Using Gamma-Ray Spectrometry and Scanning Electron Microscopy (SEM)) for assessment of Th/U ratio in soils developed on alkaline rocks: significance and implications*

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This study investigates the Th/U ratio in soils developed on alkaline rocks collected from the Ditrău alkaline massif area, Eastern Charpatians, Romania. The soil types found in the massif area are young, unevolved, being formed in situ on consolidated rocks: mafic and ultrabasic rocks, syenites, nepheline syenites and alkali granites, as well as more or less transformed varieties of these, directly reflecting the composition of the mineral substratum. Magmatic fractionation and hydrothermal alteration processes significantly influence the in-situ concentration of U and Th-bearing minerals in alkaline rocks, contributing to their relative radioactive enrichment.

Low background gamma-ray spectrometry with an n-type HPGe detector (relative efficiency of 27%, resolution of 1.80 at ^{60}Co 1.33 MeV, and peak/Compton ratio of 56:1) coupled to an ORTEC multi-channel analyzer has been used to measure the specific activity of ^{238}U and ^{232}Th in the soil samples. Scanning electron microscopy was employed to qualitatively assess the U, Th- bearing minerals in the soil mass in the <2 mm fraction of the samples. The oxidizing and reducing conditions defining the uranium and thorium mobility in the soil were estimated using the ^{238}U and ^{232}Th specific activities, with the assumption of secular equilibrium.

The average specific activity of ^{238}U is 36.8 Bq/kg, whereas the average specific activity of ^{232}Th is 58.8 Bq/kg. Significant fluctuations were found in the Th/U ratio values, ranging from 1.87 to 19.54. Mineralogical analysis revealed the dominance of Th-bearing heavy minerals such as: monazite-(Ce), chevkinite and thorite, besides xenotime-(Y), niobian rutile, zircon, titanite and gadolinite-(Y).

The unaltered mineral fraction from the bedrock influences soil Th/U ratio values, expressed in the interdependence between rock nature, Th/U ratio relative value, and soil weighted values. The accessory minerals concentrate the two elements, and the Th/U ratio oscillation indicates on the one hand the proportion of U and Th in these minerals, and on the other hand allows to estimate the abundance of these minerals in the rock mass, and respectively, in the soil mass. Among the accessory minerals, the Th/U ratio is very different: monazite contains more Th than U, while xenotime has more U. These variations in the U and Th contents of accessory minerals in late magmatic differentiates can be explained by oxidation at a later stage in the magma, and the lack of the normal Th/U ratio in accessory minerals of relatively early differentiates (apatite, zircon) influencing the selective incorporation of one element over another in the same mineral assemblage. The soil mobility of U and Th depends on physico-chemical parameters. U is easily oxidized in aqueous environments, while Th is insoluble in water, organic matter and sulfates. The redox conditions are illustrated by the Th/U ratio. Th/U values above 7 signify uranium removal in oxidizing conditions and redeposition under reducing settings, whereas values below 2 suggest an preferred concentration of uranium relative to thorium.

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Tritium- and 14C-labelled tracers in geospheric tracing operations – advantages and potential pitfalls

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The application of radioactive atoms and radiolabelled molecules to trace fluids in various streaming and mixing processes in industry and geosphere has over years shown to be a highly valuable technique. Two specific areas of application are the tracing of fluid flow in petroleum and geothermal reservoirs. The tracers are applied to follow injected gas or water in the reservoirs to monitor direction of flow, flow velocities, sweep efficiency and, for geothermal reservoirs, the effectiveness of heat extraction. So-called passive tracers (not degraded by environmental factors) are required.

A typical tracer campaign consists of injection of a pulse of, for instance, tritiated methane or tritiated water. The amount may vary, subject to the size of the actual reservoir, in the range 1-50 Ci (37 – 1850 GBq). For ^{14}C-labelled compounds the amount of activity is at least a factor of 10 lower. This tracer pulse may spend years in the reservoir before it appears in one of the production wells. During this process the tracer slug is considerably diluted. A dilution factor of more than 10^{10} may be experienced for large reservoirs. In well prepared tracer tests the activity injected is set to a minimum, though high enough to ensure detectable amounts in the production wells. During this time the tracer compounds are in contact both with reservoir water and, for petroleum reservoirs, oil and gas. One of the mechanisms which may contribute to loss of tracer is exchange of the radioactive label (^{3}H (T) or ^{14}C) with non-radioactive hydrogen and carbon isotopes in the reservoir fluids. This process is called isotope exchange and may be composed of several mechanisms.

