Downward migrating microplastic in lake sediments is a tricky indicator for the onset of the Anthropocene

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Abstract

Plastics are a particulate novel material in Earth's history. Due to its persistence and wide-range presence, it has a great potential of being a global age marker and correlation tool between sedimentary profiles. Hence, microplastics are currently considered among the array of proxies to delimit the Anthropocene Epoch (starting from year 1950 and above). Here we present a study of microplastics deposition history inferred from sediment profiles of three lakes in north-eastern Europe. The sediments were dated with independent proxies from nowadays back to the first half of the 18th century. Surprisingly, regardless of the sediment layer age, we found microplastic particles throughout the cores in all sites. The factor driving microplastic particles to penetrate deeper in sediment layers appears to be particles' dimensional (aspect) ratio: less elongated particles tend to be transported deeper while more elongated particles and fibres have a decreased ability to be mobile. We conclude that interpretation of microplastics distribution in sediment profiles is ambiguous and does not strictly indicate the beginning of the Anthropocene Epoch.

Introduction

Microplastics (MPs) are modern pervasive pollutants of anthropogenic origin that pose an environmental and health risk. Since the beginning of the production of synthetic polymers in the 20th century, more and more plastic materials with versatile features have been invented and adopted into use. Cumulative global plastic production reached 8 300 million metric tonnes (Mt) during 2017, and since then, more than 360 Mt of plastics have been produced annually. It is estimated that only about 9% of all plastic ever produced is recycled and 12% incinerated, leading to the conclusion that over 6 000 Mt of waste plastic has the potential to leak into the environment and become incorporated in natural cycles and food chains. Significant amounts of MPs are found even in arctic deep-sea and rural lake sediments in glaciers and in air of remote sites. Due to the prominent growth of plastic accumulation across natural environments, as well as their potential to persist in geological formations in the form of plastiglomerates, pyroplastics, plasticrusts and anthropoquinas, MPs are widely suggested as markers of the Anthropocene.

In the geological time scale, the Anthropocene is an unofficial unit proposed to describe the new geological ongoing event/epoch, characterized by human altered natural processes. Human activities have left traces on the stratigraphic record during the last few millennia. However, qualitatively significant changes occurred with the “Great Acceleration” of population growth and industrialization. Hence, the Anthropocene Working Group (AWG) of the International Union of Geological Sciences (IUGS) has suggested the year 1950 to be the starting point of the Anthropocene Epoch. This time coincides with the beginning of industrial mass production of plastic, consequently, plastic deposits have risen among the array of proxies discussed related to the selection of an appropriate Global boundary Stratotype Section and Point (GSSP). Proxies chosen must have global correlation potential in various sedimentary matrices. Precise dating of sediments as young as 1950 presents significant challenges. Methods that employ short-lived natural and artificial atmospheric fall-out radionuclides (²⁴¹Am, ¹³⁷Cs, ²¹⁰Pb) are most widely used to obtain reliable chronologies for such short time scales and therefore suggested as primary proxies due to their sharp and globally widespread signal. Among these methods, ²¹⁰Pb dating is commonly considered a powerful technique for estimating the age of recently deposited sediments. However, there are also caveats related to some factors (i.e. water depth, sediment composition, bioturbation) that influence the vertical activity profiles of ²¹⁰Pb in sediment cores. Thus, the dating results should only be accepted if they are
consistent with other stratigraphic marker horizons, e.g. $^{137}\text{Cs}$ activity peaks, spheroidal carbonaceous particles (SCP), tefra layers, well-dated event layers. Potentially, a significant increase in MP concentrations after 1950 would also serve as a marker horizon and ideal addition to the chronological tool box.

However, despite exponential growth in the number of studies on MPs in sediments in general, there are very few studies reporting MP pollution findings from well-dated sediment profiles$^{9,10,25–28}$. Hence, the usability of MP profiles as supplementary marker for Anthropocene remains speculative.

Here, we provide evidence of MP deposits from three lakes (Seksu, Pinku and Usmas) in the north-eastern part of Europe (Supplementary Fig. S1). The lakes represent different degrees of access restrictions due to the status of a specially protected natural area or being a part of the drinking water supply system. There was also a considerable difference among lakes regarding the distance to urbanised areas. The use of well-established dating methods with various proxies (i.e. $^{210}\text{Pb}$, SCP) enabled the evaluation of MP concentration change rates through the 20th century and earlier with precise time control, which is critical in terms of stratigraphy. The presented research demonstrates an exponential growth of MP concentrations introduced into sedimentary records and related to human-induced activities, but not necessarily being time-synchronous. The objectives of this study were: to measure MP concentration throughout dated lacustrine sediment archives at and below year 1950; to observe variables that might affect MP accumulation in the sediments; finally, to set MPs in a sedimentary context and evaluate MP as a chronostratigraphic marker for the Anthropocene.

