequent storm events increases suspended sediment load and accumulation of minerogenic material during winters with open water conditions (Ojala *et al.* 2013; Salmela *et al.* 2022). This is seen in increased susceptibility rates and sediment fluxes in WS19-20 and WS20-21 (Fig. 4 and 6) and positive correlations between sediment flux and susceptibility (Table 5; Fig. 10).

During growing seasons minerogenic and organic material are transported mainly from terrigenous sources such as rivers and as a result of precipitation on the catchment (Jokinen *et al.* 2015; Salmela *et al.* 2022). In addition, primary production increases towards late summer which leads to enhanced sedimentation of organic matter and depletion of oxygen in bottom sediment (Meyers and Ishiwatari 1993; Jokinen *et al.* 2015). During cold winters, primary production and general sedimentation decreases but sedimentation of autochthonous organic matter increases whereas terrigenous minerogenic material decreases (Ojala *et al.* 2013; Salmela *et al.* 2022). In mild winter seasons which lack the ice and snow cover, terrigenous minerogenic material and sediment flux increases due increased riverine transport and precipitation (Salmela *et al.* 2022). Organic matter decreases compared to cold winter, but the content is lower than in summer growing season samples due to increased minerogenic matter accumulation (Salmela *et al.* 2022).

Variation in organic content and susceptibility reflect seasonal and local variations between inorganic and organic sediment loads and conditions in growing seasons (Thompson *et al.* 1975; Wakeham and Lee 1993) in the Halikonlahti Estuary. Due the shallowness of the shelf and the discharge of the Uskelanjoki and Halikonjoki Rivers, the organic matter content was low in the sediment traps 1 and 2 near the town of Salo whereas minerogenic matter was dominating in these sediment traps. Organic content increased and inorganic material decreased towards the open sea (Fig. 4 and 5) which could indicate of increased resuspension of organic matter (Salmela *et al.* 2022) and decreased transport of minerogenic sediment (Thompson *et al.* 1975; Knab *et al.* 2006). This is also seen as a negative correlation between susceptibility and organic content (Table 5; Fig. 10). However, local variation occurred in both organic and inorganic matter at both openings probably due to high flow velocity events, costal erosion and resuspension which occur especially at the northern opening of the Halikonlahti Estuary (Jokinen *et al.* 2015; Salmela *et al.* 2022).

These variations are also present in the sediment flux data: Sediment fluxes generally had decreasing trend towards the open sea (Fig. 6). On the other hand, sediment traps 8, 9, 10 and 11 had distinctive sediment flux patterns. Sediment flux was especially high in sediment trap 9 and 11 which indicate strong flow velocity events throughout the season which increase the channel borne sediment load and littoral resuspension potential (Salmela *et al.* 2020; 2022). This indirect connection is seen in negative correlation between sediment flux and organic content: the sediment flux decreases, and organic matter increases towards the open sea (Table 5; Fig. 10).

6.2 Microplastics in the research area

Urban environments, wastewater treatment plants, combined sewer overflow systems and drainage networks as well as storm waters are pathways of microplastic waste to the marine environment (Talvitie *et al.* 2015; Schernewski *et al.* 2020; Kallenbach 2022). Uskelanjoki and Halikonjoki Rivers drain directly through the town of Salo and the wastewater treatment plant to the Halikonlahti Estuary which both can be considered as the main microplastic sources in the study area. This is supported by the microplastic results: microplastic fluxes and concentrations were highest at the samples from upper estuary (sediment trap 1) and decreased towards open sea (Fig 8 and 9). Decreasing trend in microplastic fluxes and concentrations from urban to open water conditions are observed previously by Talvitie *et al.* (2015), Schernewski *et al.* (2020), Saarni *et al.* (2023).

