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The impact of a uranium mining site on the stream sediments (Crucea mine, Romania)

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Abstract

XRF methods were used to evaluate the impact of uranium mine dumps on the stream sediments from Crucea region (Romania). In order to estimate the natural and anthropogenic inputs of radioactive and heavy metals in the sediments, normalization to Al was applied. The pollution degree of the bottom sediments show that U, Th and Pb reach medium and punctual high values, while the rest of the elements appears in concentrations close to the background or lower. The measurements carried out in the surroundings of a local uranium mine show that the impact of Crucea mine on water quality downstream of mining area is insignificant.

Keywords:

impact of mine wastes ; stream sediments ; uranium ; thorium

I. Introduction

Uranium and thorium are omnipresent in our human environment. Various anthropogenic activities involving the processing or use of uranium rich materials in may modify the natural abundance of uranium in stream sediments. These activities include various mining operations and the industrial processing for the manufacturing of nuclear fuel and of other products.

Between 1962 and 2004, the National Company of Uranium (former Romanian Autonomous Administration for Rare Metals), mined over 1,200,000 tones of pitchblende ore in the East Carpathians. Traditional mining methods rely on the relocation of large volumes of mineralized and waste rock. These intensive mining operations have created over 30 solid radioactive mining wastes in Crucea-Botusana area (Bistrita Mountains).

In this paper we present data from four main tributaries of Bistrita River (*i.e.* Crucea, Troaca Gavanului, Gavan and Cracul Rau creeks) and from two sampling points locating in the upper course of this main stream (one point located downstream and the other located upstream of the confluence with Crucea creek). The aim of this paper is to investigate the impact of mining activities on the stream sediments in the area.

II. The study area

II.1. Geography

The study concerns the uranium mineralization located within Crucea ore deposit, in the East Carpathians, Romania. The uranium ore deposit found in the eastern part of the Bistrita Mountains (40 km southeast of the town of Vatra Dornei) in the headwaters of Crucea, Lesu

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and Livezi valleys. At present, this is the largest uranium mine in the country. In the past, the mining area covered 18 km², but was gradually overtaken by logging activities. The area has a steep mountainous relief cut by narrow valleys. The surface streams are tributaries of Bistrita River.

II.2. Geological background

The host rocks belong to the Crystalline-Mesozoic zone of the northern part of the East Carpathians. The uranium mineralization is confined to a body of brecciated retrometamorphic micaschists, containing carbonates and clay minerals. The richest uranium mineralization is associated with four NW-SE faults with E or W strike. Most mineralized areas occur along fractures, thus denoting a significant structural control over the emplacement of the ore-bodies. Uranium ore bodies form darkgrey lenses or veinlets with thicknesses ranging from decimetres to meters. Primary mineralization consists of pitchblende U₃O₈ included in bitumen.

The intimate association between pitchblende and bitumen is characteristic to this uranium ore deposit. The sulphide content is lower than 10% and consists of pyrite, marcasite, chalcopyrite, and minor galena, sphalerite, arsenopyrite and tetrahedrite in a carbonate gangue. The mineralization is considered to be of hydrothermal origin (Petrescu, 2004).

The geochemical background of uranium in the surrounding area is lower than 3-mg.g⁻¹, whereas in the mining area, it reaches 5.39-mg.g⁻¹ in the waste rocks (rocks with sub-economic mineralization) and 7.26-mg.g⁻¹ in soils (Petrescu and Bilal, 2007).

The exploration and mining works include thirtytwo adits, situated between 780 and 1040 m above sea level. Radioactive waste resulted from mining are disposed next to the mining facilities (Petrescu and Bilal, 2007). The waste rock was disposed in piles of variable sizes that are spread over an area of 364,000 m². The average geochemical content of the waste rocks is similar to that of the ore. The average particle size of the waste material is large (>5 cm). Older dumps (18) have been already naturally reclaimed by forest vegetation, which played an important role in stabilizing the waste dump cover and in slowing down the uranium migration processes.

