The long road to determine microplastic trends in a Baltic Sea catchment

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The behaviour and accumulation of microplastics (MPs) in the marine environment has been studied for years but is still poorly understood. In this context, the interdisciplinary MicroCatch_Balt consortium, consisting of environmental scientists, microbiologists, modellers, computer scientists, and ocean managers, is investigating the significance of land-based inputs as a source of MPs into the ocean.

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MicroCatch_Balt focuses on the catchment area of the Warnow, the second-largest German freshwater Baltic Sea inflow. It includes a wide variety of land uses and integrates a high population density with industrial and agricultural areas (Figure 1). Thus, this river catchment can be considered representative of many areas of the Baltic Sea.

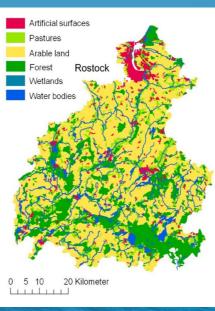


Figure 1: Overview of the different types of land use in the Warnow river catchment area (modified from CORINE Land Cover (CLC2006) by Inga Krämer).

Sampling, processing and analysis

Most of the MicroCatch Balt partners already had prior experience with the Warnow catchment-not only in the field of MPs (Labrenz, 2017) but also in modelling the Warnow catchment. its estuary and the Baltic Sea itself. Nevertheless, it quickly became clear during the project that fundamental optimisations and new developments were necessary in the field of MP sampling, processing and analysis to obtain meaningful results for MP modelling. In principle, the identification of MPs from the environment was far too labour intensive and time-consuming to obtain the amounts of data needed by the models. Not specific to MicroCatch Balt, this is a limiting factor worldwide.

For example, it turned out that net-based methods for sampling MPs in water are inadequate for the study area. These nets usually have mesh sizes of about 100- 300μ m. Comparable to most aquatic systems, however, MPs in the Warnow and the Baltic Sea are predominantly smaller, are not caught by nets and are lost to analysis. For this reason, MicroCatch_Balt developed the mobile sampling device 'Rocket' (Figure 2).

Based on filtration cartridges, this device captures all particles >10 μ m (Lenz and Labrenz, 2018), a first and essential advance for the evaluation of MPs in the aquatic environment. The Rocket allows sampling of about 1m³ of water, depending on water quality. A second crucial step was to increase the volume of Warnow water to be investigated to 1000m³. This was achieved by identifying MPs from the drinking water treatment sludge of the Rostock waterworks. The Rostock drinking water treatment plant intakes surface water from the Warnow river and purifies it by coagulation/flocculation and filtration processes. From the MPs contained in the accruing treatment sludge, MP numbers in the Warnow itself can be derived in an integrative way, as the sampling covers a period of at least three hours of flow in the Warnow river. Both methods independently estimated MP concentrations in the lower part of the Upper Warnow amount to ~200 particles/m³ of water (Siegel et al., 2021).

Time is the critical factor in MPs processing. Therefore, MicroCatch Balt also tested new procedures for sediments/soils in order to accelerate work processes. Sediments/soils have a high content of natural organic and inorganic matter and thus, have to be cleaned in a complex way. By developing and applying electrostatic separation, especially for MPs >0.5mm, MicroCatch Balt succeeded in significantly concentrating MPs from coarse-grained sediments. This method allows the removal of significant amounts of natural contaminations before further processing of the MPs,



Figure 2: Microplastic sampling system; the 'Rocket' (Foto: Robin Lenz).

so that MP purification steps could be simplified (Enders *et al.*, 2020a).

The subsequent processing of MPs from the environment was also fundamentally improved. To enable MP identification via Raman/FT-IR spectroscopy, organic particulates must be greatly reduced without harming the plastics themselves. This is possible via enzymatic and oxidative digestion. The enzymatic approach is gentle but very technical and time-consuming. However, it remained unclear whether MP, <100µm in particular, might be modified or impaired by the faster oxidative treatment. MicroCatch Balt was able to prove that this is not the case and that chemical treatment can save time and reduce complexity (Lenz et al., 2021).

The final identification of MPs from the environment was an anticipated challenge from the beginning. MP particles cannot be reliably identified by the eye or with purely microscopic methods. For this purpose, Raman/FT-IR spectroscopy, as already mentioned, are adequate methods. Again, the procedures were very time-consuming, and the identification of MP particles was a considerable bottleneck in the MPs pipeline.



Gepard Enabled PARticle Detection

MicroCatch Balt provided the scientific community with a self-developed, opensource software package allowing particle analysis using Raman microspectroscopy.

The GEPARD (Gepard Enabled PARticle Detection) software enables the acquisition of an optical image, then detects particles and uses this information to drive the spectroscopic measurement. This results in a multitude of possibilities to efficiently check, correct and report all obtained results (Brandt et al., 2020). The final implementation to reduce measurement time is to refine total sample numbers by using representative subsamples. However, these must still provide reliable results.