**Results**

**Microplastic throughout sediments in time and space**

The combination of $^{210}\text{Pb}$, SCP, and age-depth modelling techniques provided reliable chronologies for the investigated sediment cores and allowed testing and verifying the potential of MP as a marker horizon. $^{210}\text{Pb}$ displayed a regular decrease in activity concentrations with sediment depth and only minor irregularities (Fig. 1, Supplementary Fig. S2), while SCP indicated an expected concentration pattern, which proves the absence of significant disturbance of the sediment column and allows reliable sediment dating. The age-depth model for Lake Seksu was almost linear with limited uncertainty indicating a relatively young age of sediments at the basal part (46 cm, age range 1925–1943; mean age 1934). Age-depth models for lakes Pinku and Usmas showed reasonable uncertainty until 11 cm (age range 1921–1949; mean age 1936) and 25 cm (age range 1890–1910; mean age 1900), respectively. Beyond these depths, age was extrapolated because lower parts of the cores were below the dating horizon of $^{210}\text{Pb}$ and SCP methods. However, in all three lakes, the age-depth models can be used to reliably establish the boundary between sediment layers older and younger than 1950, which is 39 cm in Lake Seksu, 10 cm in Lake Pinku, and 15 cm in Lake Usmas. Sections of the sediment cores below these depths represent the so-called pre-Anthropocene period, dating before year 1950$^{14,19,20}$.

In total 14 types of polymers and polymer groups were detected in the three lakes – 10 types of polymers found in Lake Pinku, 13 in Lake Usmas and 14 in Lake Seksu. The most abundant polymers found at all depths were PA (polyamide), PE (polyethylene), PUR (polyurethane) and PVA (polyvinyl acetate). Group of rubbers (i.e. BIIR (butyl rubber), BR (butadiene rubber), SR (synthetic rubber)), same as PES (polyester), PP (polypropylene) and PS (polystyrene) were found both in deep and upper layers, but not in every layer of the cores. Biodegradable plastics - polyactic acid (PLA) and polyhydroxybutyrate (PHB) were found occasionally. In all lakes, the highest total concentrations of MPs were detected in upper sediment layers decreasing towards deeper parts of the core. The
most common polymers in the topmost 15 cm (representing years 2019 – 1997) of Lake Seksu were PE and PUR constituting in total 26.6% of all polymers while in Lake Pinku 78.9% of all polymers in the upper layer (topmost 5 cm representing time period 2019 – 2002) were PUR and rubber polymers. Rubbers were the most frequent polymers in the topmost 5 cm (years 2019 – 1997) in Lake Usmas, employing 46.2% of all identified MPs (Figs. 1 and 2, Supplementary Table S1). The sediment layer 5–10 cm (1997 – 1971) of Lake Usmas was damaged during sample processing and therefore excluded from the further analysis.

The average concentration of MP throughout the core in lakes Usmas, Pinku and Seksu was 2.4, 4.1 and 33.9 particles per gram of dry sediments (particles g$^{-1}$) accordingly (Supplementary Tables S1 and S2).

**Drivers of microplastic downward migration**

According to dry bulk density (BD) data, sediment of Lake Seksu were substantially more loose (0.12 g cm$^{-3}$) than the sediments of lakes Pinku and Usmas (0.68 and 0.44 g cm$^{-3}$, respectively; Supplementary Table S3). The low density of Lake Seksu sediment is related to exceptionally high organic content (on average 55%), compared to lakes Pinku and Usmas (for both the average organic matter was 21%) (Supplementary Fig. S4). The sedimentation rate was highest in Lake Seksu (5.3 mm year$^{-1}$) and lowest in Lake Pinku (1.3 mm year$^{-1}$).

Principal component analysis (PCA) coupled with factor analysis were performed to understand which variables and factors affect the transportation of MP particles into deeper layers. We acknowledged the following variables: sediment depth and age, sediment organic content, BD, relative bulk density (RBD), MP material density, MP particle size (including major and minor dimension), and shape i.e. aspect ratio (AR). RBD is equal to the ratio between the BD of each sediment layer and the densest layer of the lake. AR is the relation of minor dimension to major dimension. Hence, we further conventionally categorized particles according to the AR into four classes: <0.25, 0.25–0.50, 0.50–0.75 and 0.75-1. All polymers showed a wide variation of AR at every depth, although the general trend was - the greater the AR (less elongated particles), the deeper particles tend to penetrate within a core (Fig. 3, Supplementary Fig. S5).

The individual AR of the MP particles was the only variable correlating with the depth (Fig. 4A). The PCA analysis showed that transportation of MP into the deeper layers was neither affected by such geological variables as BD of sediments and organic matter content, nor MP density and particle size.

Spearman's rank correlation analysis of the pooled data from the three lakes showed a strong positive correlation (Fig. 4B) between the age of the sediment layer (date, as a proxy of depth for pooled data of three different lakes) and the proportional abundance of the most elongated particles (AR < 0.25) found in the layer, as well as a strong negative correlation with the proportional abundance of the least elongated particles (AP 0.5–0.75 and 0.75-1). Equivalent Spherical Diameter (ESD) is a particle size descriptor which allows the comparison of irregularly shaped objects via the calculated diameter of a sphere of equivalent volume. Only the proportional abundance of the smallest fraction with ESD below the first distribution quartile (ESD < 62 µm) showed a strong positive correlation with the age of the sediment layer, but the result should be interpreted with caution because, according to the ESD equation, a smaller minor dimension for the same major dimension results in a lower ESD, which may mean that the particle has a lower AR, but not the size itself. The results indicate that particle shape plays an important role in the ability of a particle to be mobile.

