Chemosphere

Radioisotope and metal content in a Lake Nakuru sediment core – accumulation rate and inventories --Manuscript Draft--

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Abstract:	The Nakuru environment is a hot spot both for human population and for biological conservation with a large number of species protected in the well visited Lake Nakuru National Park. Reoccurring mass die-off of the Lesser Flamingo in Lake Nakuru as well as cases of intoxication of humans within the water catchment area have gained attention and dedicated a significant amount of research over the recent decades. The toxicological histories of natural and anthropogenic activities are reflected by accumulated compounds in the water body sediments. In this study, a sediment core obtained from the central and deepest point of Lake Nakuru was sliced with 5 mm resolution and analyzed with the 210Pb dating method. The results show a linear accumulation rate of 1.3 mm y-1 and a mass accumulation rate of 0.027 g cm-2 y-1. Further analysis resulted in core profiles of organic material decay, phosphorus concentration gradient and total content of heavy metals in the lake water and in the sediment. In addition, analysis of 226Ra, 137Cs, 239+240Pu, 228Th/232Th was performed.				
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- 19 cases of intoxication of humans within the water catchment area have gained attention and
- 20 dedicated a significant amount of research over the recent decades. The toxicological histories
- of natural and anthropogenic activities are reflected by accumulated compounds in the water
- body sediments. In this study, a sediment core obtained from the central and deepest point of
- Lake Nakuru was sliced with 5 mm resolution and analyzed with the ²¹⁰Pb dating method.
- 24 The results show a linear accumulation rate of 1.3 mm y⁻¹ and a mass accumulation rate of
- 25 0.027 g cm⁻² y⁻¹. Further analysis resulted in core profiles of organic material decay,
- 26 phosphorus concentration gradient and total content of heavy metals in the lake water and in
- 27 the sediment. In addition, analysis of ²²⁶Ra, ¹³⁷Cs, ²³⁹⁺²⁴⁰Pu, ²²⁸Th/²³²Th was performed.

1 Introduction

- 2 Lake Nakuru is a closed basin hypereutrophic alkaline salt-water lake in Kenya. It symbolizes
- a biological hot spot exhibiting a large number of species concentrated to a small area that is
- 4 protected within Lake Nakuru National Park, which in turn is one of the most visited national
- 5 parks in Kenya. Amongst the ~400 bird species observed, the most spectacular often refers to
- 6 the large numbers of Lesser Flamingo (*Phoeniconaias minor*) that occasionally can add up to
- 7 several hundred thousands of birds. (Vareschi, 1979) The large primary production in the
- 8 alkaline saline lake constitutes a feedstock of algae where in particular the cyanobacterium
- 9 Spirulina (*Arthrospira fusiformis*) comprises the main food source for the Lesser Flamingo.
- 10 (Vareschi, 1978, 1979, 1982, 1984a, 1984b, 1985, 1987; Nogrady 1983)
- 11 The abundance of Lesser Flamingo is naturally fluctuating but after observations of
- mortalities with >10,000 birds involved during the years 1993, 1995, 1999, 2001, 2006 and
- 2008 (Krientiz and Kotut, 2010), flamingo ecology have been devoted a significant amount of
- research. Flamingo health and mortality have been addressed to fluctuation in algae crop,
- toxins associated with other species of naturally occurring cyanobacterium, organic toxins or
- heavy metal pollution originating from human activities. (Greichus et al., 1978;
- 17 Krientiz et al., 2016)
- 18 The water catchment area in the Lake Nakuru basin is estimated to 1938 km² (Greichus et
- al., 1978) and by planar projection to 1800 km² (Vareschi, 1982). The basin comprises the
- Lake Nakuru National Park of 188 km² (KWS, 2017) wherein the Lake Nakuru covers
- 21 approximately 60 km² (Schultz and Zabel, 2000). The remaining area is to the majority
- represented by a densely populated country side with farms and villages, with little forest
- cover. Consequently, erosion facilitates mobility of potential toxic compounds from
- precipitation or human origin. The large regional city of Nakuru having about 260 000
- inhabitants (WPR, 2017) is located about 1 km from the lake shores and has two sewage
- treatment plants draining into the lake. The main road between east Africa's coastal port city
- of Mombasa, via Nairobi and further to the African inland via the Uganda capital city of
- 28 Kampala passes through the city with heavy commercial traffic that increase air pollution as
- 29 well as pollution from vehicle tyres and oil products. During the last century, leaded petrol
- was used. Nakuru has a history of developed industrial production, including textile, battery,
- 31 tannery and galvanizing industries. (Vareschi, 1978) Toxic compounds originating from
- 32 anthropogenic activity resulting in human toxicity have been identified in the water catchment
- area and targeted for investigations. (Odongo et al., 2016)
- Lake Nakuru is a shallow saline pan with an average depth slightly below 1 m, it has no
- outlets and is regulated by precipitation within the water catchment basin and evaporation,
- 36 thus the lake surface area varies between \sim 45 60 km². The area around the lake is
- accordingly flat and has in historical time constituted lake bottom as a part of a larger lake
- including Lake Elementaita and Lake Naivash. Furthermore, the area has on a geological
- 39 timescale received extensive volcanic activity. (Vareschi, 1982) Over time, dissolved
- 40 organic- and inorganic compounds as well as particulate matter have accumulated to compose
- 41 the alkaline salt lake and its sediment. (Schultz and Zabel, 2000; Stumm and Morgan, 1996;

