

# DEINSEA



## Radiometric properties of marine mammal fossils from the Westerschelde Estuary (Province of Zeeland, the Netherlands)

Robert J. de Meijer<sup>1,2</sup>, Emiel R. van der Graaf<sup>3</sup> & Klaas Post<sup>4</sup>

<sup>1</sup> Stichting EARTH, Weehorsterweg 2, 9321 XS Peize, the Netherlands

<sup>2</sup> Department of Physics, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

<sup>3</sup> University of Groningen, KVI- Center for Advanced Radiation Technology, Zernikelaan 25, 9747 AA Groningen, the Netherlands

<sup>4</sup> Natural History Museum Rotterdam, Westzeedijk 345 (Museumpark), 3015 AA Rotterdam, the Netherlands

### ABSTRACT

This paper reports on the radioactivity in fossil bones dredged from the bottom of the Westerschelde Estuary, the Netherlands. The fossil bones' radioactivity was measured with three techniques and their results are compared and found to be complementary. Enhanced levels of radioactivity are found to be related to concentration of natural uranium. Thorium is hardly present and the concentrations of potassium are low. The details of the uranium concentrations of the bones are not yet clear. Various hypotheses may explain the limited data of this exploratory investigation. The uranium concentrations in some of the bones are such that they are subdued to the Dutch regulations concerning radioactive substances. Working in the collection rooms where the fossils are stored does not result in higher exposure to ionised radiation compared to working in normal museum offices.

**Keywords** Westerschelde, Breda Formation, radioactivity, uranium

**Cite this article** de Meijer, R.J., van der Graaf, E.R. & Post, K. 2016 - Radiometric properties of marine mammal fossils from the Westerschelde Estuary (Province of Zeeland, the Netherlands) - *Deinsea* 16: 10 - 18

Submitted 17 November 2015

Revised 21 September 2016

Accepted 23 September 2016

Published 31 December 2016

**Author for correspondence**

Robert J. de Meijer:

rmeijer@geoneutrino.nl

**Editor**

Jelle W.F. Reumer

Copyright ©

2016 de Meijer, van der Graaf & Post

Distributed under Creative Commons

CC-BY 4.0

DEINSEA online

ISSN 2468-8983

### INTRODUCTION

The subsurface of the southern parts of the Netherlands houses sediments of the Miocene-earliest Pliocene Breda Formation. This formation contains radioactive minerals and phosphorite pebbles with up to 300 ppm uranium (Rijks Geologische Dienst 1971, Harsveldt 1973). Slupik *et al.* (2007) and Slupik & Janse (2008) noted that these phosphorites occur within three separated units of the Breda Formation (Langhian, Tortonian and

early Zanclean). The Breda Formation is exposed at riverbeds of the Westerschelde, an estuary known for its wealth of vertebrate fossils and especially vertebrae of marine mammals (Post & Reumer 2016). There are rumours that parts of the Westerschelde bottom and their sediments and fossils are 'radioactive' due to effluents from the Nuclear Power Stations at Borssele (the Netherlands) and/or at Doel (Belgium). On the other hand, it has been established that the Westerschelde transports efflu-

ents of the phosphate and gypsum production in Flanders (Pari-daens & Van Marcke 2001) and that phosphate was produced at Vlissingen-Oost until 2013. These releases have resulted in enhanced radioactivity due to  $^{226}\text{Ra}$  (from the  $^{238}\text{U}$  decay series) and Th being incorporated into sediments in and along the Westerschelde. Rumours and publications have in common the absence of research on the nature and origin of the actual levels of radioactivity of vertebrate fossils from the estuary.

This article aims to: (1) determine the concentrations of radio-nuclides in vertebrate fossils from one specific Westerschelde site, (2) analyse the source and origin of the radioactivity of these fossils, (3) analyse the implications of eventual differences in radioactive levels of marine mammal fossils, and (4) check the possible consequences for public collections where these fossils are stored.

## MATERIAL AND METHODS

In 2014 the Natural History Museum Rotterdam (NMR) decided to (re)check the potential of various fossiliferous sites of the Westerschelde. The aim was to study important finds, and to make relevant information accessible to the general public.

The euro-cutter UK 190 (86 GT, 300 HP) was leased from February 10–13th and June 3–5th. From December 15–18th the UK 12 (48 GT, 300 HP) was used. Both vessels were equipped with specially constructed 4 meter beams, nets without chains and minimum 12 centimetre mesh. Positions and depths were recorded with the relevant equipment on board of the vessels.

The choice of sites was based on oral information of fishermen. The sites were plotted on International Chart map 1475: ‘Westerschelde van Vlissingen tot Antwerpen met Kanaal van Terneuzen naar Gent’ (Fig. 1). All fossils sampled for radiometric tests were collected in area 6, an area where massive volumes of isolated skeletal elements of marine mammals may be encountered (Post & Reumer 2016).

Three instruments were employed to investigate the radiometric properties of the fossil bones: a dose-rate meter (Gamma Scout), a portable gamma-ray meter and a low-background gamma-ray spectrometer (HPGe) housed in a lead shielding at the KVI-Center for Advanced Radiation Technology (KVI-CART). Each of these instruments has its own pros and cons with respect to their sensitivity to various types of radiation, mobility and costs, but together they cover a range of precision and accuracy as briefly explained below.