III. Material and methods

The sediment samples were collected at seventeen sampling points (*e.g.* 1, 3, 6, 11, 16, 19, 23, 25, 27, 29, 32, 33, 35, 41, 43 and 45) (Figure 1) from the bottom of the stream waters. To ensure the representativity of samples, bulk sediments were obtained by mixture of several cores collected. The pool of sediments were collected by manual coring (0–5-cm) from the moist shore and stored in glass jars. They were dried in an oven at 50°C for 48 hr, ground using an agate grinder to pass a 100-µm sieve and analyzed for the following:

III.1. Total elemental concentration

The total metal concentrations of bottom sediments were determined using a SRS3400 Bruker AXS wavelength dispersive X-Ray fluorescence spectrometer (WD-XRF). Thus, 1.3-gram of calcinated powder was added to 1.3-g of oxides (lithium nitrate) and 6.5-g of flux (lithium tetraborate 20%, lithium metaborate 80 %) and then mixed in a crucible that is placed in an automated fusion-fluxing device. The fusion is performed at 1100°C. The cooling is forced to avoid crystallization, and then fused beads with a vitreous, homogeneous structure and flat surface were obtained. The detection limits, in mg.g⁻¹, were: 4 for U, 5 for Th, 5 for Pb and 10 for V.

III.2. Statistical data analysis

The reliability of the chemical analyses was calculated from the four duplicate samples with the analysis of variance. The F-ratio, which is a measure of the ratio of total data variance to error variance (sample inhomogeneity, analytical error) and which has to be > 4 to be significantly high at the 99% level of confidence, was >1000 for Ca, Cr, Cu, Mn, Pb, V, Na and Zn, >100 for U, Th, Sr, Al, Co, Fe, K, P and Mg and 54 and 32 for Si and Ni respectively.

Hence, any pattern or absence of pattern of any of these elements in the data set is not due to analytical or sampling error.

Single correlation analysis was performed to assess relationship among heavy elements concentration. Linear correlation coefficients (r) were calculated between the different samples parameters. For each correlation, statistical significance (p -value) was determined. Traditionally, results that yield p -value < 0.05 are considered borderline statistically significant, *i.e.* the probability of concluding that two variable are different when they are actually the same is $\leq 5\%$.

The STATISTICA 7.1 for Windows (StatSoft®) program was used for the statistical analyses mentioned above.

IV. Results and discussion

Table 1 shows levels of heavy metals, aluminium oxides and total organic matter (lost on ignition =LOI) found in bottom sediments sampled at the sixteen stations. In all the areas, similar variations in the concentrations of uranium and thorium in sediment samples were observed. The bottom sediment samples collected from mining area show a wide range of total uranium content from 17.20 to 5023.96-mg.g⁻¹ with a mean value of 246.81-mg.g⁻¹ (dry wt.) (Figure 2). Total thorium concentration in sediments collected from Crucea site ranged from 18.70 to 6643.92-mg.g⁻¹ with an average of 391.17-mg.g⁻¹ (dry wt.) (Figure 2). This indicates that the adsorption of the radioactive elements by the sediments is high and variable, influenced by the ore dump - sample relationship. There is a decrease in the concentrations of U and Th in the stream sediments downstream from the Crucea uranium ore (Figure 2).

The fate and transport of uranium is governed by its oxidation state, which is either hexavalent (U(VI)) or tetravalent (U(IV)). When mine wastes containing low-grade uranium mineralization are exposed to surface waters containing carbonate ions, the pitchblende is altered, uranium (IV) oxidizing to uranyl carbonates, without producing any megascopically observable changes. This can be illustrated by the following equation:



A previous study performed in this area (Petrescu and Bilal, 2006) showed that in the pH range of waters from Crucea area, more than 85% of the uranium was present as the carbonate complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2\text{CO}_3(\text{OH})^{3-}$, UO_2CO_3 and $\text{UO}_2(\text{CO}_3)_3^{4-}$ and 17% as the hydroxide complexes $\text{UO}_2(\text{OH})_2$. The anionic carbonate complexes are extremely important because they increase uranium mobility by limiting the extent of uranium adsorption in oxidized waters and by increasing the solubility of uranium minerals (Langmuir, 1997).

Strong correlation of uranium with thorium in the sediments ($r=1$; $n=17$; $p<0.0001$) suggests that unspecific co-precipitation dominates over selective adsorption according to valence and ion sizing.