- Schlargerl and Burian, 2016) The deepest part, around 2-5m deep depending on surface water
- 2 level, centered in the lake corresponds to the final deposition point in the basin thus
- 3 representing the historical archive for compounds of natural and anthropogenic origin.
- 4 (Schultz and Zabel, 2000; Appelby and Oldfield, 1978; Koide et al., 1973; Christensen and
- 5 Chien, 1981)
- 6 In order to evaluate any time trend in the environment affecting the lake, it is useful to try and
- 7 extract data from a sediment profile. Sediment chronology can often be established either by
- 8 using well documented events (e.g. tephra layers from known volcano eruptions or excess
- 9 137Cs from the Chernobyl NPP accident in 1986) or by applying radioisotope techniques
- based on isotopes in the natural decay chains originating from the ²³⁸U, ²³⁵U and ²³²Th decay.
- 11 The earth's content of ²³⁸U originates from when our planet was formed and the nuclide has a
- half-life of 4.6 million years. One decay product is ²²²Rn which is a noble gas and diffuses
- from the ground to the air with a constant flux, but because of its short half-life of 3.8 days,
- the particle reactive daughter nuclide ²¹⁰Pb with a half-life of 22.86 years is washed out from
- the atmosphere and re-deposited to the ground, particularly during precipitation. The ²¹⁰Pb
- may thus be mobilized with surface water run-off due to the main inventory of ²¹⁰Pb is
- associated to small size mobile particles. Because of the small area of a deposition bottom in a
- lake compared to the lake's water catchment area, ²¹⁰Pb, like other pollutants from
- 19 atmospheric deposition, will often become accumulated with a higher concentration in the
- 20 bottom sediments at the deepest point such as in the basin located in Lake Nakuru. The ²¹⁰Pb
- 21 found in the sediment accumulation areas thus originate both from direct deposition on the
- lake surface and due to focusing from surrounding lake sediments and catchment run-off. If
- 23 this process is appearing at a relatively constant rate so that the atmospheric deposition is
- constantly balanced by the removal due to erosion and radioactive decay, the system is in
- equilibrium, for ²¹⁰Pb with a half-live of 22 years such an equilibrium system takes roughly
- some 60 to 70 years to develop. The amount of ²¹⁰Pb at a given surface area of the sediment
- will then be constant with time and a depth profile will show a gradient with a slope only
- depending on the sediment accumulation rate (cm per year or g per m² and year). Therefore a
- method for determining chronology in stratified sediment is by analyzing ²¹⁰Pb activity with
- sediment depth. (Appelby and Oldfield, 1978; Bollhöfer et al., 1994; Blais et al., 1995;
- 31 Matthews et al., 2007; Brown et al., 2011)
- 32 The isotope 232 Th with a half-life of 10^{10} years occurs naturally in the earth's crust. Thorium
- in aqueous solutions quickly hydrolyses and attaches to any surface thus making its residence
- time in lakes and oceans very short. The daughter isotope ²²⁸Ra (5.8 years half-life) on the
- other hand is considerably more mobile and may migrate from soils to lake reservoirs where it
- eventually decays to the short lived ²²⁸Th. The daughter nuclide ²²⁸Th with a half-life of 1.9
- years share the same chemical properties with ²³²Th and thus becomes attached to particles
- and thereby transfer into the sediments. Although the 228 Th / 232 Th ratio in soils may be less
- than 1 (due to the ²²⁸Ra migration) it is often larger than 1 in surface sediments due to the
- 40 excess input of ²²⁸Th from ²²⁸Ra decay. This allow for using the ²²⁸Th / ²³²Th as a measure of
- sediment accumulation rates in recent time scale of approximately 10 years of age.

- 1 Naturally occurring ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu exist in concentrations below detection levels, thus the
- 2 measurable contents originate from human activity. The period corresponding to nuclear
- bomb injection of these isotopes into the earth's atmosphere corresponds to 1950-1960's with
- 4 a peak around 1963. The Chernobyl nuclear plant disaster in 1986 left a measureable peak of
- 5 137Cs in the northern hemisphere. The re-entry of the satellite Snap-9A in 1964 caused a
- 6 significant injection of ²³⁸Pu from its evaporated radioisotope battery exclusively in the
- 7 southern hemisphere. (Hardy et al., 1972; Levy et al., 2011). The analysis of the above-
- 8 mentioned radioisotopes in a sediment core thus may provide information about the sediment
- 9 accumulation rate or its mixing since the inputs are well described in time.
- 10 In this study we have collected a sediment core from the center deposition bottom in Lake
- Nakuru that was analyzed to obtain 1) activity profiles of ²¹⁰Pb, ²²⁶Ra, ¹³⁷Cs, ²³⁹⁺²⁴⁰Pu,
- 12 ²²⁸Th/²³²Th, 2) concentration profiles of organic material and phosphorus and 3) content of the
- heavy metals Cd, Cr, Cu, Hg, Ni, P, Pb and Zn.

14 Materials and methods

- 15 <u>Site description and sampling</u>
- 16 The sediment core was sampled in Lake Nakuru, Kenya, at the approximate position
- 17 0°21'33.77"S, 36°5'16.44"E located by using a hand held GPS. The site constitute the deepest
- area in the central part of the lake (WLD, 1979) thus represented the sediment accumulation
- bottom. A light weight sediment core sampler closing at both top and bottom ends of the
- sampler tube was constructed especially for sampling in Lake Nakuru. The sampled core had
- a diameter of 100 mm and was sliced at 5 mm resolution. Upon visual inspection of the
- sediment matrix, the surface layers revealed blackish, fluffy layers with distinct smell of
- 23 decay of organic matter including bird fecal, the sediment consistency became more firm with
- 24 increasing depth and did not show any discrete horizons or layers. The sampling took place at
- 25 mid-day the 20th October 2001 followed by core slicing the same day. Slices were air dried
- before transport. The season was dry and hot resulting in a maximum water depth of ~0.85 m
- 27 located at the sampling site. The lake had a concentrated smell of bird dropping and was at the
- moment visited by a large amount of Lesser Flamingo. Two soil samples (15 · 15 · 15 cm)
- were collected in an elevated grass land and forest area, respectively, approximately one km
- 30 west from the lake.