Identification and quantification

MicroCatch Balt comprehensively evaluated different proposed subsampling methods on a selection of real samples from different environmental compartments. It was shown that subsampling errors are largely due to statistical counting errors. However, mainly by increasing the proportion of MP particles in the samples, (Brandt et al., 2021).

optimised and highly reproducible pipeline to identify and quantify MPs from the environment. This has been incorporated into a universal framework of modular protocols that both meet predefined user requirements ('QuEChERS': quick, easy, cheap, effective, rugged and safe) and provide best practices for appropriate working conditions in a standard laboratory, available to the public since 2020 (Enders et al., 2020b).

MicroCatch Balt has also provided, for the first time, a modelling system that can map the complete pathway of MPs transport from source to open sea in principle and monitor the effectiveness

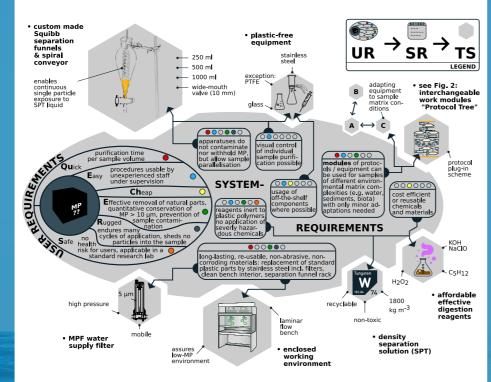


Figure 3: QuEChERS approach for identification and quantification of MP from the environment (from Enders et al., 2020b). UR (user requirement), SR (system requirement), TS (technical specification)

of mitigation measures with 'what-if' scenarios. Concurrently, this powerful tool forms the basis for the application of a multi-touch table that provides interactive learning materials. It now serves as the core element of an exhibition travelling along the German Baltic Sea coast from the subsampling error can be kept low Stralsund to Flensburg and has already been requested nationwide. Everyone is guaranteed access to the MicroCatch Thus, MicroCatch Balt has developed an Balt online app [https://microcatch. ostseeforschung.info/en/start.html (Figure 4)].



Figure 4: MicroCatch_Balt online app (Foto: Sven Hille).

Conclusion

But what have the MicroCatch Balt investigations now revealed in concrete terms for the situation in the Warnow catchment area?

Based on the mathematical simulation model RAUMIS, it can be said that sewage sludge is the most important agricultural MPs source in the Warnow catchment (0.53 g/haMP). The application of sewage sludge increases the soil load from 4 to 15MP particles/g. The mGROWA-TeMBa model system was developed to represent runoff modelling in the Warnow and from urban areas. Emissions from diffuse and point sources (atmospheric deposition, sewage sludge, wastewater treatment plants, etc.) were considered. Other pathways may not even be identified yet (Tagg and Labrenz, 2018).

Although MP concentrations in the river are highly variable, it is clear that urban emissions dominate the Warnow estuary; 49.4 per cent of MP inputs come from the catchment, and 43.1 per cent Ocean, do not exist in the Baltic Sea. It from stormwater overflows. The Rostock wastewater treatment plant contributes only 1.4 per cent. Therefore, measures to reduce MP inputs should focus on stormwater runoff and emissions from the combined sewer system (Piehl et al., 2021).

MicroCatch Balt can estimate that the annual input of MPs from the Warnow into the Baltic Sea is 152-291 billion particles (mainly 10-100 µm in size) (Piehl et al., 2021). However, a majority of the particles are already washed ashore near the point of emission. Beaches are the main accumulation areas with up to 10^9 MP/m²/a. The residence time of MPs after emission into the Baltic Sea is 14 days on average (Schernewski et al., 2020). Garbage patches, analogous to the sub-equatorial gyres of the Atlantic

even seems possible to quantitatively reduce MPs via beach clean-up. However, this alone is no solution.

It also became clear that high amounts of MPs do not even reach the Baltic Sea but remain in the sediment of the Warnow (Enders et al., 2019).

MicroCatch Balt Finally, the investigations also revealed that MPs are not degraded/assimilated by microorganisms in the Warnow or Baltic Sea but simply continue to fragment (Oberbeckmann and Labrenz, 2020), consequently continuing accumulation in distinct ecosystems. Thus, the solution to the environmental problem is a simple one: do not introduce MPs there in the first place.

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PROJECT NAME

One System: Analysing Microplastics Sinks the open Baltic (MicroCatch Balt)

PROJECT SUMMARY

The multidisciplinary MicroCatch_Balt project determines inland sources and sinks processes on its pathways to the open Baltic area. It covers the most significant aspects providing expertise to support stakeholders in designing future monitoring or mitigation

PROJECT LEAD

Prof. Labrenz received a PhD in natural sciences at the University of Kiel (1999) and worked as a postdoc in the USA and Germany. microorganisms in anthropogenic influenced at the University of Rostock (Germany) and Ecology at Klaipeda University (Lithuania).

PROJECT PARTNERS

The network project MicroCatch_Balt is partner institutes are the Leibniz Institute of Polymer Research Dresden (IPF), Fraunhofer Johann Heinrich von Thünen Institute.

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