**Discussion**
Microplastic throughout sediments in time and space

MP were present throughout every studied lake's sediment core samples regardless of “the pre-plastic age”, i.e. year 1950. Generally, our results are comparable with previous findings summarising data on polymers occurring in freshwaters and estuaries\textsuperscript{29,30}. Jones, et al.\textsuperscript{29} concluded that the highest relative abundance of polymers found in the environmental samples (including sediments) are PE, PP, PS and miscellaneous plastics representing the most produced polymers. The most frequent miscellaneous plastics were polyethylene-vinyl acetate (PEVA, referred as PVA in our study), PA, polymethyl methacrylate (PMMA) and bioplastics (cellulose derivatives)\textsuperscript{29}. We observed a comparatively low abundance and frequency of PET particles in the sediments even though PET is among top produced synthetic polymers globally. Instead, PUR was included in our dominant findings. PMMA was excluded from our results, as this polymer was used in some devices for sample preparation and consequently was found in blank samples.

The breakthrough of biodegradable plastics took place in the 1990s\textsuperscript{31}. Depending on the environment, temperature, size and shape of the particles, the biodegradable plastics (such as PLA and PHB recorded from our samples) degradation in the environment can take several years\textsuperscript{32,33}. Hence, particles found in the lake should not be older than the last decade. Still, in our study, PLA and PHB were found in sediment layers dated to the time period of 1925 – 1900 (Usmas lake) and 1953 – 1881, 1813 – 1733 (Pinku lake). In lake Seksu, PHB and PLA were present from recent down to a layer representing time period of 1979 – 1969.

Even if the found major plastic types (PE, PA etc.) were commercially available before 1950 (i.e. beginning of 1900, mostly around 1930\textsuperscript{34}), produced amounts of these materials were negligible. Hence it is not likely that particles found in Latvian lakes below 1950 represent remains of early plastic manufacture development even if historically old industrial regions in western Europe might see some evidence of early plastic production in the sediments. Furthermore, in Lake Pinku a wide range of plastic materials can be found until 1800 level and PA, and PE particles are present down to the first half of 18th century (Fig. 2).

MPs have been identified in significant amounts below 1950 also in other studies with well-dated sediment records\textsuperscript{9,10,25–28}. For example, the Santa Barbara basin record, where a varved sediment structure denotes the absence of physical mixing, shows a clearly increasing trend in fragments and films starting from sediments older than 1950 (see Brandon, et al.\textsuperscript{10} supplementary data). Nevertheless, Brandon, et al.\textsuperscript{10} treated MP findings before 1945 as core processing contamination. Due to lack of experimental controls (neither recovery samples nor air/procedural/field blanks in the study by Brandon, et al.\textsuperscript{10}), it is difficult to estimate the degree of contamination, however, based on our observations of MPs distribution in the cores, the increasing trend of MPs concentration starting from pre 1950-level is unlikely caused by artefact. Same can be concluded from other studies\textsuperscript{9,25–28}.

The highest MP concentrations at the top-parts of the sediment cores in general (varying as to estimated age) are in accordance with recent studies from well-dated sediment profiles from freshwater, marine, and estuary depositional environments\textsuperscript{35}. The increasing trend of MP concentration towards younger (surface) sediments is a well-established and understood finding related to accelerating mass production of plastic materials\textsuperscript{10,11,35}.

In Lake Pinku record, the greatest increase in particle concentration occurred immediately above the second topmost sediment layer dated to 2002 – 1953, when the concentration shifted from 0.8 to 10.6 particles g\textsuperscript{-1}. In lake Seksu record MP concentration peaked above the sediment layer 15–20 m dating back to 1997 – 1988, when the concentration increased from 11.9 to 100.1 particles g\textsuperscript{-1} (Supplementary Fig. S3). This indicates that there is no
elbow point reflecting MP pollution rise after 1950’s. Instead, an elbow reflects the beginning of the last two decades coinciding with doubling of annual production rate of plastics in 2002 compared to 1989 (from 100 to 200 Mt)\textsuperscript{36}. This is consistent with the results by Turner, et al.\textsuperscript{9} and Brandon, et al.\textsuperscript{10} reporting significant increase in MP concentrations around the time.

As to MP concentrations per sediment unit we did not compare our results with other findings since our study recovery tests revealed on average 32.6\% recovery reflecting the heavy treatment protocol involved with many procedural steps, i.e. the number of sample transfers during sample purification affects the recovery rate. Therefore, it can be assumed that the actual MP concentration in the lake sediments might be at least twice or even three times higher\textsuperscript{37}. Air background samples and procedural/field blanks were analysed in parallel with lake sediment samples and were not considered to change the results significantly (see more details in the methods section).

There are considerable differences in average concentration of MP throughout the core among lakes. Lake Seksu is a part of the drinking water system, protected by access restrictions and fence around, yet showing the highest MP concentrations compared to other two lakes (also protected). In Lake Seksu MP average concentration is 8 and 14 times higher compared to lakes Pinku and Usmas respectively. This is likely related to the Lakes Seksu location in the urban area while the other two lakes are located in rural region. Our observation extends those of Kutralam-Muniasamy, et al.\textsuperscript{38}, concluding that the conservation status does not prevent MP pollution, as protected area rules and restrictions do not address MP pollution directly. Likewise, Brahney, et al.\textsuperscript{39} have estimated that more than 1000 metric tons of wind- and rain-borne MP fall annually on US protected areas. Hence, we confirm that proximity to the urban environment and MPs transport driven by wind\textsuperscript{40,41} and runoff\textsuperscript{42} has a more significant impact on the MP concentration and composition in the sediments than protection regulations in the lake’s immediate surroundings.

