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Sediment dynamics and heavy metal pollution history of the Cruhlig Lake (Danube Delta, Romania)

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A B S T R A C T

This is the first study reporting recent sedimentation rates data (e.g. the past 120–150 years) for the Cruhlig Lake situated in the Danube Delta. The aim of this study is to analyse the recent sedimentation rates using the ^{210}Pb dating method and identifying the heavy metal pollutants and their variability in time. Five sediment cores were taken with a gravity corer and – after drying the sliced samples–physical parameters, organic material and inorganic carbon content were determined. The total ^{210}Pb content was measured via ^{210}Po by alpha spectrometry, while supported ^{210}Pb was measured by ^{226}Ra (trough short life ^{222}Rn daughters) with HPGe detectors. Heavy metals were determined by ICP-MS; from the 64 measured elements, only exceeding values of Al, As, Cd, Co, Cs, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, Pb and Zn are discussed. After applying the CRS model, ages and sedimentation rates were calculated. The average sedimentation rate of the Cruhlig Lake is 0.21 ± 0.02 g/cm^{2}y, Minimum values (0.05 ± 0.003 g/cm^{2}y) are registered along the eastern shoreline of the lake before 1913, while maximum values are recorded due to the flooding in 2006 in the western side (1.34 ± 0.12 g/cm^{2}y). Recent sedimentation rates divide the lake into three areas: the secluded eastern near shore part (0.63 ± 0.07 g/cm^{2}y), the centre of the lake (0.92 ± 0.05 g/cm^{2}y) and the dynamic western area, where most sediment transport takes place (1.13 ± 0.01 g/cm^{2}y). The sedimentation pattern proves this lake to be very sensitive to fluvial discharge fluctuations. The building of the Iron Gate dams (1972 and 1985) had a negative impact on the sedimentation decreasing it with 58.74%, while after 1989 these values grew 2.25 times. The lake received a quantity of sediment rich in heavy metals in 1992 ± 3 y, which settled mostly on the eastern part. Values for Cd, Co, Cr, Hg, Pb and Zn are up to five times higher in 1980 ± 5 y in the eastern part of the lake, while Cd, Co, Cr and Ni are twice as high as the values measured for the marine substrate. Values of As show increasing of up to 150% in 2006 ± 2 y throughout the whole surface of the lake.

1. Introduction

Determining sedimentation rates in deltas is an important task in the context of the present day concern on sinking and shrinking deltas worldwide (Ericson et al., 2006; Syviski et al., 2009; Marriner et al., 2012). Reconstruction of sedimentation rates within deltaic lakes yields important information on recent sediment circulation and sedimentation patterns as well as on their controlling factors and alludes to future sedimentation trends which bear mostly in the endeavour to project sustainable management schemas for the fragile deltaic ecosystems. Therefore, reconstructing sedimentation rates by means of high accuracy depth profiles of ^{210}Pb determination on cores retrieved from a representative lake sediments settled in calm conditions, lacking any trace of reworking processes is an important step in detecting sedimentation pattern. Moreover, assessing the sedimentation pattern into the wider context encompassing climatic and anthropogenic components evolution in the Danube Delta during the last 150 years for which meteorological, hydrological and hydro technical records are available could help estimate the future trends of deltaic lakes.

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The presence of ^{210}Pb in most environments (Ivanovich and Harmon, 1982) is the reason for it being a widely used radioisotope in tracing recent environmental changes (Appleby et al., 1997; Olid et al., 2013) such as oceanic and marine studies (Settle et al., 1982; Henderson and Maier-Remier, 2002; Sanders et al., 2011), atmospheric fallout, deposition and contamination (Walling et al., 1995; Walling and He, 1990; Bikit et al., 2004; Baskaran, 2011; Krmar et al., 2013), sedimentary processes, such as transport, erosion and mixing (Jeter, 2000; Sanders et al., 2006) and sediment radiochronology (Baskaran et al., 2014). Despite of its wide use, the ^{210}Pb radiometric method needs to be validated by independent means for the obtaining of reliable data, therefore the use of an independent chronological marker such as the record of artificial radionuclides (^{90}Sr, ^{137}Cs, ^{241}Am and $^{239+240}Pu$ isotopes) from nuclear weapon testings (1954–1963) and the Chernobyl nuclear facility accident (1986) must be taken into consideration (Pennington et al., 1976; Appleby et al., 1991; Smith, 2001).

^{210}Pb is a natural radionuclide decaying from the ^{238}U radioactive chain, having a half-life of 22.23 y and is suitable for dating materials (soils, sediments, ice cores, corals, mosses, peats etc.) up to 120–150 years (Olid et al., 2013; Baskaran et al., 2014). In sediments ^{210}Pb has two sources: the supported ^{210}Pb, which is continuously decaying in the sediments from its parent radionuclide, ^{226}Ra, with which it is assumed to be in secular equilibrium, and the unsupported ^{210}Pb formed by the emanation of ^{222}Rn from soils, which then decays into a series of short lived radionuclides, and which are finally deposited in the catchment area and directly of the lake. The unsupported ^{210}Pb is calculated by subtracting the supported activity from the total activity and is then used for a series of environmental determinations (Putyrskaya et al., 2015).