Initially a hand-held Gamma-Scout Geiger-Müller counter was used, which in principle detects  $\alpha$ ,  $\beta$ , and  $\gamma$ -radiation with a calibrated scale of 0.01  $\mu\text{Sv/h}$  to 1000  $\mu\text{Sv/h}$ . [Note: The dose rate is given in Sv/h, where Sv stands for Sievert (unit for dose in J/kg but weighted for radiation and tissue type involved in the exposure)]. The instrument was used to obtain a very rough indication of the radiation dose rates on board of the vessels and (by 24-hours average counts) in the following museums: Naturalis Biodiversity Center, Leiden; Natural History Museum Rotterdam, Rotterdam; and Zeeuws Museum, Middelburg. Next a SCINTREX-GIS5 hand-held detector was employed. This

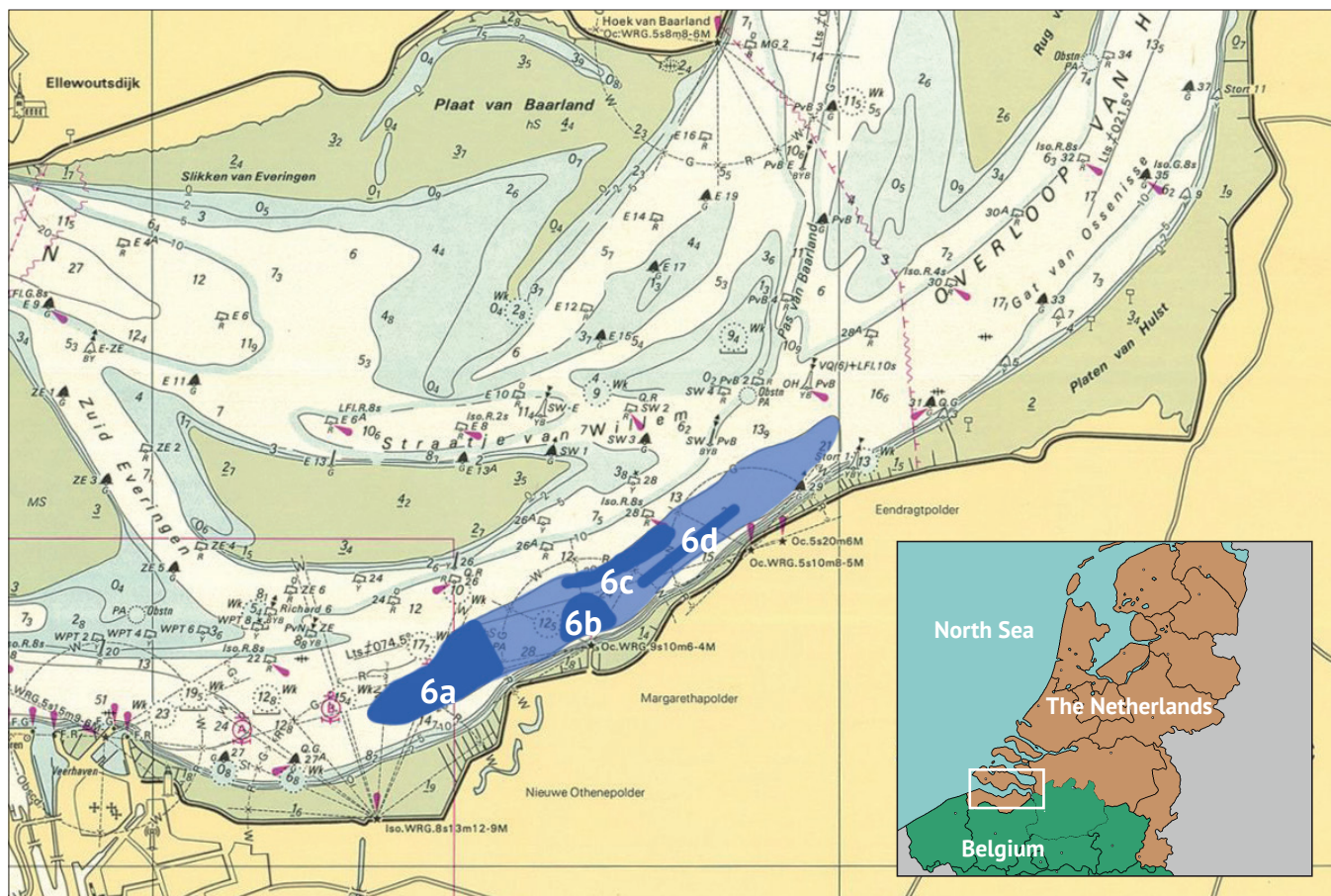


Figure 1 Detailed map of the Westerschelde with the sample locations (6a-d) of fossil bones used in this study.

detector consists of a 2.5 cm diameter and 2.5 cm long cylindrical NaI crystal mounted onto a photomultiplier tube (PMT). The crystal produces scintillation light in its interaction with  $\gamma$ -radiation, the amount of light is proportional to the energy deposited in the detector. The light is converted into an energy spectrum and the detector comes with four pre-set regions of interest: total count rate (TC) and three 'gates' related to the specific energies emitted by the natural radionuclides  $^{40}\text{K}$ , and the nuclides from the decay series of  $^{235}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$ . In the present work the detector was used for scanning the fossil samples by measuring the TC for 30 or 100 seconds depending on the count rate of the fossil bone relative to background. The detector is equipped with a read out and the counts (hereafter noted as cps = counts per second) have to be noted manually. In addition it has an option of alarm, allowing to search for radioactive substances.