31 Radiometry

- 32 Atmospherically deposited ²¹⁰Pb (²¹⁰Pb_{excess}) was determined by subtracting the supported
- 33 ²¹⁰Pb (²¹⁰Pb_{supported}) from the total ²¹⁰Pb inventory (²¹⁰Pb_{tot}). It was assumed that the supported
- 34 ²¹⁰Pb formed through ²²⁶Ra decay in the sediments were at steady state and no losses occurred
- 35 through radon emanation. In this case determination of ²¹⁰Pb_{supported} was made from the lowest
- obtained value of ²¹⁰Pb in the core. (Appelby and Oldfield, 1978)
- 37 Activity of $^{210}\text{Pb}_{\text{tot}}$ was determined by measuring the α emission from $^{210}\text{Po} \rightarrow ^{206}\text{Pb}$ (stable)
- according to Flynn (1968) and Appleby and Oldsfield (1978). Sediments of ~1 g were dried at
- 39 95°C for 48 h, homogenized and weighed. A well-known amount of a yield determinant
- 40 (about 0.1Bq ²⁰⁸Po) and 30 ml *aqua regia* was added to the sample which were then reflux-

- boiled over night followed by filtering. The fluid was evaporated to dry salt and re-dissolved
- 2 with 1 M HCl, repeated three times. 2 ml conc. HCl, 50 mg ascorbic acid and 5 ml H₂O was
- added and the solution placed in a cell with a bottom mounted Ni plate. After 2 h at 65°C the
- 4 Ni-plate was removed, rinsed with water, ethanol and ammonia and dried for 1 h at 65°C.
- 5 Alpha spectrometry was done using Canberra PIPS-detectors. Activity of ²⁰⁸Po and ²¹⁰Po was
- 6 corrected for decay according to equation [1] $A_t = A_0 \cdot e^{-k \cdot \Delta t},$ where
- 7 $k = \ln 2 / t_{1/2} (^{208}\text{Po } t_{1/2} = 1058 \text{ d} \text{ and } ^{210}\text{Po } t_{1/2} = 138 \text{ d}), \Delta t = \text{the time from disequilibria}$
- 8 (deposition time) until the time for measurement. (Appelby and Oldfield, 1978; Henriksson et
- 9 al., 2011). Decay correction of ²¹⁰Pb between sampling and Po-separation was negligible due
- to the short waiting time (< 2 months).
- 11
- Sediment accumulation rates obtained from ^{210}Pb decay (^{210}Pb t_½ = 22.26 years) were
- acquired by plotting log A as a function of d and applying linear regression in the form
- $ln\ A_t = -k/\Delta t + ln\ A_0\ (eq.\ [1])\ where\ \Delta t = (d\cdot r),\ d = depth\ (mm)\ or\ (g\ cm^{-2})\ and\ r = linear$
- accumulation rate (mm y⁻¹) or mass accumulation rate (g cm⁻² y⁻¹). (Bollhöfer et al., 1994)
- 16
- Analysis of 137 Cs was performed by gamma spectrometry by recording γ radiation at 662 keV
- directly from a weighed quantity of dried sediment.
- 19
- 20 Analysis of $^{239+240}$ Pu and 228 Th / 232 Th was done by α spectrometry after chemical separation
- 21 from the bulk. According to Holm (1984), a weighed quantity of 2-3 g dried and
- 22 homogenized sediment was ashed in 550°C overnight. ²⁴²Pu tracer as a yield tracer was added
- 23 and the sediment was dissolved in *aqua regia* overnight. The solution was evaporated and the
- remaining salt dissolved in HCl, followed by filtration. The filtrate was precipitated as mixed
- 25 hydroxides by adding ammonia and then centrifuged. The supernatant was removed and the
- precipitate was dissolved in 8M HNO₃ with an addition of some 100mg NaNO₂. The solution
- passed through an ion exchange column absorbing Pu and Th where Th was eluted with 9M
- HCl and Pu eluted with 9M HCl+ 0.1M NH₄I. Some tens of milligrams of Na₂SO₄ was added
- 29 to the Pu and Th eluates and then evaporated. The salt was dissolved in H₂SO₄ and pH
- adjusted with NH₃/H₂SO₄ to pH 1.8 2.1. Electroplating of Pu and Th onto stainless steel
- 31 discs from the solution was done at an applied current of 1 A during 1 h. The steel plates were
- 32 rinsed in water, ammonia and acetone before being analyzed by alpha spectrometry for Pu and
- 33 Th-isotopes using Canberra PIPS detectors.
- 34 35
- Determination of organic material
- 36
- 37 Organic material content in the dry sediments were determined by oxidation at 550°C during
- 38 24 hours. The results were calculated as ash weight / dry weight and presented as ash free dry
- 39 weight (%). (Bydén et al., 1996)
- 40 <u>ICP-OES analysis</u>
- The elements Cd, Cr, Cu, Hg, Ni, P, Pb and Zn were analyzed with ICP. Dry sediment
- samples were weighed, heated in concentrated HCl overnight, filtrated with paper filter
- 43 (Munktell no. 5) followed by cellulose filter (22.5 µm pore size) and analyzed on
- an ICP-OES 3520B (ARL Instruments) calibrated with Atomic Spectral Standards (Analytical
- 45 Standards AB). Four sediment samples following the same procedure were also heated in

- 1 aqua regia and used to obtain a relative correction factor between the two methods. The
- 2 results in (ppm) were calculated from dry sediment weight and presented as an average for the
- 3 entire core 0 325 mm depth. Coefficient of variation, CV, from ICP-OES analysis was
- 4 expressed in (%).