Positive and moderate correlations between microplastic flux and sediment flux and microplastic flux and susceptibility could indicate that microplastic accumulation concentrates close to the source of plastic materials (Schernewski *et al.* 2020; Saarni *et al.* 2023) where following the human activities, sediment flux and detrital input are high as well (Knab *et al.* 2006; Table 5; Fig. 4, 6, 8, 9 and 10). However, sediment and microplastic fluxes does not seem to have connection towards the open sea due to increased sedimentation by resuspension and decreased major sources of plastic. Previously Saarni *et al.* (2023) reported that sediment and microplastic fluxes does not always have connection in freshwater environment. Microplastic fluxes were mostly higher during growing seasons than winter seasons (Fig. 8) due the increased sedimentation in growing seasons and freezing of surface waters and catchment in winter which prevents the microplastic transport to the sediment traps (Saarni *et al.* 2023). In addition, microplastics are reported to be frozen in the sea ice (Geilfus *et al.* 2019)

Major roads and bridges around the Kemiönsaari Island are able to affect the leaching of microplastics to the Halikonlahti Estuary by the mechanical abrasion of vehicle tires, and paint on the road surface (Kallenbach 2022). Agricultural and farmland sources have multiple pathways to transport microplastics to the environment (Rehm *et al.* 2021; Kallenbach 2022). For example, soil conditioners and fertilizers which are applications from sewage sludge-derived biosolids on land, plastic materials which are used in farming (plasticulture) and irrigation water that contains microplastics can be such sources and pathways (Kallenbach 2022). These could be the reasons to relatively high microplastic fluxes and concentrations for example in sediment traps 6 and 9 in both openings, both surrounded by large, cultivated lands (Fig. 8 and 9). In addition, the catchment area of Uskelanjoki and Halikonlahti Rivers are heavily cultivated where microplastics could transport to the Halikonlahti Estuary (Salmela *et al.* 2022).

Majority of the plastic types in the sediment traps were polystyrene (PS) which is the one of the most used plastic type in Europe among PE and PP (Gewert *et al.* 2015; Geyer *et* al. 2017). PS was the most common plastic type in the research area and the majority of it accumulated at the river mouth (Sediment trap 1) which located near to the industry areas (Table 3). Other plastic types were more dispersed in the sediment traps.

At the moment, there are very few studies reporting microplastic flux rates. Previously average microplastic flux has been recorded from Santa Barbara Basin, California with 7,8 particles m^{-2} a^{-1} with methodological lower limit of 66 µm (Brandon *et al.* 2019). In Arkona Basin at the Baltic Sea microplastic flux of 37 particles m^{-2} a^{-1} was measured with methodological lower limit of 25 µm (Enders *et al.* 2019). In Northeast Atlantic between Azores and Canary Islands, microplastic flux varied from 1,13-3146,81 particles m^{-2} d^{-1} with methodological lower limit of 10 µm (Reineccius and Waniek 2022). The annual average microplastic flux in Halikonlahti Estuary (50 735 MPs m^{-2} a^{-1}) was higher than microplastic fluxes in Santa Barbara basin, California (Brandon *et al.* 2019) and Arkona Basin at the Baltic Sea (Enders *et al.* 2019). The minimum calculated microplastic flux in Northeast Atlantic between Azores and Canary Islands (1,13 m^{-2} d^{-1}) was lower than minimum calculated microplastic flux in Halikonlahti Estuary (9,0 MPs m^{-2} d^{-1}) but maximum measured microplastic flux in Northeast Atlantic (3146,81 particles m^{-2} d^{-1}) was higher than maximum measured microplastic flux in Halikonlahti Estuary (1656,0 MPs m^{-2} d^{-1}) (Reineccius and Waniek 2022).

The higher fluxes in Halikonlahti Estuary compared to previously mentioned studies from open sea sites were expected because the sources of microplastic were significantly closer in our research site. Furthermore, the water depths were significantly higher, for example, sediment traps in Northeast Atlantic between Azores and Canary Islands were placed in the depth of 2000 m where sea depth was 5300 m (Reineccius and Waniek 2022).