Since part of the count rate originates from the surrounding terrestrial radiation sources and the cosmic rays, the samples were taken to a low-background location at the attic of de Weehorst at Peize, The Netherlands. Here background was measured for five periods of 100 seconds. The samples were measured twice for 100 or 30 seconds, depending on their activity for two geometries facing the fossil. The measurements were conducted for wet samples, shortly after rinsing them with tap water and a month later when the bones were dried to air as part of the measurements described below.

Initially five fossil vertebrae (#1-5, see Appendix 1) were selected for a detailed, non-destructive measurement on the low-background set-up at KVI-CART. In the low-background set-up with a 10 cm lead shielding, the fossil sample was placed on top of a 6 cm diameter 8 cm long Hyper Pure Germanium crystal (HPGe). This crystal, housed in a vacuum container and kept at liquid nitrogen temperature, is a diode in which the radiation releases electron-hole pairs, which are collected on the electrodes of the detector, causing an electric pulse that is shaped, amplified, digitised and stored in energy spectrum. Due to the good resolution of the detector the full energies of the detected  $\gamma$ -rays form a spectrum (see Fig. 2) that shows a set of very narrow and isolated peaks from which the energy and

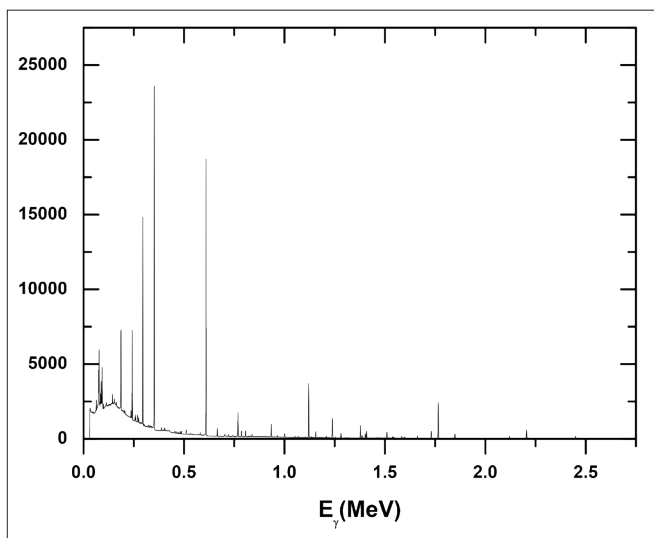


Figure 2 Gamma-ray spectrum of sample 5 measured at the HPGe detector of KVI/CART, University of Groningen, The Netherlands.

intensity of the radiation can be deduced.

The natural radionuclides expected to be present in the samples are  $^{40}\text{K}$ , and members of the decay series of  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{235}\text{U}$ . The activity concentrations of the members of the  $^{238}\text{U}$  decay series are determined from the intensity of the  $\gamma$ -rays in the decay of  $^{214}\text{Bi}$  and  $^{214}\text{Pb}$ . For the activity concentrations in the  $^{235}\text{U}$  series the  $\gamma$ -rays at  $E_{\gamma}=144, 163, 205$  (decay of  $^{235}\text{U}$ ) and 236 (decay of  $^{227}\text{Th}$ ) keV. For the activity concentration of  $^{232}\text{Th}$  several  $\gamma$ -rays of decay products are used. In all these three decay series a so-called secular equilibrium is assumed which implies a situation in which for all radionuclides the production and the loss of activity is equal. Under this condition the activity concentrations of all members of the decay series are the same. The  $\gamma$ -ray at  $E_{\gamma}=1461$  keV is used to determine the activity concentration of  $^{40}\text{K}$ .

An additional set of fossil bones (#6 to 24, see Appendix 1) was measured in this way by the SCINTREX to select extra samples for further (partly destructive) analysis. Moreover bones #1-5 and bones #20-24 were also measured with the Gamma Scout at the low background attic of de Weehorst, Peize, The Netherlands to allow for a comparison between the various measuring techniques and their related quantities.

For precise activity measurements, samples have to be homogenised and placed in a well-defined geometry and kept for about 20 days in a sealed environment to allow the nuclei of the  $^{238}\text{U}$  decay series to be in secular equilibrium. As at this stage we were mainly interested in approximate values, except for sample #13, samples were not destroyed to fit the standard geometry, nor were they stored for 20 days to establish equilibrium. The standard geometry for which the efficiency is calibrated consists of a 100 mL cylindrical pillar box and assumes a density of 1.2 kg/L. The size of the bones exceeds this geometry largely. The analysis assumes that the detector only measures the radiation emitted in the 100 mL volume. In reality also radiation emitted outside that volume is detected and hence the reported activity concentrations overestimate the activity concentrations. The concentrations derived from this analysis are therefore only indicative and likely overestimate the actual values by a factor 1.5 based on the results of the measurements for sample #13 (described below).

After measuring all samples in a non-destructive way, sample #13 was destroyed by breaking it into pieces to fit into a 100 mL cylindrical pillar box for which the HPGe detector efficiency is calibrated. Moreover the sample in the pillar box was firstly measured without a lid and subsequently with a sealed lid. In the latter case the pillar box was stored for 20 days to ensure secular equilibrium in the  $^{238}\text{U}$  decay series.

### Basic data

Appendix 1 presents the basic data of all relevant fossils, and their masses. The samples are stored in the collection of the Natural History Museum Rotterdam (NMR).