6 Results

- 7 ²¹⁰Pb decay profile and sediment accumulation rates
- 8 The activity of excess ²¹⁰Pb was plotted against sediment depth, see Figure 1. The resulting
- 9 profile showed that the activity near the surface was ~20 % lower than the maximum seen at a
- depth of ~90 mm, hereafter the activity decreased exponentially with sediment depth. At the
- depth of 322.5 mm the activity was 0.077 Bq g⁻¹ and this value was used to determine the
- sediment ²¹⁰Pb support level resulting from uranium series background. Linear regression of
- data below 140 mm depth, see insert in Figure 1, resulted in k = -0.0247 ($R^2 = 0.84$) thus
- calculations according to equation [1] resulted in a linear sediment accumulation rate of
- 1.3 mm y^{-1} (± 0.2 mm y^{-1}). The ²¹⁰Pb activity plotted against the mass depth is presented in
- Figure 2. Linear regression of data > 2 g cm⁻², see insert in Figure 2, resulted in k = 1.1478
- $(R^2=0.85)$ thus the mass sediment accumulation rate was calculated by equation [1] to
- 18 $0.027 \text{ g y}^{-1} (\pm 0.004 \text{ g y}^{-1})$. Total inventory of ²¹⁰Pb in the surface soils were 0.104 Bq g⁻¹ in
- the savanna and 0.126 Bq g^{-1} in the forest. The excess ^{210}Pb in the upper 150 mm of the
- sediment core accumulated to 0.138 Bq g⁻¹.
- 21 Decay profiles of ¹³⁷Cs, ²³⁹⁺²³⁹⁺²⁴⁰Pu and ²²⁸Th/²³²Th
- The results from ¹³⁷Cs and ²³⁹⁺²³⁹⁺²⁴⁰Pu analysis did not show any clear trend between
- 23 15 280 mm depth, nor did the 228 Th/ 232 Th ratio in the analyzed interval of 15 100 mm
- depth (Figures S4-S5).
- 25 Profiles of sediment density, organic material and total Phosphorus
- 26 Sediment dry mass relative to organic material and total Phosphorus content was plotted
- against depth and presented in Figure 3. The result clearly showed that sediment density
- 28 increased with depth inversely proportional to the decrease of organic material content. The
- 29 concentration profile of total Phosphorous followed the trend of the organic material.
- 30 Content of heavy metals
- 31 The results from ICP measurement of heavy metal content in sediment are presented in
- Table 1. For most metals the concentration showed insignificant variation with sediment
- depth, thus presented as an average of 0 325 mm depth. However, notably lead
- concentrations increase by some 10-20% below 150mm depth (Figure S7).
- 35 Discussion
- 36 ²¹⁰Pb decay profile and sediment accumulation rates

- 1 ²¹⁰Pb profiles with a decreased or flattening activity near the surface of the sediment have
- 2 previously been reported (Donazzolo et al., 1982; Koide et al., 1973; Christensen and Chien,
- 3 1981) and ascribed to a physical or biological mixing zone. Considering that Lake Nakuru
- 4 often have relatively strong afternoon winds, wave motion may likely reside in force through
- 5 the shallow water column consequently moving particles. The wave motion occurs in a
- 6 horizontal ellipse where the amplitude decline with depth by increased viscosity and friction,
- 7 particularly as the motion enters the sediment. (Kundu, 1990). Vareschi (1982) however
- 8 argued that wind-speed rarely was of a magnitude large enough to cause significant sediment
- 9 resuspension. This must however be regarded in connection with the variable water depth.
- During low water levels resuspension should be more frequent at a given wind speed.
- 11 (Vareschi, 1982)
- 12 The benthic zone in Lake Nakuru has been reported to be deficient in larger organisms that
- could possibly cause bio-turbation of the sediment. (Vareschi, 1978) Vivid microbial activity
- in the lake result in a highly oxidized potential close to the surface of the water column that
- sharply decrease with depth where large amounts of organic material including bird faeces
- cause anaerobic conditions near- and in the sediment. (Vareschi, 1978; Greichus et al., 1978)
- 17 This is consistent with 1) observations made at the slicing of the sediment core where viscous
- organic material caused difficulty to define the water-sediment interface and 2) the resulting
- 19 profiles of organic material and total Phosphorous seen in Figure 3.
- 20 It may therefore be expected that the resulting ²¹⁰Pb decay profile obtained from Lake Nakuru
- 21 is a consequence of slow physical sediment mixing to an approximate depth of 90 mm. In
- addition, the difficulty in identifying the exact water-sediment interface opens for a possibility
- that the absolute level of 0 mm depth was determined with inaccuracy. Thus, to allow for
- tolerance in absolute sediment depth, it was decided to avoid the flattened decay profile
- around 90 mm depth and calculate the sediment accumulation rate below 140 mm depth
- 26 where the ²¹⁰Pb decay profile demonstrated exponential decay. Assuming the depth of the
- 27 mixing zone has been roughly constant with time the exponential decline in ²¹⁰Pb below the
- 28 mixing zone is a measure of the sediment accumulation rate. Tolerance of the absolute
- 29 sediment depth does not affect the calculated sediment accumulation rates because these are
- 30 relative calculations. Due to the amphoteric nature of lead it may be anticipated that both
- stable lead and ²¹⁰Pb partly may exist as soluble forms. The integrated ²¹⁰Pb level of 4250
- 32 Bq/m² (equaling a steady state flux of 130 Bq per m² and year) is however within expected
- range or even a bit higher than what would be expected. Unfortunately published ²¹⁰Pb fluxes
- on the African continent are relatively rare so values to compare with are scarce but in general
- 35 ²¹⁰Pb fluxes are proportional to the annual rain rate.
- The sampling spot was chosen at the deepest central part of the lake. This spot is the most
- unlikely place for a mammal to visit, or, the flamingo to be standing because of the bird's
- 38 limitation of standing in deep water, nor any other large bird. Furthermore, if hippopotamus
- 39 had disturbed the sediment where the sediment core was obtained, there would indeed be no
- 40 variation of ²¹⁰Pb decay with depth. The spot chosen for sampling most likely represent the
- best area for obtaining sediment cores, however it can still not be excluded to 100% certainty