In Kallavesi Lake in Finland, microplastic flux was 1,5-9,5 particles m^{-2} d^{-1} with a methodological lower limit of 100 µm (Saarni *et al.* 2023) and in Huruslahti Bay in Haukivesi Lake in Finland, microplastic flux was 61,3-130,6 particles m^{-2} d^{-1} with methodological lower limit of 100 µm (Saarni *et al.* 2021). Both sites lack major river inflow but are located close to urban activities. The fluxes at Kallavesi Lake are generally lower than in the Halikonlahti Estuary while the Huruslahti Bay show similar fluxes with estuarine values, excluding the upper estuarine site (sediment trap 1), where the microplastic fluxes are significantly higher. This implies the importance of riverine transport (Strokal *et al.* 2023). Versatile microplastic fluxes in different locations are also likely related to different

sedimentological and bathymetric conditions. However, the size of microplastics in Halikonlahti Estuary were mostly under 100 µm (Table 3) which indicate that the results in Kallavesi Lake and Huruslahti Bay probably underestimate the microplastic fluxes because the methodological lower limit was 100 µm in both studies (Saarni *et al.* 2021; 2023). In addition, removal of PP and PE from the results likely underestimate the real microplastic fluxes in Halikonlahti Estuary.

In the Bay of Brest in France mean microplastic concentration was 0.97 ± 2.08 MP kg^{-1} in dry sediment with methodological lower limit of 1,6 µm (Frère *et al.* 2017). Along the beaches of German Baltic coast microplastic concentration was 0-7 MP kg^{-1} with methodological lower limit of 63 µm (Stolte *et al.* 2015) and at the Belgian coast highest microplastic concentration was 390 particles kg^{-1} and lowest 48,7 particles kg^{-1} with methodological lower limit of 38 µm (Claessens *et al.* 2011). In Gulf of Lion at Northwestern Mediterranean Sea microplastic concentrations varied from 33 to 798 particles kg^{-1} with methodological lower limit of 63 µm (Constant *et al.* 2019).

Microplastic concentrations were lower in the Bay of Brest in France (Frère *et al.* 2017), German Baltic coast (Stolte *et al.* 2015), at the Belgian coast (Claessens *et al.* 2011), Gulf of Lion at Northwestern Mediterranean Sea (Constant *et al.* 2019) research than the average concentration in Halikonlahti Estuary (0,24-25,9 MPs/g). However, the comparison between different microplastic concentrations and separate places are difficult due the various timescales, differences in basin properties, methods and units in results (Saarni *et al.* 2021). Microplastic fluxes and concentrations varies significantly depending on the different sedimentation processes and anthropogenic plastic sources around each study site. The observed high concentrations of microplastics in the sediments of this semi closed estuary support the previously made suggestion that estuarine systems could be hot spots for microplastics (Vandermeersch *et al.* 2015; Nel *et al.* 2020).

6.3 Background contamination

Possible contamination sources could be plastic containers (PP) where the sediment was poured in the research vessel and plastic centrifuge tubes (PP) which were used in the density separation as well as bottles (PE) which were used to rinse bottle top device and filters during the enzymatic purification process. Other plastic materials were not used in the process.

7. Conclusion

The sediment fluxes are the highest at the river opening and decreases towards the open sea which represents the common trend in the Halikonlahti Estuary. Variation in sedimentation in different sediment traps are mainly due to changes in riverine sediment transport, channel narrowness and shallowness which promote the sediment resuspension: the shallower and narrower the channel is the more sediment accumulate in sediment trap. Minerogenic and organic matter is mainly terrigenous, transported from rivers with transport peaks as a result of precipitation on the catchment to the Halikonlahti Estuary. During winter seasons snow coverage determined the character of the sediment: mild winters with low or no snow cover resulted to high fluxes of minerogenic and organic matter and overall high sediment flux whereas ice and snow cover and frozen soil led to lower minerogenic fluxes, low organic matter burial and low sediment flux.