**Drivers of microplastic downward migration**

Our results suggest significant downward migration of MPs in sediment profiles. Several mechanisms can transport MP particles deeper - core smearing during sampling, sediment reworking through resuspension or turbidity flows and bioturbation\textsuperscript{43}. There is no evidence of significant particle movements resulting from coring in our results nor in the literature\textsuperscript{44}. The volume of material close to the liner walls is comparatively low compared to the rest of the sediment core sample volume. Moreover, large cores tube diameter that we used, with short penetration depth and loose surface sediments are considered less prone for core smearing\textsuperscript{45}. Due to precise and consistent time control of the investigated sediment cores, sediment reworking including bioturbation can be excluded. In lake Pinku, more than 40\% of MPs occurred below the sediment layer of the 1950’s and noticeable MP concentrations are found in deeper layers of lakes Seksu and Usmas compared to the total MP concentration throughout the core and to our contamination controls (see further in the text, methods section). The high number of MP particles below 1950-level supports our argument, that occurrence of MP downward migration cannot be explained as an artefact of sample preparation. Hence, we question the use of pre-1950 sediments as core processing contamination controls in MP studies.

Downward migration through low-density organic sediments is described in cryptotephra studies, explained by the higher density of the tephra shards (1–2 g cm\textsuperscript{-3}) leading to particle sinking through soft, porous sediments until higher density facies\textsuperscript{44,46}. MP downward migration is previously related to low sediment density and small particle size of MPs as well as large grain size of the sediment matrix\textsuperscript{47}. Pore water movement within porous sediments is also discussed as a possible mechanism\textsuperscript{49}. The density of most plastic materials is significantly lower than that of tephra shards, and our analyses did not support the density driven penetration of MP particles as a primary
explanation. In fact, PE, which has a density $< 1 \text{ g cm}^{-3}$, was one of the most frequent polymer types found below 1950-level. Leiser, et al. 49 have observed that aggregation to iron-organo flocs causes faster burial of PE particles and downward migration within sediment column up to 11 cm in unconsolidated muddy lake sediments49. Such mechanism can well have an important role. In the eutrophic dimictic lakes with cycles of anoxic and oxic conditions at the bottom as a consequence of stratification and mixing, favour floc formation. Leiser, et al. 49 also suggested that the consequent gas formation within the anoxic sediment following the breaking of the flocs can have caused PE particles to sink further within the sediment column44a. Although Leiser, et al. 49 only tested PE particles, the mechanism can have importance in the burial of other plastic polymers as well.

In addition, compaction of loose surface sediment can play a significant role in vertical MP penetration within the sediments. Loose, water rich surface sediments can be compared to porous sediments, where movement of particles can occur driven by gravitation, compaction process or pore water movement. Sediment compaction resulting from the weight of overlying younger sediment deposits, reduces porosity leading to loss of water and labile sediment fractions such as organic matter50,51. The detailed investigation of the compaction process of a varve record showed that the compaction is most effective in the topmost 5 cm of the sediment column but occurs generally in topmost 12 cm51. This, of course, is expected to depend on sediment composition and can vary from lake to lake. Unfortunately, our records do not reach deep enough below the 1950-level to evaluate if MPs occur or significantly decrease beyond the potential compaction depth.

Furthermore, sedimentation rate can be an important factor influencing temporal occurrence of MP particles in pre-Anthropocene level. It is likely that low sedimentation rate (e.g. Lake Pinku) causes slower sediment compaction51 and hence can lead to MP penetration into older sediments compared to sites with high sedimentation rates (e.g. Lake Seksu). Deeper burial of MP-containing iron-organo flocs in unconsolidated sediment sequences is previously anticipated49. While there is a wide range of plastic materials in the deepest layers of all investigated lakes showing varying sedimentation rates and sediment densities, this issue cannot be assessed using our short cores.

Zheng, et al. 52 suggested the deeper the sediments, the smaller ESD of the MP particle. In contrast, Waldschläger & Schüttrumpf53 claimed that infiltration depth increases with decreasing ESD of the MP particle, moreover the infiltration depends on ratio between diameters of the MP particles and the sediment fraction. Our results showed that less elongated particles tend to penetrate deeper into sediments, while particles $\frac{1}{2}$ length wide or larger (AR 0.5-1) are more likely to remain in the upper layers. There is also a trend for larger (according to major dimension) particles to be located in layers more towards the surface (Fig. 2, Supplementary Fig. S6) suggesting that migration might be size/shape selective to a certain extent. This is in line with Leiser, et al. 49 finding, smaller PE particles incorporated with iron-organo flocs penetrated deeper in the sediment column. This can also be influenced by MP degradation versus residence time in sediments. Moreover, ESD metric alone, without consideration of particle’s shape can lead to a biased conclusion, because a small AR.