## RESULTS

As indicated above, the measurements are not taken in a calibrated geometry and hence should be regarded as indicative. In view of this restriction not all samples have been measured with all three techniques. To allow a comparison between the results of the various measuring techniques the dose rate in  $\mu\text{Sv/h}$  measured by the Gamma Scout, the readings of the Scintrex in cps/kg and the activity concentrations in Bq/kg measured with the HPGe are listed in Table 1. [Note: The activity concentration is expressed as Bq/kg, where Bq stands for Becquerel and corresponds to the number of decaying nuclei per second. The relation between the mass of a radionuclide and its activity is given in Appendix 2]. All values are corrected for environmental background.

In Table 1 the numbers in parentheses reflect the standard deviations. In the last column the ratio of the  $^{235}\text{U}/^{238}\text{U}$  activity concentration is presented. The results indicate that the mass corrected count rates for the mysticete bones are orders of magnitude higher than for the mammoth bones. For that reason

we concentrate for the activity concentrations on the mysticete bones.

The results indicate that U is the dominant radionuclide in these fossil mysticete bones and that Th is hardly present. The concentration of K is low. It should be kept in mind that these uncertainties only reflect the counting statistics. These uncertainties are much smaller than the systematic uncertainties due to the non-standard source detector geometry for all three instruments. Moreover the samples have not been measured in a condition in which the nuclei in the  $^{238}\text{U}$ -series may be considered to be in secular equilibrium. In the measurements of sample 13a in a pillar box, the concentration of  $^{238}\text{U}$  is about 3% higher than before sealing. This result indicates that the distortion of secular equilibrium is relatively small for this crushed sample.

The comparison between the activity concentration of samples #13 and #13a shows that for  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{40}\text{K}$ , the ratio of the derived activity concentrations is 1.451(0.018), 1.12(0.08) and 1.33(0.24), respectively. This gives an indication for the overestimate of the activity concentrations listed in Table 1.

Table 1 Dose rates, count rates, activity concentrations and  $^{235}\text{U}/^{238}\text{U}$  concentration ratios for selected samples from the Westerschelde. ND indicates a non-detectable concentration.

sample	dose rate ( $\mu\text{Sv/h}$ )	count rate (cps/kg)	$^{238}\text{U}$ (Bq/kg)	$^{235}\text{U}$ (Bq/kg)	$^{40}\text{K}$ (Bq/kg)	$^{232}\text{Th}$ (Bq/kg)	$^{235}\text{U}/^{238}\text{U}$
1	0.04(0.04)	19.3(0.3)	1590(14)	51(10)	129(7)	ND	0.032(0.006)
2	0.06(0.04)	26.8(0.3)	3230(30)	133(11)	332(11)	37.6(1.2)	0.041(0.006)
3	0.27(0.06)	165.0(1.2)	14940(130)	720(40)	168(18)	ND	0.048(0.003)
4	0.39(0.07)	137.2(0.8)	15880(140)	580(30)	102(18)	ND	0.037(0.002)
5	0.49(0.14)	143.4(0.8)	17470(150)	640(40)	160(20)	ND	0.037(0.002)
6		5.94(0.13)					
7		24.6(0.3)					
8		103.3(1.1)					
9		46.0(0.4)					
10		162.4(0.9)					
11		86.6(0.9)					
12		4.7(0.3)					
13		271(6)	8680(80)	440(20)	93(13)	ND	0.051(0.003)
13a*			5980(50)	396(16)	70(8)	ND	0.066(0.003)
14		14.6(0.7)	1161(10)	34(6)	89(6)	9.5(1.2)	0.029(0.005)
15		141.9(2.0)					
16		107(2)					
17		185.4(1.8)					
18		53.4(0.6)					
19		0.10(0.12)					
20	0.01(0.04)	0.1(0.2)					
21	0.01(0.05)	1.3(0.5)					
22	0.02(0.05)	0.28(0.14)					
23	0.03(0.05)	2.84(0.19)					
24	0.00(0.05)	9.1(0.4)					

\* Measured in the pillar box geometry after 20 days of sealing.

As a consequence the activity ratio  $^{235}\text{U}/^{238}\text{U}$  is underestimated by a factor of about 0.77.

Natural uranium contains 0.7% of the isotope  $^{235}\text{U}$ , the remaining part being  $^{238}\text{U}$ . Due to the difference in half-life time the activity ratio is 0.046 (see Appendix 2). The numbers in the last column indicate that we are dealing with natural uranium in the fossils and not with enriched (up to 5%  $^{235}\text{U}$ ) uranium as used in the nuclear power plants of Borssele (the Netherlands) or Doel (Belgium). The result for sample 13a suggests that the slight difference from the expected value is not likely to be caused by the escape of the gaseous decay product  $^{222}\text{Rn}$  (radon) from the fossils. It may indicate a mass effect in the exchange process between minerals in the bone and U, increasing the observed  $^{235}\text{U}/^{238}\text{U}$  ratio by about 20 to 50%.

Another possibility is that the  $^{238}\text{U}$  concentration is underestimated by the breaking of the secular equilibrium condition by the solution of  $^{226}\text{Ra}$ . This will be one of the topics in a follow-up study.