Microplastic accumulation follow the similar trend as sediment fluxes where microplastic fluxes and concentrations decrease towards open sea. However, the amount of microplastic accumulation is more related to the anthropogenic activities and location of the plastic sources such as urban areas, major roads and cultivated lands than sediment accumulation rates. Microplastic fluxes were mostly higher during growing seasons than winter seasons due the increased sediment availability in growing seasons and freezing of surface waters and catchment in winter. Removal of PP and PE plastic types from the results due possible contamination potentially underestimate the real microplastic fluxes in Halikonlahti Estuary.

Relatively high microplastic fluxes and concentrations were expected because the sources of microplastic were significantly closer in our research site than in compared microplastic studies around the world. The accumulation of microplastic varies significantly depending on the different sedimentation processes and anthropogenic plastic sources around each study site. Therefore, the comparison is difficult due the various timescales, differences in basin properties, methods, methodological lower limits and units used in microplastic results. However, the high concentrations of microplastics in the sediments of Halikonlahti Estuary support the suggestion that estuarine systems could work as a sink for microplastics.

Contamination was a major issue in this research but valuable knowledge to more successful enzyme purification process was obtained. To prevent the contamination in the future all used plastic items during sampling and microplastic analysis should be replaced with non-plastic materials if possible.

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9. References

Amaneesh, C., Balan, S. A., Silpa, P. S., Kim, J. W., Greeshma, K., Mohan, A. A., Antony, A. R., Grossart, H. P., Kim, H.-S. and Ramanan, R. 2023: Gross Negligence: Impacts of Microplastics and Plastic Leachates on Phytoplankton Community and Ecosystem Dynamics. Environmental Science and Technology 57 (1), 5–24.

Andrady, A. L. 2011: Microplastics in the marine environment. Marine Pollution Bulletin 62 (8), 1–10.

Arthur, C., Baker, J. E., Bamford, H. A., Barnea, N., Lohmann, R., McElwee, K., Morishige, C. and Thompson, R. 2009: Executive Summary. In: Arthur, C., Baker, J. E. and Bamford, H. A. (eds) Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris. NOAA Technical Memorandum. Tacoma, USA. 7–18.

Ashter, S. A. 2016: New developments. In: Ashter, S. A. (ed) Introduction to Bioplastics Engineering William Andrew Publishing, Elsevier Science. Oxford, UK. 251–274.

Brandon, J. A., Jones, W. and Ohman, M. D. 2019: Multidecadal increase in plastic particles in costal ocean sediments. Science Advances (5), 1–7.

Carbery, M., O'Connor, W. and Palanisami, T. 2018: Trophic transfer of microplastics and mixed contaminants in the marine food web and implications for human health. Environment International 115. 400–409.

Carpenter, E. J. and Smith, K. L. 1972: Plastics on the Sargasso Sea Surface. Science 175, 1240–1241.

Central Chemical Consulting 2018: The Home of LST Heavy Liquid- webpage: https://www.heavyliquids.com/index.html [14.03.2023].

City of Salo 2020: General information on Salo: https://salo.fi/kaupunki-ja-paatoksenteko/organisaatio/tietoa-salosta/ [3.06.2023].

Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K. and Janssen, C. R. 2011: Occurrence and distribution of microplastics in marine sediments along the Belgian coast. Marine Pollution Bulletin 62 (10), 2199–2204.

Claessens, M., Van Cauwenberghe, L., Vandegehuchte, M. B. and Janssen, C. R. 2013: New techniques for the detection of microplastics in sediments and field collected organisms. Marine Pollution Bulletin 70 (1-2), 227–233.

Cole, M., Lindeque, P., Halsband, C. and Galloway, T. S. 2011: Microplastics as contaminants in the marine environment: a review. Marine Pollution Bulletin 62 (12), 2588–2597.

Colton, J. B., Burns, B. B. and Knapp, F. D. 1974: Plastic Particles in Surface Waters of the Northwestern Atlantic. Science 185, 491–497.