Material characteristics such as hydrophobicity could further influence MP migration. Gao, et al. 47 found the plastic materials with higher contact angle (hydrophobic > 90°) penetrating in lesser depths within soil formation. Within the aquatic environment decreased water content occurs deeper in the sediments in contradiction to increasing humidity deeper in the soil formations. Hence this behaviour is expected to oppose findings from soil studies. Water column and wet surface sediments may drive hydrophilic particles downward within the sediment profile during the compaction process. PVA with contact angle around 60°54 is less represented deeper within sediment profiles despite their common occurrence in surface sediments and larger density compared to hydrophobic PE (96° or
more)\textsuperscript{55} with density lower than that of water yet being more frequent plastic material observed in the layers older than 1950s. Further experimental laboratory and field studies are required to fully understand the drivers of downward migration. However, being one of the first plastic materials to generalise, PE particles have likely prevailed in nature for a longer time which can be reflected in the deeper occurrence of PE materials.

While particle density and sediment characteristics are not recognised as the primary controlling factor of MP migration, particle shape seems to have the strongest influence. Because rounded particles show stronger tendency to penetrate deeper in the sediment profile, our results agree with previous study by Bancone, et al.\textsuperscript{15} suggesting that fibres have more potential as dating tool than fragments.

**Conclusions**

According to this study based on results from three lakes in Latvia, there is no doubt that sediments serve as a significant accumulation spot for MP in freshwaters. Comparing the deeper sediments with surface ones, there is a trend for MP concentration to increase towards younger sediments, i.e. in surface layers. Hence, these findings are consistent with the global plastic production and pollution history. The highest concentrations per sediment unit are associated with the last decades' time span. Nevertheless, a considerable part of the total MP pollution is accumulated in the sediments deposited before 1950\textsuperscript{35}. Such findings are often treated as artefacts of sample processing. However, we suggest that these findings show a true natural phenomenon. We recommend the use of procedural/field blank samples and air contamination samples to trace field and laboratory contamination, hence to be able to reliably investigate the occurrence of MPs in sediment cores also from pre-1950 sediments.

Together with the increasing amount of evidence reporting MPs from pre-1950 sediment layers from well-dated sediment records\textsuperscript{35}, our results raise a significant concern related to the use of MPs as an additional stratigraphic marker for the post-1950 great acceleration. Although all these records show great acceleration regarding MP accumulation rates and concentrations equivalent to growing global net plastic production mass, the first appearance of MPs in the sedimentary archives does not reflect the onset of plastic production and hence fail to reflect the onset of Anthropocene.

Due to the downward migration of MPs to varying depths through unconsolidated sediment profiles, the occurrence of MPs cannot directly be used as a time-synchronous marker horizon for the Anthropocene. The migration depth likely depends not only on particle shape but also on sediment porosity and sedimentation rate. A slow sedimentation rate can lead to larger temporal errors due to slow sediment compaction. Hence, especially organic rich low density sediments and locations with low sedimentation rates should be investigated with a severe caution. In addition, careful dating with ideally several independent and robust dating methods should be widely introduced. Consequently, MP becomes not rational as a chronostratigraphic marker due to low confidence and high costs. Observed phenomena on vertical distribution of MP in the sediments needs to be studied and confirmed in other environmental matrices apart from marine and lacustrine sediments, i.e. in soil and fluvial systems.

**Methods**

**Study site description and sampling.**

Sediment cores (one core per each lake from the deepest part of the lake) were taken from three lakes in Latvia (Supplementary Fig. S1). Lake Pinku is oligotrophic/mesotrophic lake located in a glacier depression. It is of high water quality and since 2004 the lake and its surrounding area has been a part of a protected nature park. The
nearest regional motor road is approximately 600 m away. The lake's surface area is 29 ha, length 1.3 km, greatest width 0.3 km, average depth 4.3 m, greatest depth 20 m. There is one inflow ditch and another outflow ditch. The core (25 cm length) was taken in August 2019 (Lat: 56° 59' 58.20", Long: 21° 41' 14.72") by a 5.2cm inner diameter Kajak corer.

**Lake Usmas** is among Latvia's largest lakes, with a surface area of 3469.2 ha and a water volume of 0.19 km$^3$. It is mesotrophic/eutrophic lake, located in a glacier depression and has several islands. Part of the lake (outside sampling area) belongs to a nature reserve. Apart from this area, the lake is a famous destination for recreational activities. The major motor road is approximately in 680 m distance. The lake is also surrounded by several local roads. Lake's length is 13.5 km, greatest width 6.2 km, average depth 5.4 m, greatest depth 27 m. There are more than 10 inflow rivers and ditches and one outflow river. The core (25 cm length) was taken in August 2019 (Lat: 57° 13’ 45.32", Long: 22° 10' 26.97") by a 5.2cm inner diameter Kajak corer.

