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# From floodplain to aquatic sediments: Radiogeochronological fingerprints in a sediment core from the mining impacted Sancho Reservoir (SW Spain)

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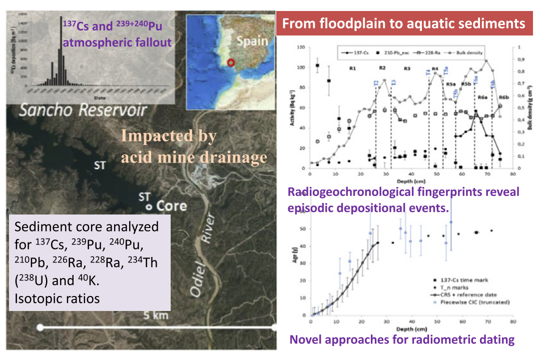
## HIGHLIGHTS

- Sancho Reservoir (1962), in SW Spain, is impacted by acid mine drainage.
- Sediment core studied with multi-tracer approach by Gamma spectrometry and ICP-MS.
- Radiogeochronological fingerprints and isotopic ratios for decoding past conditions.
- Sediments grew over the floodplain soil with depositional events and continuous SAR.
- Novel radiometric dating with numerical solutions, STA, piecewise CIC and CRS models.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The Sancho Reservoir (SW Spain) was built in 1962, about the time of maximum $^{137}$Cs fallout, and it has been affected by acid mine drainage (AMD) particularly since the mining cease in 2001. This is a unique scenario for studying the radiogeochronological fingerprints in AMD-affected sediments deposited over the former flood plain. A sediment core sampled in 2011 was analysed for bulk density, $^{137}$Cs, $^{239}$Pu, $^{240}$Pu, $^{210}$Pb, $^{226}$Ra, $^{228}$Ra, $^{234}$Th ($^{238}$U) and $^{40}$K, and studied with various radiometric dating models. Bulk density revealed unsteady compaction and likely depositional events. The activity concentrations of $^{226}$Ra, $^{228}$Ra, $^{234}$Th ($^{238}$U) and $^{40}$K were uniform down-core, but declining overall in the upper 0–25 cm, revealing changes in provenance except for $^{238}$U, which increased in the top 10 cm likely due to its supply by AMD. The AMD fingerprint was also found in the $^{239+240}$Pu/$^{137}$Cs activity ratio, which increased in the top sediment layers. The $^{137}$Cs and $^{239+240}$Pu profiles show well defined peaks at the same depth, with inventories being about four times higher than the expected integrated atmospheric deposition in the area. The unsupported $^{210}$Pb ($^{210}Pb_{exc}$) showed a complex non-monotonic profile interrupted at several sections, particularly around the $^{137}$Cs peak. The whole dataset cannot be interpreted in terms of continuous sedimentation processes. Based upon correlated features in the bulk density and $^{210}Pb_{exc}$ profiles, a series of depositional events (likely linked to peaks in the rainfall records) have been identified in the core. These events date back to the period comprised since the construction of the dam until its increase in height in 1972, which likely displaced upstream the main depositional area of riverine loads, as

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inferred from sediment trap data. The CRS (with a reference date) and (a piecewise) CIC models have been used for complementing and discussing the chronology.



## 1. Introduction

Since the beginning of the Industrial Revolution, human influence on the environment has increased substantially. For this period of time, several radionuclides have proved useful tools for establishing chronologies in sediment cores and other reservoirs, which allows examination of the impact of the anthropogenic influence in the surrounding environment (Asmund and Nielsen, 2000; Audry et al., 2004).

The $^{210}$Pb dating method is based on the particular cycle of this radionuclide in nature (Appleby and Oldfield, 1992; El-Daoushy, 1988; Robbins, 1978). After its production in the atmosphere (from radioactive decay of $^{222}$Rn), $^{210}$Pb is removed primarily by precipitation and dry deposition processes and it can follow a wide diversity of pathways to reach the sediment-water interface (SWI). This is known as the $^{210}$Pb unsupported fraction or in excess ($^{210}Pb_{exc}$), while the supported fraction of $^{210}$Pb is produced by the radioactive decay of $^{226}$Ra present in the sediment, and is generally assumed to be in secular equilibrium with its parent radionuclide. The $^{210}Pb_{exc}$ decays with its own half-life (22.3 y) and is the basis of $^{210}$Pb dating technique (Robbins, 1978). Since the first time it was used in glaciers from Greenland (Goldberg, 1963), the $^{210}$Pb-based dating of freshwater and coastal sediments has been extensively applied over the past 50 years for studies of reconstruction of pollution records, sediment focusing, sediment accumulation rate (SAR), and mixing rate determination (e.g. Baskaran et al., 2014; Couillard et al., 2004; San Miguel et al., 2003).

There are many factors that can alter the $^{210}$Pb versus depth profile in the sediment, such as sediment mixing, the biologically-mediated alteration of SARs, or chemical remobilisation (Putyrskaya et al., 2015; Robbins and Edgington, 1975). Unfortunately, there is no universal model that can be applied to any case study. Moreover, for any given $^{210}Pb_{exc}$ profile, and in absence of restrictive assumptions, there is an infinite number of mathematically exact solutions for the chronology (Abril, 2015). The validation of the $^{210}$Pb-based chronologies with some additional chronostratigraphic marks is then essential to be confident with results (Smith, 2001). This is commonly accomplished by the combination of $^{210}$Pb with $^{137}$Cs measurements in the sediments (e.g. Jha et al., 2003; San Miguel et al., 2003).