Tracer compounds with sufficiently high chemical and thermal stability are the radiolabelled variations of fluids already existing in the reservoir, i.e. HTO for water and CH_3T or $^{14}CH_4$ for gas. Such tracers are called intrinsic radiotracers.

The aim of the present study has been limited to examine the potential for isotopic exchange, as a sink mechanism, for the gases tritiated and ^{14}C-labelled methane and ethane to water and oil in petroleum reservoirs. The highest exchange rate found is 3,2% of tritium from radiolabeled ethane to water at 150 °C after 6 months. All factors considered, this level of exchange is considered acceptable for the labelled compounds to be considered as passive tracers for gas injection in oil reservoirs.

The $^{233}U/^{236}U$ signature for emission source identification in environmental tracer studies

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Analysis of the atomic $^{233}U/^{236}U$ ratio in environmental reservoirs suggests that this signature allows to distinguish anthropogenic Uranium (U) emitted by civil nuclear industry from U deposited as nuclear weapons fallout [1]. In addition, U is known to be transported conservatively with the water masses over long distances in the marine environment, which would make the $^{233}U/^{236}U$ signature a superior oceanographic tracer. The $^{233}U/^{236}U$ ratio of $0.1 \cdot 10^{-2}$ detected in environmental archives was attributed to releases from nuclear power production while a ratio of up to $3.7 \cdot 10^{-2}$ could be assigned to nuclear weapons fallout in this initial work. Consequently, significant amounts of ^{233}U were only released by nuclear weapons; either produced by fast neutron capture on ^{235}U or directly by ^{233}U fuelled devices. However, the exact production and release pathways of ^{233}U still remain unclear which limits the application of this isotope signature as environmental tracer on a global scale. Sources of ^{233}U including a possible contribution from natural production on ^{232}Th have to be fully characterized first.

To be able to narrow down the time span of the maximum ^{233}U release, we studied the $^{233}U/^{236}U$ ratios in samples from different locations, partly time-resolved or of well-known age. Samples comprised e.g. air filters from 1961-1965 collected in Austria, i.e. the period of maximum deposition of global fallout, a lake (lake Hallstatt, Austria) and an ocean sediment core (Beppu Bay, Japan), a peat bog core (Pürgschachen Mire, Austria) and sediment from the layered urban artificial ground of Vienna (Austria). Whenever possible, the new $^{233}U/^{236}U$ data was directly compared to other isotopic signatures such as $^{240}Pu/^{239}Pu$ or ^{237}Np. The data generally support a ^{233}U deposition before the 1963 bomb peak and generally are in agreement with the ratios attributed to the emission sources mentioned above. However, the maximum $^{233}U/^{236}U$ ratio in the lake sediment was found to be a factor 20 higher than the ratio attributed to global fallout [1] even exceeding the maximum value of a Baltic Sea sediment core published previously [2]. These occasionally occurring high values point to a missing / still unkown source of ^{233}U, which calls for a systematic investigation of the ^{233}U inventory.

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Towards a sediment reference material database for the Danube River - from the Black Forest to the Black Sea

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The Danube is the second longest river in Europe. Its Delta is Europe's largest natural wetland, a very complex ecosystem with unique features. The third largest biodiversity in the world is an open school for today and tomorrow's biologists, geologists and many inter- and crossdisciplinary scientists. Information from the perspective of ecology is huge and opens the way to interpretations that help preservation, protection and natural evolution in a world where anthropogenic hazards unfortunately deteriorate essential parameters for equilibrium.