Many studies have been undertaken worldwide to assess the changes experienced by the European deltaic regions (Tolmazin, 1985; Boyer et al., 2005; Simeoni and Corbau, 2009; Stănică and Panin, 2009; Syviski et al., 2009; Fatori and Chelleri, 2012; Kakroodi et al., 2012; Giosan et al., 2013; Ibánez et al., 2014; Anthony, 2015; Kakroodi et al., 2015; Olliviera et al., 2015), results indicating changes in the sedimentation rates caused by human activities such as shoreline displacements, via alteration of sediment transport and modification of littoral sediment budget.

In case of the Danube Delta, the first significant human interventions were made approx. 150 years ago (Driga, 2004; Stănică et al., 2007), while dams and dikes along its banks as well as along its tributaries were extended continuously over the past approx. 100 years. Also some of the late sedimentation in the Danube Delta and its development may be due to increasing deforestation in the drainage basin in the last 1000 years (Kaplan et al., 2009). The drainage basin of the Danube has a long history of precious and base metal mining (Hungary, Serbia, Bulgaria and Romania), having 12 major metal ore deposits; minings are being made for Au, Pb/Zn, Cu –Massive Sulphide, Cu –Porphtry, Pb/Zn/Cu (Bird et al., 2010). Metal contaminants are released in the drainage basin of the Danube, part of these reaching the Danube Delta (Sakan et al., 2011).

After the beginning of the industrial age (1850) the sediment intake has increased, but the construction of dams have caused the retention of sediments (Mann et al., 2013). The building of the Iron Gates hydro energetic power plant has led to a dramatically reduced sediment discharge to the shoreline of the Black Sea. The building of the dam (1972) was made at 943 km from the mouth of the Danube River, between Romania and Serbia, by forming the Iron Gate Reservoir having under average hydrologic conditions a volume is $3.5 \cdot 10^9$ m^3, meaning an increase of $2.1 \cdot 10^9$ m^3 compared to the volume of the natural channel of the Danube. This construction has disturbed the equilibrium of both up and downstream the dam (Vukovic et al., 2014).

2. Materials and methods

2.1. Sampling site

The Cruhlig Lake is situated in the marine Danube Delta, south of the Sf. Gheorghe branch (Fig 1.). Its genesis is bound to the gradual closing of a back barrier lagoon by the landward migration of a series of barrier islands and spits ca. 840–680 years ago (Preoteasa et al., 2016). Its location within the general context of the Danube Delta together with the morphometric characteristics render this lake an ideal location for sediment sampling in order to determine the fluvial driven sedimentation pattern in the terminal part of the delta. The access to this lake is granted through a approx. 3.5 km long channel, having the width ranging from 0.5 to 1 m and the depth up to 1 m, which makes the connection with the Sf. Gheorghe distributary having currently the lowest discharge (2.7×10^6 m^3/an) of the Danube. By its position within the Danube delta, this lake evolved without any local anthropogenic interferences (it is isolated from the common boating route; no dredging activities have been reported in this area). This is a N–S elongated lake of 0.8 km length, 0.13 km width and 0.7–1.2 m depth, while its banks are made up entirely by dense reed curtain which protect the lake's water surface in case of high energy winds. Therefore, no significant waves can form so that to affect the bottom lake sediments.

Five sediment cores were taken from this lake during two sampling campaigns with care to avoid any sediment reworking; their location and parameters are shown in Table 1. The dating horizon has been reached at 32–35 cm.

2.2. Sampling and analysis

The sediment cores were subsampled into 1–2 cm thick slices. After measuring their wet masses, sediments were put to dry in a drying oven for 24 h at 75 °C; dries masses were measured and physical parameters such as water content and porosity were calculated. Determination of the organic mass and the total carbonate content was made using the LOI (Loss On Ignition) technique, by drying the samples at 350 °C and, respectively, 750 °C.

The $^{210}Pb_{supported}$ was determined via ^{226}Ra (^{222}Rn short lived daughters) by high resolution gamma spectrometric measurements using an ORTEC GMX HPGe detector (FWHM of 1.92 keV at 1.33 MeV and a 0.5 mm Be window), using 294 keV, 351 keV and 609 keV gamma lines.

The $^{210}Pb_{total}$ content has been measured via its alpha particle emitting progeny, ^{210}Po. The ^{210}Po sources were prepared by adding to the measured 0.5 g sediment 0.3 ml 100 Bq/l ^{209}Po tracer for determination of the chemical yield. Samples were then put to acidic digestion using a series of acids (2×10 ml 65% HNO_3, 2×10 ml 35% HCl, 10 ml 6 N HCl and 10×3 ml 8:1 35% H_2O_2: 35% HCl), after which they were deposited onto high nickel content stainless steel discs (3 h at 85 °C in a drying oven), interferrents (iron ions) being eliminated with ascorbic acid. The obtained alpha sources were measured by an ORTEC SOLOIST 900 mm^2 PIPS detector, having a resolution of 19 keV and an ASPEC-92 data acquisition system. All uncertainties of measured data is given with 2σ confidence interval.

The total concentrations of metals for subsamples of the CR2, CRII1 and CRII3 cores were determined using an Inductively Coupled Plasma Mass Spectrometer (SCIEX Perkin–Elmer Elan DRC II). Analyses were made in triplicate and the mean values are reported. The samples with ion concentrations exceeding the