**Lake Seksu** is eutrophic, small (surface area 7.9 ha, length 550 m, greatest width 350 m) and shallow (average depth 2.5 m, greatest depth 6 m) lake located in the vicinity of Latvia's capital city, Riga. Major motor roads are located on both sides of the lake (the nearest - one of the most extensively used major motor roads in the country is in approximately 850 m distance). Inland dune forests mainly surround the adjacent catchment. The lake is part of the drinking water supply system enriching the groundwater level near the drinking water pump station. Due to that, access to the lake is limited, and a fence surrounds the lake. Water in the lake was artificially replenished between 1953 and 1965 from close to the eutrophic lake in order to increase the water level. The lake has no outflow, and there is an inflowing ditch. The core (45 cm length) was taken in February 2019 (Lat: 57° 2’ 10.35", Long: 24° 21’ 6.73") by an 8 cm inner diameter Kayak/HTH gravity corer.

The sediment cores were divided in the field into 1 cm sections, placed in specially prepared (washed and muffled) glass jars, covered by aluminium foil and metal lids. Samples were stored in a cold room. Part of the material (4 to 5 cm$^3$) of each section was dried and used for $^{137}$Cs/$^{210}$Pb and spheroidal carbonaceous particles (SCPs) dating as well as for dry weight estimation, chemical and physical analyses.

**Microplastic samples preparation and analysis**

MP samples were prepared as a consecutive section with 5 cm intervals of mixed subsamples of the core. However, due to the very high water content of the topmost samples of Lake Seksu, the upper sample of the core consisted of 10 cm. Samples purification was done by applying a multi-step treatment method (Supplementary Fig. S7) adapted from ref. 59–64.

Samples were analysed using Fourier Transform Infrared micro-Spectroscopy (µFTIR (Perkin Elmer Spotlight 400). A sub-sample of the total 5 mL sample (at least 0.5 mL) was taken using a capillary glass pipette (micro-classic, Brand GmbH, Germany) and filtered through 11×11 mm Si-filter (Fraunhofer Institute for Reliability and Microintegration, Germany). In case sample contained low number of particles and for the blank samples the total volume of the sample (5 mL) was analysed. Filters were left to dry for 12 h at room temperature. The analysis was done applying µFTIR-Imaging technique in transmission mode in a spectral range of 4000 – 750 cm$^{-1}$ at 8 cm$^{-1}$ resolution. The whole surface of the filter was scanned, and IR spectra of particles were obtained. The polymer assignments of the analysed particles were based on comparison with a FTIR spectral library developed at Tallinn University of Technology and in Leibniz Institute for Polymer Research Dresden. Spectral libraries comprise spectra of artificial polymers and natural organic and inorganic materials. The threshold for accepting the match was set to
70%, but all matches were verified by the operator as well. Cross-validation of measured spectra between Tallinn University of Technology and Aalborg University, Department of the Built Environment was made. At the same time a light microscope image of the inspected particles was produced for visual inspection and size determination. Plastic particulates were also identified and categorised by size class for greatest length and width dimensions (major dimension is the longest side of the particle and minor dimension is the shortest side of the particle). Principles of measuring particles were taken from Sun & Liu protocol for measuring cell bio volume and surface area. We followed only measurement instructions from this work. To present measurements, we used 50µm intervals from 51 to 550 µm. One size step (50 µm) below and above fractioning sieves size was chosen to recover fibres as much as possible.

**Quality control and blank tests**

In order to avoid airborne and cross-contamination or unintentional loss of MP particles, several precautionary measures were taken. All equipment that was used for samples storage and treatment or came in contact with the samples in any other way, was made from either glass, PTFE or metal when possible and was thoroughly rinsed with filtered Milli-Q water before use. The polymer spectrum of all plastic materials, which were in contact with samples and not possible to replace with glass or other alternatives (e.g. sediment corer, gloves, bottle corks etc.) was recorded and excluded from further polymer analysis. Cotton laboratory coats of a specific colour (green) and blue or green nitrile gloves were worn while working with samples. The samples treatment was performed in the laminar flow cabinet. The same beaker was used when possible throughout the treatment process for each sample, rinsing it with filtered Milli-Q water between each treatment step. Samples were covered with aluminium foil when not processed or when placed in the shaking-heating bath located in the fume hood. All reagents were filtered through a glass fibre filter (pore size 1.2 µm).

Laboratory and field blanks were run parallel to real samples, applying the same processing steps to collect information on sample contamination degree during sample treatment. The air background sample showed contamination of 3.4 fibers h⁻¹ (only, no fragments) on average. Procedural and field blanks contained mostly viscose (65.7–100% of all polymers found in the blank samples), most likely from the clothing. Viscose was consequently removed from the further data analysis. Other polymer particles were detected only in very low numbers (few particles per blank sample). Recovery tests were performed with triplicate lake sediment samples spiked with standardised 100 red ø 100 µm PS beads, density 1.05 g/cm³ (Sigma-Aldrich product no. 56969-10ML-F). The spiked samples were processed as described in the protocol for sediment samples. Extracted beads were easily identified due to their distinct appearance and were counted under a light microscope Leica DM400 B LED.