The lack of correlation between uranium and vanadium in sediments samples ($r=0.16$; $n=17$; $p<0.0001$) is related to ore type. In the Crucea uranium mineralization the vanadium concentration range between 60.7 - 335.9-mg.g⁻¹ and we can state that the surrounding rocks are the source of this element. This affirmation confirms the absence of the uranium minerals with vanadium (such as carnotite). Through the weathering of the rocks, vanadium migrates as vanadic acid and in supergene conditions this metal easily concentrates in clay minerals and oxy-hydroxides.

In order to estimate the natural and anthropogenic inputs of actinides and heavy metals into sediments, their total concentrations were correlated with Al concentration. Since Al originated from the natural background it was chosen as the normalizing factor. These data are presented in Table 2. It can be seen that only vanadium shown a linear relationship with the concentration of Al, fact indicates his natural background origin. For the rest of selected elements their origin was anthropogenic. This indicates the impact of mining waste disposal on the environment.

The total concentrations shown in Table 1 have been used for the determination of the degree of pollution with radioactive and heavy metals. At this time, no regulations exist for levels of heavy metals in sediments; however several sets of sediment quality criteria have been reported. Thus, the pollution degree of the sediments was classified using the geo-accumulation index (I_{geo}), which is applied for separate element characteristic in the examined sediments and determines the contribution of each element to overall sediment contamination. I_{geo} was calculated as follows:

$$I_{geo} = \log_2[C_n / (1.5B_n)] \quad (\text{Pinto } et al., 2004),$$

were: C_n = total element concentration ($\text{mg}\cdot\text{g}^{-1}$); B_n = background concentration for each element ($\text{mg}\cdot\text{g}^{-1}$). Therefore, based on the concentration levels of these metals, the stream sediments are categorized into seven classes, with the "0" class corresponding to the values close to the geochemical background. The background concentrations were taken from Petrescu and Bilal (2007) (Table 3).

The pollution degree of the bottom sediments is shown in Table 4. The I_{geo} of U, Th and Pb presents medium and punctual high values that represent sediments belonging to classes of strong to extreme pollution ($I_{geo} > 6$). A proportion of 47.05% of Th and U concentration values are categorized into the highest pollution class (I_{geo} class 6) (Figures 3 a and b), while the rest of the elements presents concentration close to the background values or lowers (Figure 3d). These high concentrations of U, Th and Pb are distributed preferentially in the proximities of 5, 8, 9 and 1bis mine dumps. Table 4 also shows that I_{geo} of U and Th from the sediments taken from downstream of the mineralized zone (P27 and P29) are lower than those taken from the mineralized areas. This indicates that uranium and thorium are not very mobile in the waters and that these elements are precipitated close to the mining dumps.

V. Conclusions

The knowledge concerning uranium and thorium concentration in stream sediments is essential for predicting natural actinide migration and for drafting strategies concerned with the rehabilitation of contaminated sites.

The pollution degree of the bottom sediments shows that U, Th and Pb are characterized by medium and punctual high values, while the rest of the elements are in concentration close to the background values or lower.

Although neither U nor Th have an appreciable "exchangeable" fraction, the isolation of specific U- and Th-rich sediment fractions helped to identify connections between bioavailability and genesis of sediments, which control the natural cycling of U and Th. However, if the geochemical conditions it happens to be changes, the surface sediments could act as a future source of actinides and heavy metals to the above water body.

The measurements carried out in the surroundings of a local uranium mine show that the impact of Crucea mine on sediment quality downstream of mining area is insignificant.