- that the sediment have been disturbed by any animal in recent history during abnormally low
- 2 water levels.
- 3 Sediment dry weight plotted against depth in Figure 3 demonstrate scattering of data points
- 4 which reflects the difference in wet volume of each slice generated during slicing. Ideally, the
- 5 profile should in general have an appearance of a smooth line with variations in certain
- 6 chronological layers of different sediment density

8 Determination of ground content of ²¹⁰Pb

- 9 Organic surface soils at non-erosion locations are considered to contain excess ²¹⁰Pb due to
- integrated accumulation from precipitation. [Bro11, Per11] As expected, the excess ²¹⁰Pb in
- the upper 150 mm of the sediment was higher than the control samples obtained from the
- surface soils in the forest and savannah, however, the soil sample from the forest may show
- too high activity because the bottom 30 mm of the sampled cube was composed of dense
- mineral soil rather than organic soil. Mineral soil could possibly contain support ²¹⁰Pb due to
- slow diffusion of ²²²Rn. (Brown et al., 2011; Persson and Holm, 2011). Assuming a supported
- 16 ²²⁶Ra of about 50 mBq/g and a unit density the areal inventory of excess ²¹⁰Pb at the two
- terrestrial sites becomes 8100 and 11400 Bq/m² respectively, thus very high compared to the
- world average. The dense mineral soil appeared to be originating from volcanic material, thus
- 19 the lake and its wide stretched flat surroundings likely constitute one large pan. The terrestrial
- soil sample should probably be better represented if collected at a site further away from the
- 21 lake, at a slightly higher altitude and with deeper content of organic type of soil.

22

23

¹³⁷Cs, ²³⁹⁺²⁴⁰Pb and ²²⁸Th/²³²Th

- The absence of bomb ¹³⁷Cs and ²³⁹⁺²⁴⁰Pb peaks in the sediment profile, as well as an absence
- of a decreasing decay profile of ²²⁸Th/²³²Th in the upper 100 mm is a likely consequence of
- slow physical sediment mixing to an approximate depth of 90 mm. This may indicate that
- 27 either the sediments are mixed or that transport of particle reactive material (where ²²⁸Th and
- Pu-isotopes are attached to) occur with a delay and at a slow rate so that the time lag between
- deposition in the catchment area and the transport + deposition in the lake sediments takes in
- 30 the order of years.
- 31 Levels of radiocesium deposition in the equatorial regions from global fallout was very low
- 32 (UNSCEAR) and other sources are in practice absent at these latitudes. It is well-known that
- clay minerals, e.g. Illite (Comans et al., 1989), are the main trap for dissolved cesium in fresh
- and marine waters. Although it has been reported that anoxic conditions in the lake water are
- unlikely due to daily mixing caused by wind (Vareschi, 1982), the high organic load most
- likely cause the interstitial water in the sediments to become anoxic with high NH₄⁺
- 37 concentrations as a consequence. Temporarily bound radiocesium thus probably experience
- 38 extensive ion exchange reactions and are becoming solubilized shortly after burial, especially
- 39 when sediments are poor in clay minerals. The integrated ¹³⁷Cs of about 850 Bq/m² is roughly

- what is expected at these latitudes of the deposited from fallout. Similarly the Pu may be
- 2 released due partly to carbonate complexation and partly due to colloidal formation of organic
- 3 material in the sediment deposits (Cleveland et.al., 1983; Sanchez et.al., 1986). It is however
- 4 interesting that the integrated ²³⁹⁺²⁴⁰Pu of 40 Bq/m² is nearly twice that is expected at these
- 5 latitudes (UNSCEAR, 1980) which indicates that the sediments is a main reservoir for
- 6 deposited Pu in the lake. Ratios ²³⁸Pu/²³⁹⁺²⁴⁰Pu were all lower than 3% showing that the
- 7 contribution from the SNAP-9A event in 1965 was negligible as expected.

8 ICP measurements and heavy metal contents

- 9 The elements Cd and Zn generate a larger error in ICP-OES analysis than the other elements
- due to closeness of atomic spectral lines. The results from heavy metal analysis of the
- sediment show that there is no significant change of concentration with depth except for lead
- which show concentrations by some 10-20% higher below 150mm depth (Figure S7). In
- general the concentrations are rather high for a lake, however alkaline salt lakes in volcanic
- bedrock may well have high natural concentrations of heavy metals. (Loberg, 1999) The only
- metal that impose a noteworthy difference in comparison to previous measurements is Cd
- which in our study was higher, 4 ppm compared to 0.27-0.48 reported by Ochieng et al.
- 17 (2007) and Greichus et al. (1978).

18 **Summary**

- In summary, the conditions in Lake Nakuru of 1) shallow water body 2) frequent afternoon
- 20 winds resulting in motion of the water column and loose surface sediments and 3) a viscous
- 21 water-sediment transition zone introducing tolerance in determination of absolute sediment
- depth eliminated the possibility to obtain accurate sediment chronology in a recent time scale
- using ²¹⁰Pb. Instead, by calculation of data below the mixing zone, sediment accumulation
- rates were successfully obtained. In general, the sediments contained high amounts of heavy
- 25 metals. The integrated levels of artificial radioisotopes and the natural ²¹⁰Pb are at, or
- somewhat above, what would be expected which shows that the sediments themselves are the
- 27 main reservoir for deposited radioisotopes in spite of the very different water chemistry.