Constant, M., Kerhervé, P., Mino-Vercellio-Verollet, M., Dumontier, M., Vidal, A. S., Canals, M. and Heussner, S. 2019: Beached microplastics in the Northwestern Mediterranean Sea. Marine Pollution Bulletin 142, 263–273.

Dame, R. F. 2008: Estuaries. In: Jørgensen, S. E. and Fath, B. D. (eds) Encyclopedia of Ecology. Academic Press, Charleston, USA. 1407–1413.

Dearing, J. A. 1999: Environmental Magnetic Susceptibility, Using the Bartington MS2 System, 2. Edition. Bartington Instruments Limited. Oxford, UK. 1–54.

D-maps.com 2023: Baltic Sea map: https://d-maps.com/carte.php?num_car=5038&lang=en [1.10.2023].

Enders, K., Käppler, A., Biniasch, O., Fedens, P., Stollberg, N., Lange, X., Fisher, D., Eichhorn, K-J., Pollehne, F., Oberbeckmann, S. and Labrenz, M. 2019: Tracing microplastics in aquatic environments based on sediment analogies. Scientific Reports 9, 15207.

Fjäder, P. 2016: Merten roskaantuminen, muovit, mikromuovit ja haitalliset aineet. Suomen ympäristökeskuksen raportteja 37, Suomen ympäristökeskus (SYKE), Helsinki. 1–62 (in Finnish).

Frère, L., Paul-Pont, I., Rinnert, E., Petton, S., Jaffré, J., Bihannic, I., Soudant, P., Lambert, C. and Huvet, A. 2017: Influence of environmental and anthropogenic factors on the composition, concentration and spatial distribution of microplastics: A case study of the Bay of Brest (Brittany, France). Environmental Pollution 225, 211–222.

Geilfus, N.-X., Munson, K. M., Sousa, J., Germanov, Y., Bhugaloo, S., Babb, D. and Wang, F. 2019: Distribution and impacts of microplastic incorporation within sea ice. Marine Pollution Bulletin 145, 463–473.

Gewert, B., Plassmann, M. and MacLeod, M. 2015: Pathways for degradation of plastic polymers floating in the marine environment. Environment Science: Processes Impacts 17, 1513–1521.

Geyer, R., Jambeck, J. R. and Law, K. L. 2017: Production, use, and fate of all plastics ever made. Science Advances 3 (7), 1–5.

Gingele, F. X. and Leipe, T. 1997: Clay mineral assemblages in the western Baltic Sea: recent distribution and relation to sedimentary units. Marine Geology 140 (1–2), 97–115.

Gourmelon, G. 2015: Global Plastic Production Rises, Recycling Lags. Worldwatch institute, Vital Signs 22, 91–95

Gregory, M. R. 1977: Plastic pellets on New Zealand beaches. Marine Pollution Bulletin 8 (4), 82–84.

Hartmann, N. B., Hüffer, T., Thompson, R. C., Hassellöv, M., Verschoor, A., Daugaard, A. E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M. P., Hess, M. C., Ivleva, N. P., Lusher, A. L. and Wagner, M. 2019: Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. Environmental Science and Technology 53, 1039–1047.

Heiri, O., Lotter, A. and Lemcke, G. 2001: Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results, Journal of Paleolimnology 25, 101–110.

Jokinen, S. A., Virtasalo, J. J., Kotilainen, A. T. and Saarinen, T. 2015: Varve microfabric record of seasonal sedimentation and bottom flow-modulated mud deposition in the coastal northern Baltic Sea. Marine Geology 366, 79–96.

Kallenbach, E. M. F., Rødland, E. S., Buenaventura, N. T. and Hurley, R. 2022: Microplastics in Terrestrial and Freshwater Environments. In: Bank, M. (ed) Microplastic in the Environment: Pattern and Process. 1. Edition. Springer International Publishing. Amherst, USA. 87–130.