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Figures

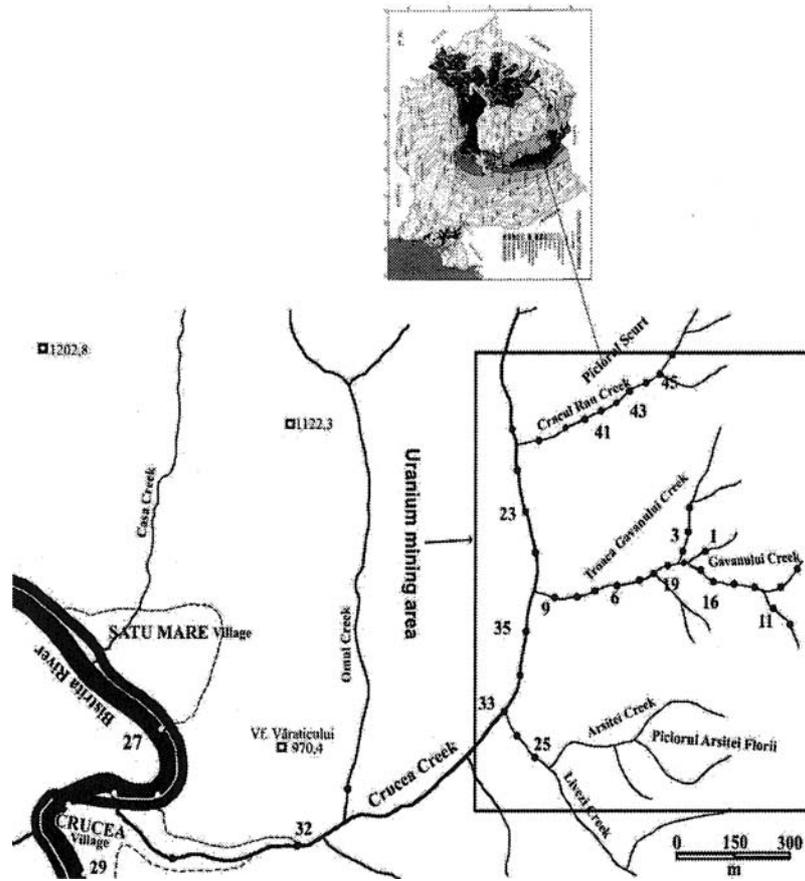


Figure 1: Topographic map of the investigated area with the distribution of sampling points.

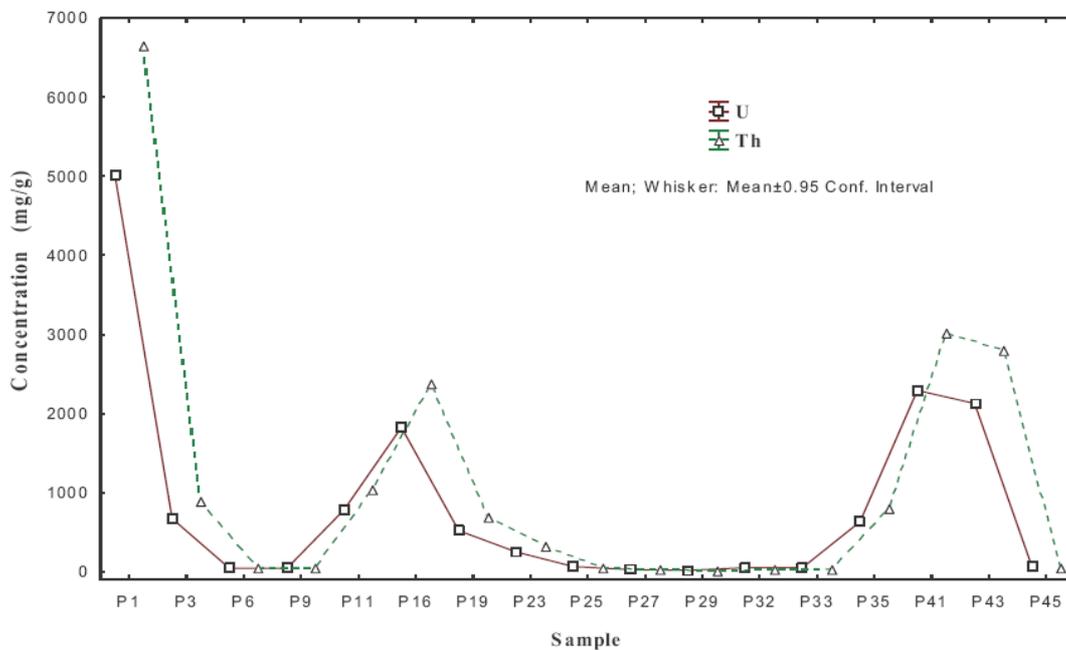


Figure 2: Variations in actinide concentrations in bottom sediments along Crucea zone. For location of sampling sites see Figure 1.