**Core chronology samples preparation and analysis**

The activity of total lead isotope $^{210}$Pb was determined indirectly by measuring polonium isotope $^{210}$Po using alpha spectrometry. Freeze-dried sediment samples of 0.2 g were spiked with a $^{209}$Po yield tracer and digested with concentrated nitric acid HNO₃, perchloric acid HClO₄, and hydrofluoric acid HF at a temperature of 100°C (CEM Mars 6 microwave digestion system, USA). Next, the solution was evaporated with 6 M hydrochloric acid HCl to dryness, and then dissolved in 0.5 M HCl. Polonium isotopes were spontaneously deposited within 4 h on silver discs. After deposition, the discs were washed with methanol and analysed for $^{210}$Po and $^{209}$Po using a 7200-04 APEX Alpha Analyst spectrometer (Canberra, USA) equipped with PIPS A450-18AM detectors. The samples were counted for 24 h. A certified mixed alpha source ($^{234}$U, $^{238}$U, $^{239}$Pu, and $^{241}$Am; SRS 73833-121, Analytics, Atlanta, Georgia, USA) was used to check the detector counting efficiencies, which varied from 30.9–33.9% for the applied geometry. Two blank samples were analysed with each sample batch to additionally verify the quality of the chemical procedure.
According to the black carbon combustion continuum model of Hedges, et al.\textsuperscript{68} and Masiello\textsuperscript{69}, SCP only form during industrial fuel combustion at high temperature (> 1000°C). A load of SCP along the sediment sequences were estimated and followed the methodology of Rose\textsuperscript{70}. The sediments were subjected to sequential chemical treatment using H\textsubscript{2}O\textsubscript{2}, potassium hydroxide (KOH) and HCl to remove organic material, silicates and carbonates, respectively. \textit{Lycopodium} tablets\textsuperscript{71} with a known amount of spores were added as markers allowing estimation of SCP per sample. Slides for the microscope were prepared afterwards and all SCP within the whole slide was counted under a light microscope at 400 times magnification. Identification criteria for SCP counting followed Rose\textsuperscript{72}. The concentrations of SCP were calculated as a number of particles per 0.2 gram dry mass of sediment. Across all sites, the record of SCP starts at the beginning of the 20th century and rapidly increases since the 1950s. The peak in SCP emissions in Latvia occurred in 1982+/-10\textsuperscript{73}. After rapid increase and peak in SCP concentration followed a decline which coincided with the collapse of the Soviet Union when numerous manufactures and air pollutants halted their production in the Baltic region. The SCP occurrence pattern in our study mirrors worldwide SCP pattern change\textsuperscript{74} following the fuel combustion pattern: 1950 - the rise of SCP; 1982 - the peak of SCP; 1991 - the decrease of SCP.

Results of the \textsuperscript{210}Pb dating with the CFCS (Constant Flux Constant Sedimentation) model and the SCP analyses were used to build an age-depth model using the \textit{Clam} deposition model\textsuperscript{75} package with a 95.4% confidence level in the R environment\textsuperscript{66}. The mean weighted value of the modelled age was selected.

**LOI samples preparation and analysis**

The dry weight of 1-cm-thick subsamples with a 1-cm\textsuperscript{3} volume was determined after oven-drying at 105°C until constant weight. The organic matter content of the sediment was determined by loss-on-ignition (LOI) at 550°C for 4 h. The carbonate matter was calculated as the difference between the LOI at 950°C and the LOI at 550°C. Because the weight loss after 950°C is the amount of CO\textsubscript{2} evolved from carbonate minerals, to get the actual percent of CO\textsubscript{3}, the weight after 950°C combustion was multiplied by 1.36\textsuperscript{76,77}. Dry bulk density (BD, g cm\textsuperscript{-3}) was estimated on the base of the LOI for all samples. Non-carbonate siliciclastic matter, here referred to as minerogenic matter content, was obtained by subtracting organic and carbonate matter from the total sample weight after final combustion. All values for organic, carbonate and mineral matter are expressed as percentages.

**Data analysis and statistical assessment**

Particles were categorised into size ranges (with intervals of 50 μm) up to size class 51 to 550 μm considering two diametrical dimensions (major and minor dimension). Plastic densities data were obtained from existing databases. If density range was rather wide, e.g. for PA and PUR what can be made in a variety of densities and hardnesses, particular polymers were not included in the density analysis\textsuperscript{78,79}. Principal Component Analysis (PCA) combined with factor analysis was applied to the data to understand which variables and factors are driving the transport of particles into deeper sediment layers. In order to include information about particle elongation (or shape) on a continuous scale, the Aspect ratio\textsuperscript{80} was calculated for each analysed particle. Aspect ratio is a shape descriptor defined by the ratio of the minimum to maximum Feret diameter\textsuperscript{80}:

\[
AR = \frac{X_{Feretmin}}{X_{Feretmax}}
\]

(for easier interpretation of the results, the AR is expressed in decimal fractions; in the reviewed literature, this form of expression is used less often than the length-to-width ratio). In addition, a variable such as \textit{relative bulk density}
has been added to the dataset to normalize substantial variations in bulk density between sediments of different lakes. The most representative dimensions of PCA were determined according to the commonly used methodology, implementing Kaiser–Guttman criterion together with the scree plot of eigenvalues and biplot visualization output, therefore PC1 (29.7%) and PC3 (18.8%) were selected as the best explanations of variances (PC2 was equal to 19.3%, but visualization of individuals’ groups was weaker). PCA output, variable coordinates, quality of the factor map COS2 and variable contribution can be found in Supplementary Table 3.