28 Acknowledgements

- 29 We dearly thank Asa Zazzi for conducting ICP-analysis. Kenya Wildlife Service for
- 30 supporting the study and lending a boat.

1 Figures and Table

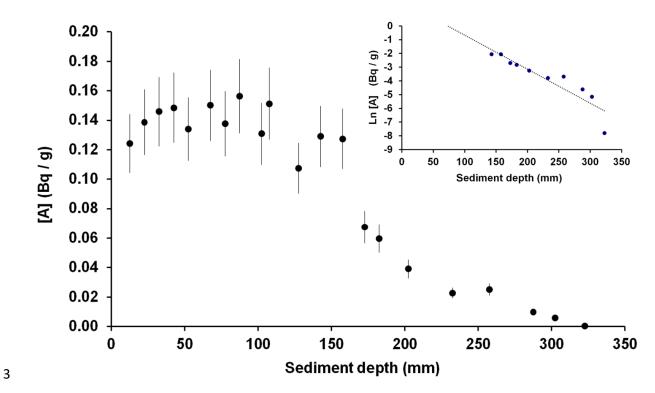


Figure 1 210 Pb decay (\pm 16%) profile in sediment from Lake Nakuru. The linear sediment accumulation rate 1.3 mm y⁻¹ was calculated from linear regression (insert).

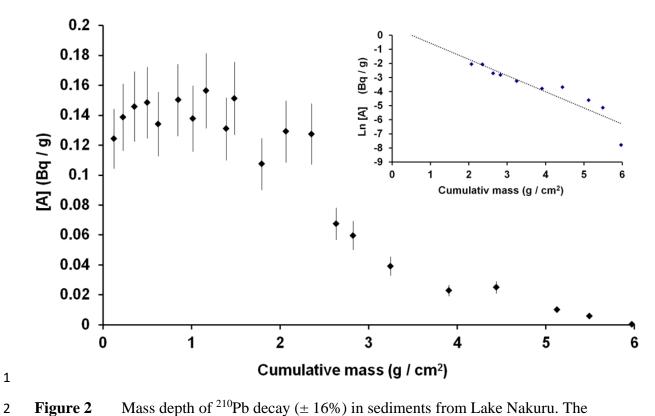


Figure 2 Mass depth of 210 Pb decay (\pm 16%) in sediments from Lake Nakuru. The sediment mass accumulation rate 0.027 g cm⁻² y⁻¹ was calculated from linear regression (insert).

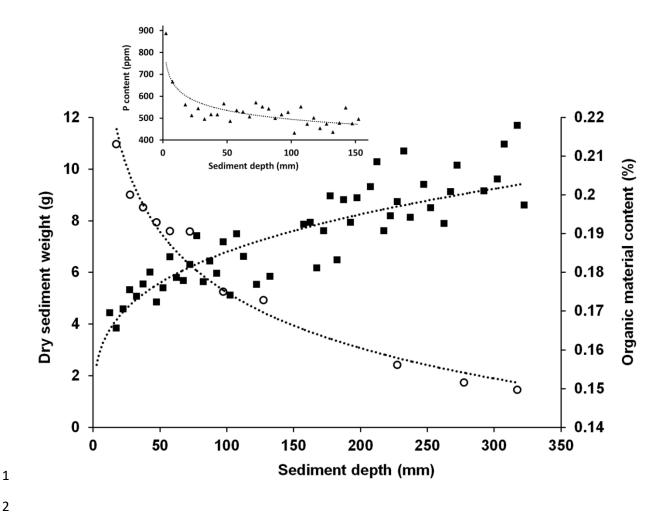


Figure 3 Graph showing sediment dry mass (left axis) increasing with depth, correspondingly, the organic material (right axis) decreases with depth in accordance with total Phosphorus content (insert). The trends are highlighted by power regression lines (dashed lines), serving as guides for the eye.

- 1 **Table 1** Heavy metal content in lake sediment calculated from dry weight in ppm $(\mu g/g)$.
- 2 Statistical error presented as coefficient of variation, CV (%). The results are compared to
- 3 three previous studies.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
This study CV (%)	4 46	10 32	8 41	<1 3	10 20	30 19	142 8
Ochieng et al., 2007 *	0.48	1.95	2.89		15.58	14.36	154.1
(±ppm)	0.10	0.075	0.06		0.31	0.75	15.3
Nelson et al., 1998 **		67	24			22	147
Range***		10-280	5-95			4-100	44-630
Greichus et al., 1978	0.27		6.2	<0.5		34	140

^{*} Average from 3 sample sites. ** Average from 11 samples sites. ***The concentration range of the

6

9

Table 2 Fall out of radioactive isotopes (Bq/m²) in Lake Nakuru in comparison to global fallout in the southern tempered zone (UNSCEAR, 1980).

	¹³⁷ Cs	²³⁹⁺²⁴⁰ Pu	²¹⁰ Pb
Lake Nakuru sediments	847	40	4250
Global fallout south temp. zone	1420	16	

^{5 11} sampling sites.