Caesium-137 ($T_{1/2}$ = 30.2 y) is an anthropogenic radionuclide originating from atmospheric nuclear weapons testing carried out from 1945 to 1972, and from some major nuclear accidents (e.g. Chernobyl in 1986 and Fukushima in 2011). If the $^{137}$Cs vertical profile in a sediment core has not been significantly affected by post-depositional processes, it is expected to show a well-defined peak corresponding to the years of its maximum concentration in the atmosphere (1962–1963). The use of $^{137}$Cs as an indicator of sedimentation processes is consistent as it binds almost irreversibly to clay and silt particles (Audry et al., 2004).

Plutonium isotopes have been also used as a complementary method of sediment dating (Putyrskaya et al., 2015). As in the case of $^{137}$Cs, nuclear weapons testing also released significant amounts of Pu which were distributed into the atmosphere. In addition, the releases from nuclear fuel cycling facilities are regional sources of Pu contamination (Lindahl et al., 2011; MacKenzie et al., 2006). The activity ratios $^{239+240}$Pu/$^{137}$Cs in environmental samples can be useful as an indicator of contamination coming from a source other than radioactive fallout (Hodge et al., 1996; Wu et al., 2010).

Several constraints have been identified in the use of $^{137}$Cs as a chronostratigraphic marker (Abril, 2003a). One of them is its potential mobility in the sediment profile, especially in saline sediments (Hancock et al., 2011). Plutonium, on the other hand, remains particle-reactive in both fresh and saline waters. Nevertheless, some cases have been found in estuarine sediments in which Plutonium is significantly associated to exchangeable phases (Lucey et al., 2004).

Radiometric dating of sediments from reservoirs is particularly challenging, with complex non-monotonic $^{210}Pb_{exc}$ profiles (Anjum et al., 2017; Chen et al., 2014). Among other difficulties we can mention: i) in those systems affected by severe erosion, SARs can surpass one metre per year (in these cases the GIS-bathymetry is a more appropriate tool; Khaba and Griffiths, 2017); ii) the watershed-dominated inputs of matter and radiotracers onto the SWI may show high temporal variability (McCall et al., 1984); iii) in most cases reservoirs are not old enough for allowing steady-state inventories of $^{210}Pb_{exc}$ in sediments (as required for applying the standard CRS model); iv) depending on their age, the expected peaks in the profiles of artificial fallout radionuclides may be absent.

Because of the above issues, the radiometric dating of recent sediments has become a complex task in which all the available tracers (e.g., stable lead, Chi et al., 2009; pollen markers, Chen et al., 2014; etc.) and sources of evidence (e.g., bulk density profiles, Abril, 2011) must be analysed.

The effects on radionuclide concentrations in sediments due to progressive acidification of the aquatic system, and particularly their implications in the radiometric dating, have not been studied in detail. This study addresses this issue by analysing bulk density and the activity concentration profiles of $^{137}$Cs, $^{239}$Pu, $^{240}$Pu, $^{210}$Pb, $^{226}$Ra, $^{228}$Ra, $^{234}$Th ($^{238}$U) and $^{40}$K in a sediment core from the Sancho reservoir (SW Spain), which has been drastically impacted by acid mine drainage (AMD). The construction of the dam ended in late 1962, about the time of maximum $^{137}$Cs and $^{239+240}$Pu fallout. It was heightened in 1972, almost doubling the capacity of the reservoir and displacing upstream the major depositional area of sediments transported by the Meca River. The reservoir is strongly affected by AMD, particularly since 2001, when the closure of the mining of Tharsis ceased the treatment of its waters (Cánovas et al., 2016). This scenario brings a unique opportunity to study the different radiogeochronological fingerprints in an AMD-affected sediment core, which records the transition from the former flood plain to aquatic sediments. The methodology (involving a multi-tracer approach and outstanding dating tools), results and discussion may be of general interest for environmental scientists.

## 2. Materials and methods

### 2.1. Site description

The Sancho Reservoir (Fig. 1) has a capacity of 58 Mm$^3$. It was built in 1962 (works ended on December 31st) to supply water to a paper mill factory, and it has been used as a domestic water supply after treatment. The dam was enlarged in height to increase (almost doubling) the capacity of the reservoir, with works ending on January 1st 1972. This water body has a surface area of 4.27 km$^2$ and a maximum depth of 40 m. It is mainly fed by the Meca River, with a catchment area of 314 km$^2$ and an average stream flow of 61 Mm$^3$/year. The studied site has a Mediterranean-type climate with an average temperature of 19 °C and an average annual rainfall of 614 mm. About 60% of rainfall occurs between October and January, although the precipitation is subject to great inter-annual and intra-annual variability (Galván et al., 2012).

In the headwaters of the Meca River, the huge mining complex of Tharsis is located (Cánovas et al., 2016). Due to the intense mining activities, there is an extensive area of flooded open-pits, galleries, shafts and mining wastes that release metal and acidity to the Meca watershed,