Figure 3 shows the surface readings of the Gamma Scout in  $\mu\text{Sv/h}$  and the Scintrex in cps. From the figure one may conclude that the correspondence between the two measurements is excellent within the statistical uncertainties introduced by the large variations in the readings of the Gamma Scout. The uncertainties in the values obtained with the Scintrex are within the size of the squares. The solid line represents a best linear fit to the data. The results indicate the much larger sensitivity of the Scintrex, which is especially useful in the domain of net low dose rates ( $< 0.1 \mu\text{Sv/h}$ ); above  $0.2 \mu\text{Sv/h}$  the Gamma Scout has enough discriminative power for indicative measurements.

Figure 4 presents the correlation between the count rates per kg measured for wet and dry bones with the Scintrex and the  $^{238}\text{U}$  concentration measured with the HPGc detector. The statistical uncertainties are mostly smaller than the size of the marks. The lines are meant to guide the eye. It must be noticed that there is not a perfect agreement, which ideally one would have expected. The deviations are indicative for systematic errors and uncertainties for example introduced by the non-standard geometries and the fact that the U may not be homogeneously distributed over the sample. In particular we like to point out to sample 13, producing an outlier in the graph most likely related to its small size and mass.

The difference between the blue and black curve indicates the effect of drying the bones. On the one hand drying causes the mass to decrease and reduces the absorption of radiation by water. This leads to a larger amount of radiation reaching the detectors. Another effect of water is that it reduces the radon emanation. The results of figure 4 indicate that during field measurements and in wet samples the net count rates are about 25% lower than when measured for dried bones.

As indicated in the previous section, sample #13 was broken up and placed in a 100 mL pillar box, sealed and measured after 20 days. The sample mass is 55 g. The deduced activity concentrations increase during the 20 day period by about 3 to 4% as is shown for the 609 keV  $\gamma$ -ray of the  $^{238}\text{U}$ -series in Figure 5.

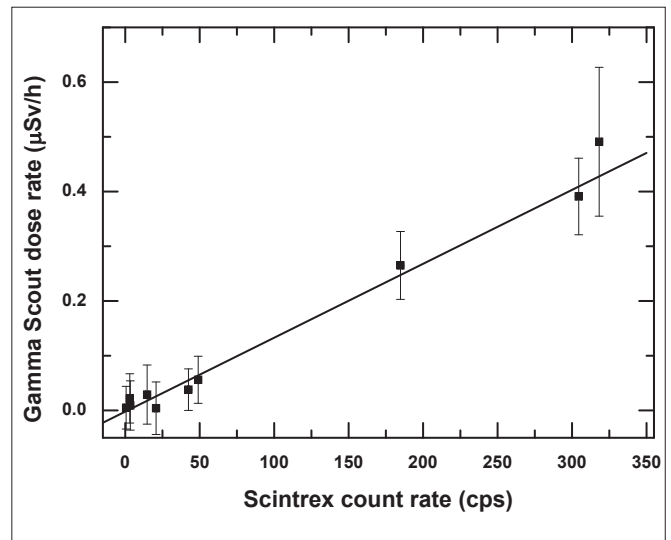


Figure 3 The relation by the dose rate measured by the Gamma Scout and the total count rate measured with the Scintrex.

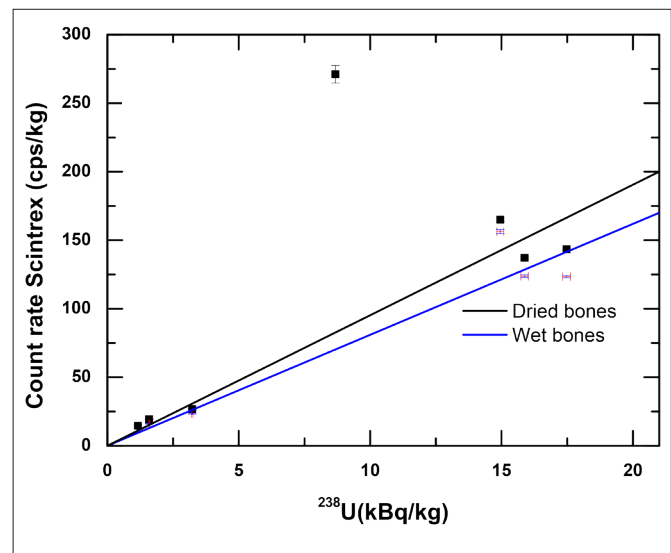


Figure 4 Count rate for wet and dry bones measured by Scintrex as function of the  $^{238}\text{U}$  concentration, measured with HPGc detector.

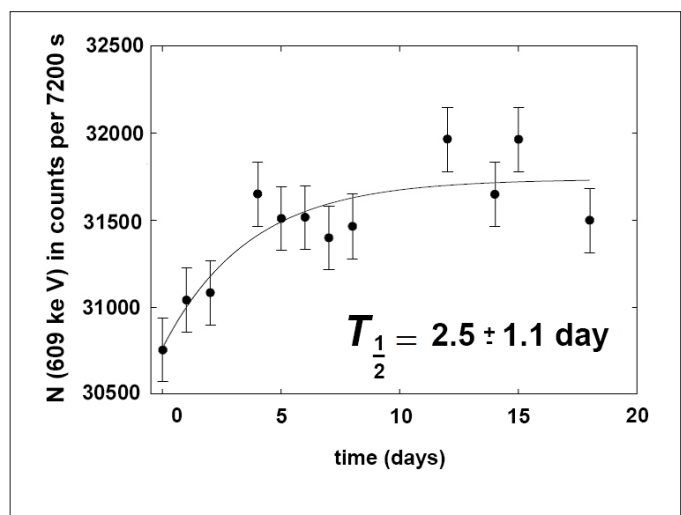


Figure 5 Count rate in the  $E_{\gamma}=609 \text{ keV}$  line of  $^{238}\text{U}$ -decay series as function of time since sealing sample #13a.