Kaiser, D., Kowalski, N. and Waniek, J. 2017: Effects of biofouling on the sinking behavior of microplastics. Environmental Research Letters 12 (12), 124003.

Kangas, A. 2017: Käsittelyvaatimusten toimeenpano in: Kangas, A. (ed) Haja-asutuksen jätevedet – Lainsäädäntö ja käytännöt. Ympäristöopas 2017, Ympäristöministeriö, Lönnberg Print and Promo. Helsinki. 31–42 (in Finnish).

Knab, M., Hoffmann, V., Petrovský, E., Kapička, A., Jordanova, N. and Appel, E. 2006: Surveying the anthropogenic impact of the Moldau river sediments and nearby soils using magnetic susceptibility. Environmental Geology 49, 527–535.

Lambert, S. and Wagner, M. 2018: Microplastics Are Contaminants of Emerging Concern in Freshwater Environments: An Overview. In: Lambert, S. and Wagner, M. (eds) Freshwater Microplastics Emerging Environmental Contaminants? The Handbook of Environmental Chemistry 58. 1. Edition. Springer Cham. Switzerland. 1–24.

Löder, M. G. J., Imhof, H. K., Ladehof, M., Löschel, L. A., Lorenz, C., Mintenig, S., Piehl, S., Primpke, S., Schrank, I., Laforsch, C. and Gerdts, G. 2017: Enzymatic Purification of Microplastics in Environmental Samples. Environmental Science and Technology 51, 14283−14292.

Meyers, P. A. and Ishiwatari, R. 1993: Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry 20 (7), 867–900.

Napper, I. E. and Thompson, R. C. 2020: Plastic Debris in the Marine Environment: History and Future Challenges. Global Challenges 4, 1900081.

National Land Survey of Finland 2023: Topograohic map raster and Hillshade elevation model: https://asiointi.maanmittauslaitos.fi/karttapaikka/ [1.10.2023].

Nel, H. A., Smith, G. H. S., Harmer, R., Sykes, R., Schneidewind, U., Lynch, I. and Krause, S. 2020: Citizen science reveals microplastic hotspots within tidal estuaries and the remote Scilly Islands, United Kingdom. Marine Pollution Bulletin 161, 111776.

Nuelle, M. T., Dekiff, J., Remy, D. and Fries, E. 2014: A new analytical approach for monitoring microplastics in marine sediments. Environmental Pollution 184, 161–169.

Ojala, A. E. K., Kosonen, E., Weckström, J., Korkonen, S. and Korhola, A. 2013: Seasonal formation of clastic-biogenic varves: the potential for palaeoenvironmental interperations. GFF 135 (3–4), 237–247.

Primpke, S., Cross, R., Mintenig, S., Simon, M., Vianello, A., Gerdts, G. and Vollertsen, J. 2020: Toward the Systematic Identification of Microplastics in the Environment: Evaluation of a New Independent Software Tool (siMPle) for Spectroscopic Analysis. Applied Spectroscopy 74 (9), 1127–1138.

Rehm, R., Zeyer, T., Schmidt, A. and Fiener, P. 2021: Soil erosion as transport pathway of microplastic from agriculture soils to aquatic ecosystems. Science of The Total Environment 795, 148774.

Reineccius, J. and Waniek, J. J. 2022: First long-term evidence of microplastic pollution in the deep subtropical Northeast Atlantic. Environmental Pollution 305, 119302.

Ritchie, H., Samborska, V. and Roser, M. 2023: Plastic Pollution. In Our World Data; Oxford Martin School: Oxford, UK: https://ourworldindata.org/plastic-pollution [26.11.2023].

Saarni, S., Hartikainen, S., Meronen, S., Uurasjärvi, E., Kalliokoski, M. and Koistinen, K. 2021: Sediment trapping – An attempt to monitor temporal variation of microplastic flux rates in aquatic systems. Environmental Pollution 274, 116568.