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1 Supplementary information

3 Table of content

- **Figure S1** Sediment profile showing total inventory of ²¹⁰Pb and support level
- **Figure S2** Sediment profile of $^{210}\text{Pb} \ge 142.5$ mm depth showing regression fit
- **Figure S3** Sediment profile of ²²⁶Ra
- **Figure S4** Sediment profile of ¹³⁷Cs
- **Figure S5** Sediment profile of ²³⁹⁺²⁴⁰Pu
- **Figure S6** Sediment profile of 228 Th / 232 Th
- **Figure S7** Sediment profile of heavy metal contents
- **Figure S8** Bathymetric map of Lake Nakuru showing the sampling sites

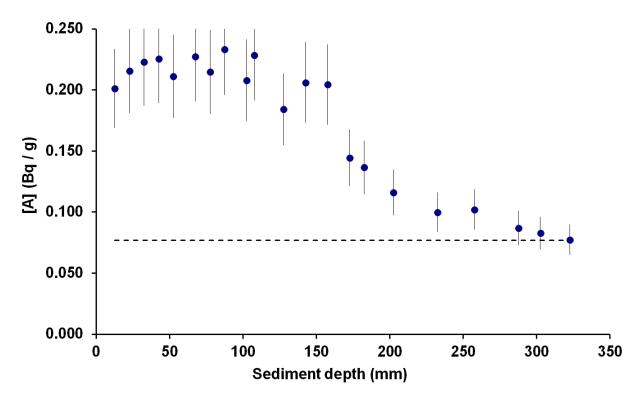


Figure S1 Total inventory 210 Pb decay profile from sediment in Lake Nakuru. The dashed line indicates the supported level of 210 Pb in the sediments. Error estimated to \pm 16%.

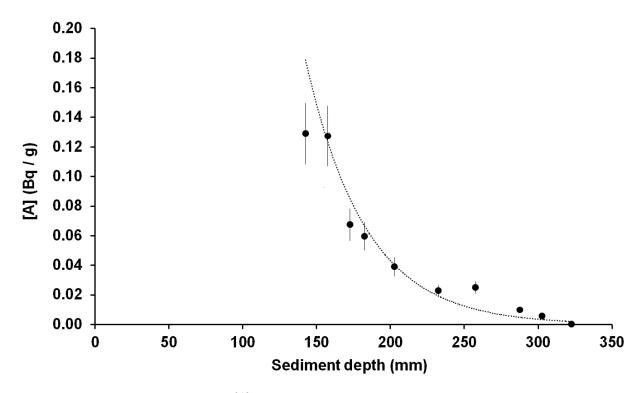
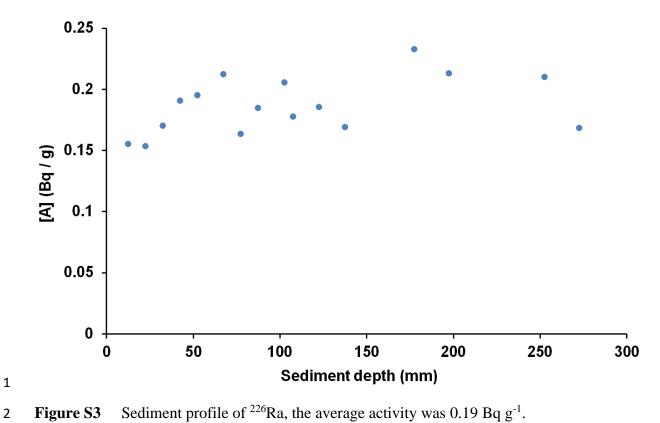
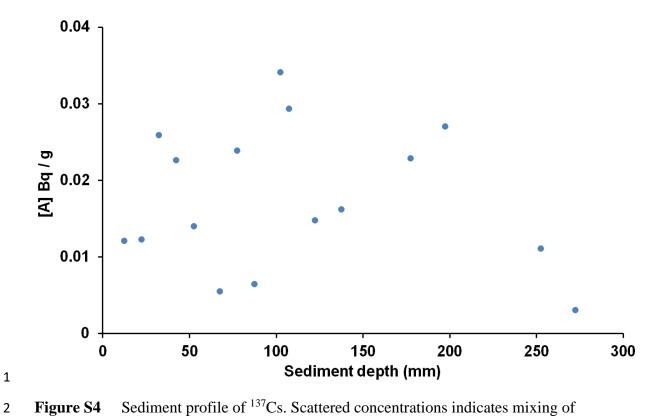


Figure S2 Sediment profile of 210 Pb below ≥ 142.5 mm depth showing a power regression line $y = 6.07e^{-0.025x}$ with a fit of $R^2 = 0.84$.



Sediment profile of 226 Ra, the average activity was 0.19 Bq g⁻¹. Figure S3



Sediment profile of ¹³⁷Cs. Scattered concentrations indicates mixing of Figure S4 sediments.

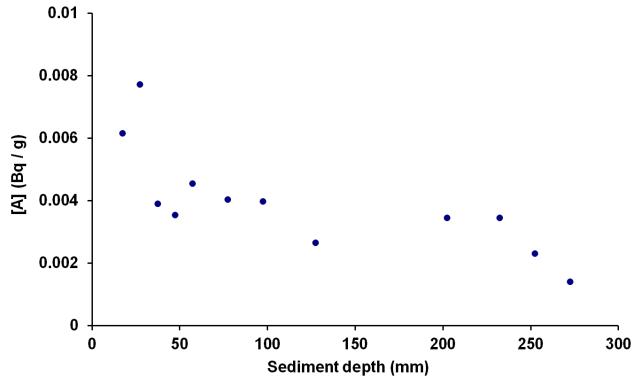


Figure S5 Sediment profile of ²³⁹⁺²⁴⁰Pu. The higher concentration at the surface may likely be a consequence of a chemical processes, for example flux of Pu bound to phosphorus precipitate or organic material. The wave motion mixing of sediment to a depth of ~90 mm would not allow for a chronological peak.

