Age dating of recent tidal sediments by means of Cesium 137 and micropollutants

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Introduction:
Tidal areas represent highly dynamic regions with immense natural (sediment and particulate matter transport) as well as anthropogenic (disposal of dredged material in scope of sediment management) transport processes. The investigation layers of sediment cores can be used to follow the sediment transport and deposition of particulate matter, to understand the transport of pollutants bound to particulate matter and to elucidate pollutant emission trends. One of the challenges is the age-dating of the sediment. The analysis of well-established Cesium-137 represents a reliable tool to date undisturbed sediments with a minimum age of about 35 years back to 1986. However, for younger sediments other tracers for age-dating have to be found. Hence, new substances like emerging pollutants such as pharmaceuticals were tested for their reliability as new tracers. For these comprehensive data regarding market launch and annual consumption data are available. Furthermore, a good correlation between consumption and particulate matter concentrations in rivers could be shown [1]. Consequently, age dating of sediment by concentration profiles of pharmaceuticals with striking concentration trends could be a promising approach.

Methods:
A 130 cm long sediment core was drilled using VibroCorer from tidal area of Elbe, southwest from Stoer mount (13.6.2019). The core was subdivided into 2 cm slices. At each slice Cs-137 activity was measured using high purity germanium detector. Afterwards each slice was freeze dried, sieved to < 2 mm, homogenized, milled and extracted using a mixture of methanol-water by means of pressurized liquid extraction (PLE) as described by [1]. After solvent exchange, concentration of chosen pharmaceuticals was measured using a LC-MS/MS system equipped with a Zorbax Eclipse Plus C18 chromatographic column and an ESI detector [1].

Results: Based on Cs-137 analysis the core can be subdivided into 2 parts: the upper 90 cm show a constant activity of about 3 Bq/kg; the lower 40 cm of about 10 Bq/kg. This suggests that two different sediment types with a different Cs content have to be considered.

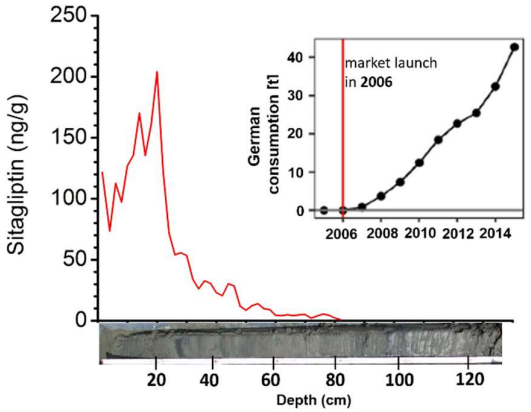

Fig. 1: Concentration profile in sediment core and consumption data (adapted from [1]) of sitagliptin.

The pharmaceuticals sitagliptin, aliskiren and citalopram showed significant concentration increases with depths above 82 cm. Consumption of these pharmaceuticals strongly increased from 2006 on due to market launches and end of patents. Hence, 82 cm depth can be used as 2006 approximation. Concentration trends correlated with consumption data up to 20 cm depth. The top of the core was close to liquid limit and as a consequence data varied strongly.

Discussion: While the CS-137 analysis reveals strong changes in sedimentation with a defined fix point, concentration profiles of micropollutants such as pharmaceuticals, deliver the future opportunity to serve as a proxy for dating based on consumption and launching data. However, catchment area specific analysis must be undertaken to find more substances with overlapping release dates and concentration trends, used as specific time-stamps.

References: [1] Boulard et al. (2020) *Water Research* **171**:115366; [2] Dimas et al. (2004) *Wasserwirtschaft* **22**:222-233.