## ANALYSIS AND DISCUSSION

Conversion of the activity concentrations to mass percentages (see Appendix 2) yields that 1 ppm natural U, containing 0.993 mg/kg  $^{238}\text{U}$ , corresponds to 12.38 Bq/kg. This implies that the samples 3, 4, and 5 contain more than 1000 ppm or 0.1% U, considerably more than the phosphorite pebbles and two orders of magnitude more than the average concentration in the Earth's crust. In commercial mining such uranium concentrations are being considered as minable.

Considering bone minerals to be  $\text{Ca}_3(\text{PO}_4)_2$  implies that 1 Mole is about 310 g, containing  $3 \cdot N_A$  atoms of Ca ( $N_A$  being Avogadro's number). Per kg we have about  $10 \cdot N_A$  atoms Ca. At a concentration of 0.238% the bone contains 2.38 g  $^{238}\text{U}$ , corresponding to  $0.01 \cdot N_A$ . From this estimate one may conclude that one in thousand atoms Ca has been replaced by a  $^{238}\text{U}$  atom. As a metal, uranium has a silvery grey colour, but after oxidation it becomes a black and shiny substance. In nature, uranium(VI) forms highly soluble carbonate complexes at alkaline pH. This leads to an increase in mobility and availability of uranium to groundwater and soil. Uranium(VI) also interacts with carbonate anions. Contrary to most carbonates, uranium carbonate is soluble in water and forms series of uranium complexes at alkaline pH levels. It is already known for almost a century (see e.g. Neuman *et al.* 1948) that in this way uranium in solution is in an ionic exchange process replacing calcium at the surface of the bone mineral. Sediments consisting of uranium bearing minerals (such as glauconite) and in an alkaline environment (such as sea shores) release uranium carbonates over time, which may lead to an accumulation of uranium in the embedded mammal bones. We propose this mechanism as the explanation of our observations.

Based on these properties of uranium, the data are consistent with a diagenetic uranification process after the mammals died and were incorporated in the sediment. From here on several possibilities can be imagined. One option is that the amount of incorporated uranium depends on the surface area of the bone and the time available for the exchange process. The uranification process seems to be most effective in whale bones and especially in isolated vertebra that were free of matrix. Bones of cetaceans are porous by nature, allowing for the storage of large volumes of fat and oil that facilitate buoyancy. More dense whale bones such as samples #1, 2, 14, 23 and 24 all contain lower concentrations of uranium. Another option is that mysticete bones were originally buried in coastal regions, and

were subsequently exposed to river water by the scouring river. This implies a change in pH-value and could have enhanced the uranification process.

The present work does not provide information to allow any conclusion on the uranification process. The data may help to e.g. decide which dating techniques may help to disentangle the possible processes.

Dating the sediments will be a likely method to identify the age of the bones. Or vice versa dating the bones by e.g. U-Pb, will determine the age of the sediments in which the mammals were buried and/or the uranification of the bones took place. A prerequisite, however, is that the system must be considered to be closed such that the condition of secular equilibrium is fulfilled. This may be questionable for  $^{238}\text{U}$ , but is likely true for  $^{235}\text{U}$ . Unfortunately, dating of fossil bones by U isotopes is not considered reliable because the condition of closed system is hardly ever met, in particular for bones with 'minable' U contents (e.g. Van der Plicht *et al.* 1989). Dating the material is however beyond the scope of this paper.

## RADIOLOGICAL ASPECTS

The obvious radiometric levels of (some of) the vertebrate fossils of the Westerschelde (and in the general sense of any fossil containing radioactive elements) inflicts the intake and storage into public and private collections. Two main concerns have to be addressed: possible health risks and storage of uranium containing sediments.

### Possible risks for museum staff and public

Dutch regulations, known as 'Besluit Stralingsbescherming' (BS; Dutch Ministry of Economic Affairs 2013a), allow effective yearly doses of 1 mSv for visitors and museum staff exposed to radioactive objects (BS, articles 49 and 76). Working conditions over and above this dose (up to 6 mSv/year, and up to 20 mSv/year) enforce special measurements and are basically drawn for industrial purposes and standards (BS, articles 77 and 79). Given these maximum levels, it is obvious that even more active Westerschelde fossils will have no harmful impact on public (and staff) admiring and passing isolated and single objects in an exhibition.

For a curator or a museum collaborator the average working year counts maximal 2000 hours. Although curators spent usually minor parts of these hours in the storage rooms where the Westerschelde fossils are being kept, these rooms must be

Table 2 Dose rates ( $\mu\text{Sv}/\text{h}$ ) at two locations in three museums in the Netherlands.

museum and location	museum entrance (public and staff)	collection depot (curator desk)
NMR, Rotterdam	0.15	0.12
Zeeuws Museum, Middelburg	0.14	0.12
Naturalis (Raamsteeg), Leiden	no public entrance	0.14

considered as potentially critical areas. Gamma checks (24 hour average) were taken at the locations of working desks in the storage rooms and at working desks at the entrance of Naturalis Biodiversity Center, the Natural History Museum Rotterdam and the Zeeuws Museum (Table 2). The results confirm that working in the collection rooms does not result in higher exposure to ionised radiation compared to working in the normal offices. Taking into account that the background radiation to which every person in the Netherlands is exposed being about 2.4 mSv/a ([www.rijksoverheid.nl](http://www.rijksoverheid.nl)), and that the average 10 hour air flight counts for an exposure of c. 0.05 mSv ([www.rijksoverheid.nl](http://www.rijksoverheid.nl)), it becomes obvious that the safe working environment in the collection rooms of the said institutes and their offices is ensured (0.3 mSv/a).