The use of natural radioisotopes and additionally neutron activated spectra is a corner stone for pattern recognition. As the background is dynamic since the very beginnings of nuclear physics, we have to adapt, no matter the provenience of changes. Detection and decision limits, standardized sample preparation&measurement protocols, U-Ra (Rn) equilibrium and uncertainty evaluation are crucial for the accuracy. Monte Carlo simulations are the key element to many corrections to be performed, but the physical processes, the relevance and precision of the parameters involved and the code algorithms must be treated with great care, in order not to turn against the purpose of the performance. From the Black Forest to the Black Sea, we need to have a clear reference for each spot, including - if possible - the history of elemental concentrations available at the time the analysis is carried out.

Albeit the enormous number of samples required for such a database and the variety of characteristics they exhibit, if we choose a simple and robust set of rules to systematize the analysis process, we can obtain an accurate, clear and meaningful database in terms of isotopic patterns (i), history (ii) and dynamics of pollutants (iii), the latter including particles uninvolved in radioactive processes, such as microplastics. The key element for the dynamics reconstruction is found within the isotopes used for dating procedures, as they help us track the concentrations in time, if the models are validated, following adaptation to specific conditions for each spot. Notably ^{210}Pb dating can help us tracking the pollutants from the industrial era, which are the most nocive ones for the ecosystems. There are many lessons to be learned from such a database, but it is urgent to start it right away, since the half-life of this radioisotope (22.3 y) allows us to have a decent uncertainty for a maximum interval of roughly 120 years; this means that if we start the effort in 10 years, the 1900-1910 period will be lost.

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Determination of ^{226}Ra in environmental samples from the analysis of the 186keV photopeak and the short-lived radon progeny in equilibrium

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One of the most important naturally occurring radionuclides to be determined in environmental samples is ^{226}Ra, mainly due to its progeny ^{222}Rn. In most cases, Radium-226 is determined through the short-lived ^{222}Rn progeny in equilibrium, a relatively straightforward and well-established procedure [1]. Another way to determine ^{226}Ra is through its 186.25keV γ-ray. In environmental samples, this photopeak overlaps with the 185.72keV photopeak of ^{235}U, producing a multiplet at ~186keV which can be difficult to deconvolute. However, very useful information can be provided by resolving the two overlapping peaks such as the activity of ^{226}Ra and ^{235}U, the existence of radioactive equilibrium as well as the isotopic abundance of Uranium in the sample.

For the analysis of ^{226}Ra and ^{235}U in environmental samples such as soil and NORM, both the direct and indirect methods are applied at NEL-NTUA for decades [1-3]. In this work, a further improvement of the method applied for the direct analysis is presented. The improved technique is based on proper calibration of the detector system together with the use of an algorithm for the resolution and quantification of the overlapping peaks at ~186keV (Fig. 1). The improved method has the advantage of being faster and providing results simultaneously from both the analysis of the multiplet at ~186keV and the γ-rays of short-lived radon progeny, thus giving the opportunity to evaluate the accuracy of the obtained results.

The analysis technique presented in this work has been applied to environmental samples with and without radioactive equilibrium among the U-series nuclides, as well as to a series of spectra experimentally constructed in the lab with the use of appropriate sources.

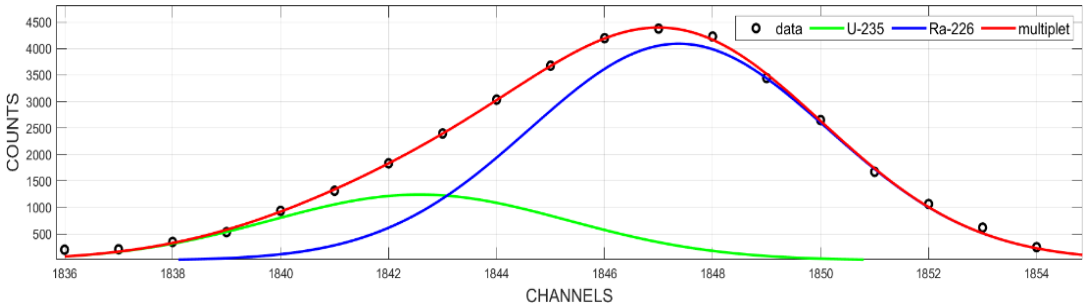

Figure 1- The multiplet at ~186 keV in a soil sample with disrupted radioactive equilibrium

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