Saarni, S., Soininen, T., Uurasjärvi, E., Hartikainen, S., Meronen, S., Saarinen, T. and Koistinen, A. 2023: Seasonal variation observed in microplastic deposition rates in boreal lake sediments. Journal of Soils Sediments 23, 1960–1970.

Salmela, J., Kasvi, E. and Alho, P. 2020: River plume and sediment transport seasonality in a non-tidal semi-enclosed brackish water estuary of the Baltic Sea. Estuarine, Coastal and Shelf Science 245, 106986.

Salmela, J., Saarni, S., Blåfield, L., Katainen, M., Kasvi, M. and Alho, P. 2022: Comparison of cold season sedimentation dynamics in the non-tidal estuary of the Northern Baltic Sea. Marine Geology 443, 106701.

Schernewski, G., Radtke, H., Hauk, R., Baresel, C., Olshammar, M., Osinski, R. and Oberbeckmann, S. 2020: Transport and Behavior of Microplastics Emissions From Urban Sources in the Baltic Sea. Frontiers in Environmental Science 8, 579361.

Setälä, O., Lehtiniemi, M., Haaksi, H. and Gustafsson, J. 2017: Roskapostia – kansalaisen tietokirja meren roskaantumisesta. Silverprnt. Sipoo. 1–68 (in Finnish).

Stolte, A., Forster, S., Gerdts, G. and Schubert, H. 2015: Microplastic concentrations in beach sediments along the German Baltic coast. Marine Pollution Bulletin 99 (1–2), 216–229.

Strokal, M., Vriend, P., Bak, M. P., Kroeze, C., van Wijnen, J. and van Emmerik, T. 2023: River export of macro- and microplastics to seas by sources worldwide. Natural Communications 14, 4842.

Talvitie, J., Heinonen, M., Pääkkönen, J-P., Nyman, E., Mikola, A., Setälä, O. and Vahala, R. 2015: Do wastewater treatment plants act as a potential point source of microplastics? Preliminary study in the coastal Gulf of Finland, Baltic Sea. Water Science and Technology 72 (9), 1495–1504.

Thompson, R., Battarbee, R. W., O'Sullivan, P. E. and Oldfield, F. 1975: Magnetic susceptibility of lake sediments, Limnology and Oceanography 20 (5). 687–698.

Thompson, R. C., Olsen, Y., Mitchell, R., Davis, A., Rowland, S., John, A., McGonigle, D. and Russell, A. 2004: Lost at Sea: Where Is All the Plastic? Science 304, 838–838.

Turner, S., Horton, A. A., Rose, N. L. and Hall, C. 2019: A temporal sediment record of microplastics in an urban lake, London, UK. Journal of Paleolimnology 61, 449–462.

Uurasjärvi, E. 2021: Instrumental techniques for analysis of microplastics. In: Hakulinen, N. (ed) Microplastics – A challenge for environmental analytical chemistry. Publications of the University of Eastern Finland, Dissertations in Forestry and Natural Sciences 433. PunaMusta Oy. Joensuu. 27–37.

Vandermeersch, G., Van Cauwenberghe, L., Janssen, C. R., Marques, A., Granby, K., Fait, G., Michiel, J. J., Kotterman, M. J. J., Diogène, J., Bekaert, K., Robbens, J. and Devriese, L. 2015: A critical view on microplastic quantification in aquatic organisms. Environmental Research 143 (B), 46–55.

Wakeham, S. G. and Lee, C. 1993: Production, Transport, and Alteration of Particulate Organic Matter in the Marine Water Column. In: Engel, M. H. and Macko, S. A. (eds) Organic Geochemistry Topics in Geobiology 11. Springer. Boston, USA. 145–165.

Wang, Y-L., Lee, Y-H., Chiu, I-J., Lin, Y-F. and Chiu, H-W. 2020: Potent Impact of Plastic Nanomaterials and Micromaterials on the Food Chain and Human Health. International Journal of Molecular Science 21 (5), 1727.