Spearman's rank correlation test between age (date) of sediments, Aspect ratio and Equivalent Spherical Diameter was performed on the entire dataset of the pooled data of the three lakes in order to increase data length and include data on Lake Usmas, which was not sufficient (only 4 data lines) for a separate analysis. Thus, it was not possible to use layer depth as a correlating variable for the pooled data due to the different bulk density and of the sediments. Instead, the age of the sediments was used as a measure of depth, normalized to bulk density. The verified relationships were considered statistically significant at p < 0.05. For the analysis, the aspect ratio was conventionally divided into 4 groups: group 1 is AR < 0.25; group 2 is 0.25 ≤ AR < 0.5; group 3 is 0.5 ≤ AR < 0.75; group 4 is AR ≥ 0.75, to show differences in proportional composition of that groups in each sediment layer. The Equivalent Spherical Diameter (ESD), as a standardized particle fraction index, was calculated according to the formula:

\[
ESD = (AC^2)^{\frac{1}{2}},
\]

where A is a particle's major dimension (or \(X_{\text{Feret max}}\)) and C is a minor dimension (or \(X_{\text{Feret min}}\)). Similarly to AR, to see how the proportion of particle fractions varies in different sediment layers, ESD was divided into four groups according to the lower quartile, median, and upper quartile of the ESD distribution: group 1 is ESD < 62 µm; group 2 is 62 µm ≤ ESD < 120 µm; group 3 is 120 µm ≤ ESD < 190 µm, group 4 is ESD ≥ 190. Spearman's rank correlation test was chosen because the AR proportional composition variables were not normally distributed, moreover Date is an ordered variable.

Elbow points of MP concentrations in sediment cores were calculated by means of \textit{akmedoids} package (version 1.3.0) in R environment. Analysis was done for lakes Pinku and Seksu only. The number of data from Lake Usmas was not sufficient for this analysis.

Data exploration, artworks, and statistical analyses were performed using R software for Windows, release 4.0.3 and GNU Image Manipulation Program (GIMP), release 21.10.30.

**Declarations**

**Data availability**

All the data supporting results presented in this study are included in the figures and supplementary materials available for downloading.

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Author contributions

I.D-D. and S.S. designed the study, undertook field sampling and field protocol design, developed the manuscript. I.D-D., M.B., N.St. contributed to samples and data preparation. N.Su. applied statistical methods to analyse data and provided visualisations. N.B. provided spectral analysis of the samples. N.St. and W.T. were responsible for chronology and associated analyses. A.V. and J.V. contributed to laboratory protocol design and conceptualisation. All authors were involved in manuscript drafting and revising for intellectual content.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at....

Correspondence and additional information request to I.D-D. and S.S.

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Figures
Figure 1

**Chronology and associated microplastic mean concentration for Lake Seksu, Lake Pinku and Lake Usmas.** The black solid line shows the weighted mean ages of all depths, whereas the light grey area indicates the reconstructed 95% chronological uncertainty band. Dates of lead isotope $^{210}\text{Pb}$ and spheroidal carbonaceous particles (SCP) with their error margin age-depth model uncertainties are displayed as light blue boxes. Horizontal red line indicates year 1950.
Figure 2

Concentrations and size (the minimum to maximum Feret diameter expressed as minor and major dimension) distribution of dominant microplastic polymers. PA – polyamide, PE – polyethylene, PUR - polyurethane; PVA - polyvinyl acetate, Rubbers – combined group of BIIR (butyl rubber), BR (butadiene rubber), SR (synthetic rubber) in sediment core layers and corresponding time period within 5 or 10 cm depth intervals (identified at right margin) of Lake Seksu, Lake Pinku and Lake Usmas.
Figure 3

Conceptual representation of microplastic particles distribution and concentration within lake sediments. General trend of microplastic particles distribution according to shape (aspect ratio (AR) - relation of minor dimension to major dimension) and total microplastic abundance distribution throughout the sediment core before, around and after 1950 in Lake Seksu, Lake Pinku and Lake Usmas. Year in brackets represents the age of the sediment core oldest possible layers studied.
Figure 4

**Principal component analysis (A) and Spearman's rank correlation matrix (B).** a. The selected (see Methods) principal component 1 (PC1) and principal component 3 (PC3) together explain 48.5% of variations. Variables: Date – dating of sediment layer, OM – organic matter content, Depth – depth of sediment layer (cm), Shape – aspect ratio (AR) of particle minor dimension versus major dimension, MN – particle minor dimension, MJ – particle major dimension, PD – density of polymer, BD – bulk density of sediments, RBD – relative bulk density of sediments (average BD of a core layer to the densest layer of the lake); Legend: P – Lake Pinku, S – Lake Seksu, U – Lake Usmas. b. Spearman's rank correlation matrix. Correlation for the composition of four particle groups with different values of aspect ratio (AR): Group 1 is AR<0.25; Group 2 is 0.25≤AR<0.5; Group 3 is 0.5≤AR<0.75; Group 4 is AR≥0.75 and relative dating of the sediment core layer in pulled data of lakes Seksu, Pinku and Usmas. The coefficients (Spearman's rho) are coloured based on their sign and strength (the legend of continuous colour scale positioned on the right side) and insignificant correlations (P > 0.05) are crossed out.

**Supplementary Files**

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