### Storage of uranium containing sediments

Dutch laws prescribe that stocks of > 1000 Bq of radioactive objects must be reported to the relevant authorities (Dutch Ministry of Economic Affairs 2013b) and may require a permit. (The human body, which contains about 5000 Bq of naturally occurring radioactivity, is excluded from this regulation.) Given the uranium contents of some vertebrae, this implies that any Dutch museum holding Westerschelde collections must report (some elements of) their collections to the authorities. Both the Natural History Museum Rotterdam and the Zeeuws Museum have reported their collections to the relevant authorities.

### CONCLUSIONS

Enhanced levels of radioactivity in certain fossil whale bones in the Westerschelde are found to be predominantly caused by the uptake of uranium. The isotopic ratio of  $^{235}\text{U}/^{238}\text{U}$  is typical for natural uranium and is distinctly different from the uranium composition in fuel rods of nuclear power plants. Hence the often suggested relation to releases from nuclear power plants at either Borssele (the Netherlands) or Doel (Belgium) is not supported by our findings. The results of the measurements are only indicative since most of the samples were measured in a non-destructive way, meaning that they were in a geometry and condition for which the instruments were not calibrated.

For the understanding of the uranium of the fossil whale bones we follow the explanation in e.g. Ivanovich & Harmon (1982). In that explanation, the uranium takes place after the animal has died and decayed such that natural uranium ions in seawater exchange with calcium ions in the bone minerals. It is to be expected that  $^{232}\text{Th}$  is below the detection limit for most bones and the  $^{40}\text{K}$  content is rather low, due to the low solubility of Th (see e.g. Van der Wijk 1987).

In the high-activity bones ( $A > 10$  kBq/kg) the uranium ions have replaced about 1:1000 calcium ions. The measurement of a sample broken up to fit into a well-defined geometry and sealed for more than 20 days to ensure secular equilibrium to be restored for radon emanation, indicates that only a small (3-4%) distortion of secular equilibrium occurs. Also, the non-standard shape of the bones overestimates the activity concentrations by up to a factor of five, but slightly affects the ratios of the radionuclide concentrations. For an exploratory study as the present one bones will not be destroyed and hence only indic-

ative values are a consequence. If accurate concentrations are required the bones have to be ground and placed in a standard geometry and effective densities have to be used.

Details of the uraniumification process (time, speed and pH-condition) are insufficiently present in our exploring investigation, hampering an explanation of the observations. It is noted that the high uranium concentrations occur in porous bones, which have - in dry form - a dark greyish colour. It is also noted that the naturally porous vertebrae of whales (and especially of young whales) seem the most affected by the uraniumification process. More dense bones occurring in the same strata like other parts of the whale skeleton (cranial parts, atlas), or geologically much younger bones from terrestrial Pleistocene mammals are lower in total count rate and may show different colour patterns.

The increased radiation levels of some of the isolated marine mammal fossils from the Westerschelde Estuary do not cause health hazards to public and museum staff, but necessitate the collections to be reported to the authorities following the valid Dutch legislation.

### ACKNOWLEDGEMENTS

Access to collections of museums was of vital importance to our research and the kind and efficient cooperation and support of Marjan Ruiter and Mark Bosselaers (Zeeuws Museum), Henry van der Es (Natural History Museum Rotterdam) and Natasja den Ouden (Naturalis) is duly noted. Arike Gill (Naturalis) shared information on procedures on radioactive objects in their collections, Olivier Lambert (Royal Belgian Institute of Natural Sciences) helped with cetacean literature, and Peter de Jong (Nuclear Research and consultancy Group (NRG)) assisted with the legal aspects on storage and handling of radioactive objects. They all deserve our sincere thanks. The suggestions and critical review of the manuscript by Hans van der Plicht (University of Groningen) are highly appreciated.

### REFERENCES

- Dutch Ministry of Economic Affairs, 2013a - Besluit Stralingsbescherming, <https://www.autoriteitnvs.nl/onderwerpen/besluit-stralingsbescherming>
- Dutch Ministry of Economic Affairs, 2013b - Uitvoeringsbesluit Stralingsbescherming EZ, <https://www.autoriteitnvs.nl/onderwerpen/stralingstoepassingen-in-nederland>
- Harsveldt, H. M., 1973 - The discovery of Uranium at Haamstede (Netherlands) - *Verhandelingen Koninklijk Nederlands Geologisch Mijnbouwkundig Genootschap* 29: 63-72
- Ivanovich, M. & Harmon, R.S., 1982 - Uranium Series Disequilibrium: *Applications to Environmental Problems* - Clarendon Press, pp 571
- Neuman, W.F., Neuman, M.W., Main, E.R. & Mulryan, B.J., 1948 - The deposition of Uranium in bone, V ion exchange studies. *Journal of Biological Chemistry* 179: 335-340
- Paridaens, J. & Vanmarcke, H., 2001 - Inventarisatie en karakterisatie van verhoogde concentraties aan natuurlijke radionucliden van industriële oorsprong in Vlaanderen - MIRA, MIRA/2001/01, SCK
- Plicht, J. van der, Wijk, A. van der & Bartstra G.J., 1989 - Uranium and thorium in fossil bones: activity ratios and dating.