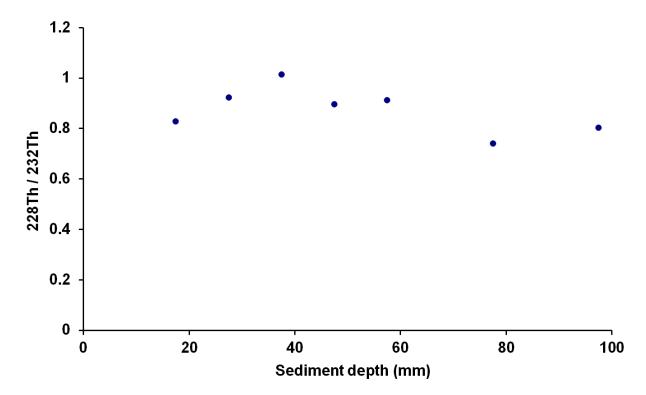


Figure S6 Sediment profile of ²²⁸Th / ²³²Th. In undisturbed sediments the fraction commonly reaches between 0.5 and 10 in an exponentially decreasing profile.

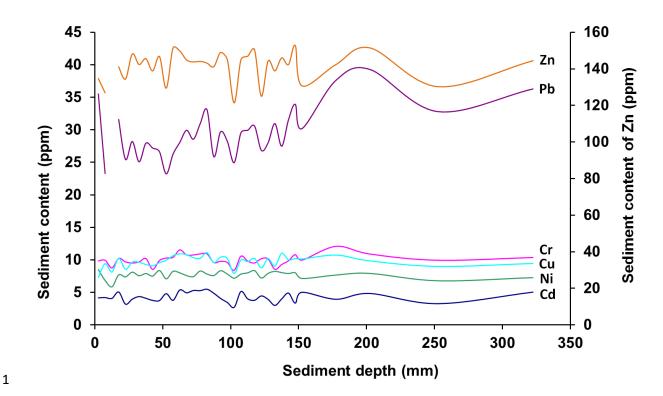


Figure S7 Sediment core profiles of heavy metal content demonstrating insignificant concentration changes with depth within errors. Average values are presented in Table 1.

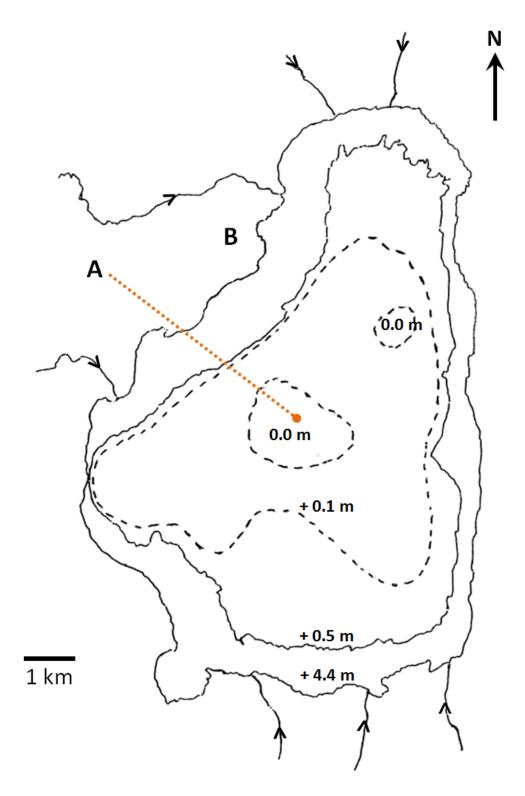


Figure S8 Illustration of a bathymetric map of Lake Nakuru with isopleths at various

- 3 heights of the water column. (WLD, 1979) The lake surface level exhibit large seasonal
- 4 variations. The sediment core was sampled from A (approx. location
- $0^{\circ}21'33.77"S$, $36^{\circ}5'16.44"E$) that represent the sediment accumulation bottom of the lake.
- 6 Ground reference samples was taken from B (approx. location 0°19'47.27"S, 36°4'12.68"E)
- 7 located above the highest lake level.

Declaration of Interest Statement

Declaration of interests

⊠The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Contribution

Paper: SVENGREN et al

Henrik Svengren; main author. Performed sampling, sample analysis, raw data processing, main authoring of manuscript.

Pär Roos; supervising and in-part-performing the practical part of sample analysis with Henrik Svengren in laboratory. Calculations. Co-authoring manuscript.

Daniel Koros; supervising sampling in situ, in Lake Nakuru, Kenya, co-operating sampling process in lake. Co-authoring manuscript.

Gunnar Svensson; main professor in the research project, co-authoring, reviewing of manuscript.

Cover Letter

Paper: SVENGREN et al

This paper presents unique sediment data of one of the world's most popular Flamingo Lakes (BBC, National Geograpic broadcasts) as well as one of the main National Park in Kenya regarding visiting numbers per year - but most of all an outstanding site for study of environmental chemistry as the surrounding landscape is densely inhabited with a human population situated in a water basin without drainage; all ends up in the salt water Lake Nakuru where only evaporation allows water to escape. The sediment collects historical events taken place in this special catchment basin. The unique data set is until now never published elswhere and no comparable research data has ever been made here. The paper represents a historical mark in the research history of Lake Nakuru and shows a method of performing sediment dating in a shallow salt lake, thus an excellent paper for contemporary research to relate to.

Yours sincerely

Henrik Svengren, corresponding author

Highlights

Highlights

Paper: SVENGREN et al

- Sediment sampling in a shallow salt water lake possible by using a core sampler
- Sediment dating using radio isotopes requires analysis results in
- Accumulation rates determined by sediment core in Flamingo habitat human population
- Lake Nakuru Kenya offers inventories heavy metal and core profiles of organic material decay
- Lead Pb 210 decay method resolution at deepest point catchment area basin