- Applied Geochemistry* 4: 339-342
- Post, K. & Reumer, J.W.F., 2016 - History and future of paleontological surveys in the Westerschelde Estuary (Province of Zeeland, the Netherlands). *Deinsea* 16: 1-9
- Rijks Geologische Dienst, 1971 - *Tweede rapport betreffende de stand van het onderzoek en de evaluatie van de uraanvondsten te Haamstede op het eiland Schouwen uitgebracht aan de Minister van Economische Zaken door de directeur van de Rijks Geologische Dienst*: 1-7
- Slupik, A.A. & Janse, A.C., 2008 - The geological record of the Breda Formation in the subsurface of the island of Noord-Beveland (Province of Zeeland, The Netherlands) from the Colijnsplaat borehole (42G24-1): A sequence-stratigraphic approach. *Deinsea* 12: 37-52
- Slupik, A.A., Wesselingh, F.P., Janse, A.C. & Reumer, J.W.F., 2007 - The stratigraphy of the Neogene-Quaternary succession in the southwest Netherlands from the Schelphoek borehole (42G4-11/42G0022) - a sequence-stratigraphic approach. *Netherlands Journal of Geosciences, Geologie en Mijnbouw* 86: 317-332
- Wijk, A. van der, 1987 - *Radiometric dating by alpha spectrometry on uranium series nuclides* - Ph.D. Thesis, University of Groningen

**Appendix 1** Sample number, mass, description, collection location and NMR catalogue number of fossil bones as collected in project Westerschelde 2014 (NMR trip 2014/3).

no	mass (g)	item	taxon	area	NMR cat. number
1	2200(2378)	Atlas	mysticete	6C	9991-0012052
2	1830(2037)	Axis	mysticete	6C	9991-0012048
3	1120(1436)	Vertebra (lumbar)	mysticete	6C	9991-0012046
4	2219(2659)	Vertebra (thoracic)	mysticete	6C	9991-0012045
5	2296(2852)	Vertebra (lumbar)	mysticete	6C	9991-0012047
6	10900	Vertebra (lumbar in sediment)	mysticete	6D	9991-0012050
7	8030	Vertebra (caudal in sediment)	mysticete	6D	
8	195	Squamosum (cranium)	mysticete	6C	9991-0012051
9	5450	Vertebra (thoracic)	mysticete	6C	9991-0012049
10	1050	Atlas	mysticete	6C	9991-0012043
11	2400	Vertebra (caudal)	mysticete	6C	9991-0012044
12	3645	Basisoccipitale (cranium)	mysticete	6C	9991-0012036
13	362	Vertebra (lumbar) on iron	mysticete	6C	destroyed
14	1644	Squamosum (cranium) on iron	mysticete	6C	
15	875	Vertebra (lumbar)	mysticete	6C	9991-0012038
16	610	Vertebra (caudal)	mysticete	6C	9991-0012037
17	2635	Vertebra (lumbar)	mysticete	6C	
18	3320	Vertebra (thoracic)	mysticete	6C	9991-0012035
19	1986	Molar	woolly mammoth	6C	9991-0012039
20	4600	Sacrum (fragment)	woolly mammoth	6C	
21	2700	Tibia (fragment)	woolly mammoth	6C	9991-0012040
22	10887	Humerus (fragment)	woolly mammoth	6C	
23	5000	Rostrum	beaked whale	6C	
24	2300	Cranium	pontoporiid	6D	9991-0012018



**Appendix 2** Basic Radiometry

A basic starting point for radiometry is the definition of activity,  $A$ , and its relation to the number of radioactive nuclei,  $N$ , in a substance and the half-life time of these nuclei,  $t_{1/2}$ . The relation is given by:

$$A = \lambda N, \quad (\text{A2.1})$$

where  $\lambda$  is the decay constant related to the half-life time by:

$$\lambda = \ln 2 / t_{1/2}. \quad (\text{A2.2})$$

If the half-life time is expressed in seconds,  $A$ , is given in Becquerel (Bq) or ( $\text{s}^{-1}$ ).

Eq. (A2.1) leads also the relation between the activity concentrations of two radionuclides,  $C_1$  and  $C_2$ , and their mass ratio  $m_1/m_2$ :

$$\frac{C_1}{C_2} = \frac{A_1}{A_2} = \frac{\lambda_1 N_1}{\lambda_2 N_2} = \frac{t_{1/2}^2}{t_{1/2}^1} * \frac{m_1}{m_2}. \quad (\text{A2.3})$$



DEINSEA - the online open-access Journal of the Natural History Museum Rotterdam publishes contributions on zoology, paleontology and urban ecology  
 editor-in-chief Jelle W.F. Reumer | editors Bram W. Langeveld & Cornelis W. Moeliker  
 design TANK | layout Jaap van Leeuwen | content, back-issues & guidelines [www.deinsea.nl](http://www.deinsea.nl)  
 submissions [deinse@hetnatuurhistorisch.nl](mailto:deinse@hetnatuurhistorisch.nl)