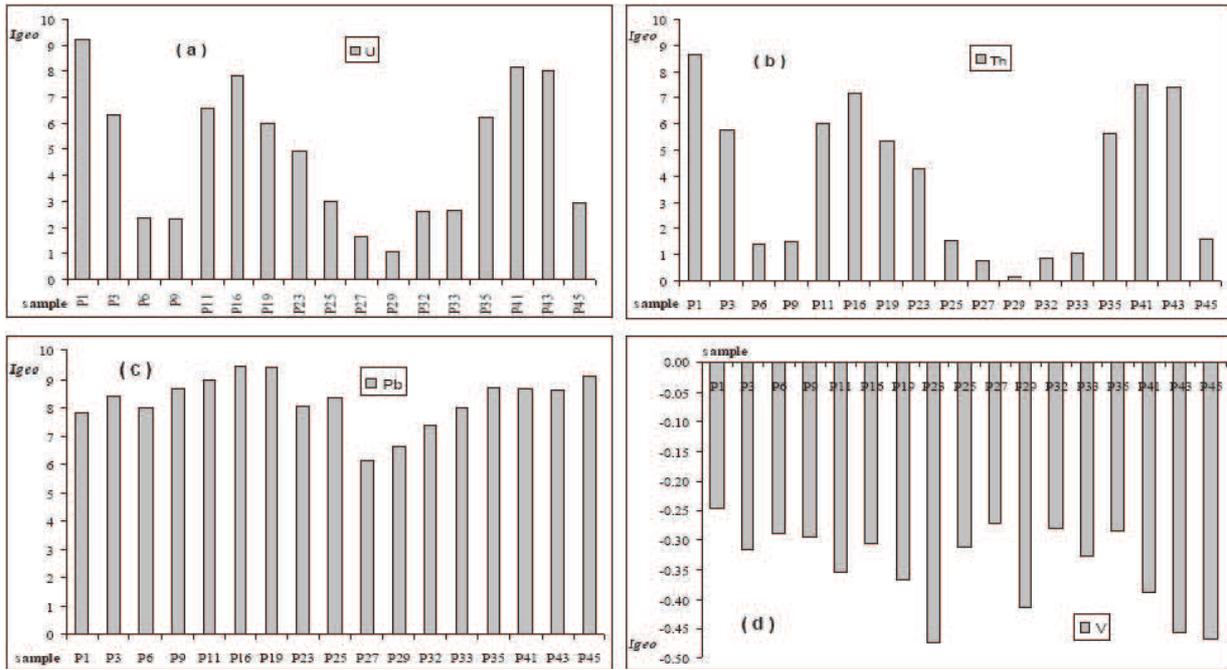


Figure 3: The geo-accumulation index in bottom sediments: (a) U; (b) Th; (c) Pb; (d) V.

Tables

Table 1: Statistics of parameters for bottom sediments samples (n = 17) collected in Crucea region (milligrams per gram $mg.g^{-1}$ except LOI^a and $Al_2O_3^b$).

| Parameter | Minimum value | Maximum value | Median value | Mean value | Standard deviation |
|----------------------------|---------------|---------------|--------------|------------|--------------------|
| LOI (%) ^a | 4.59 | 6.12 | 5.15 | 5.19 | 0.428 |
| Al_2O_3 (%) ^b | 14.55 | 17.77 | 16.71 | 18.38 | 0.948 |
| Co | 15.03 | 21.54 | 18.34 | 18.41 | 1.872 |
| Cr | 81.82 | 110.68 | 88.88 | 90.74 | 6.344 |
| Cu | 39.83 | 70.86 | 54.64 | 55.12 | 9.291 |
| Ni | 35.78 | 125.09 | 46.03 | 50.41 | 19.929 |
| Pb | 37.16 | 371.57 | 183.54 | 192.16 | 97.169 |
| Sr | 100.26 | 120.17 | 106.57 | 108.96 | 7.364 |
| Th | 18.70 | 6643.92 | 47.78 | 309.89 | 391.169 |
| U | 17.20 | 5023.96 | 63.46 | 246.81 | 291.098 |
| V | 105.23 | 123.29 | 117.39 | 115.29 | 5.703 |
| Zn | 124.63 | 161.68 | 142.00 | 141.18 | 10.483 |

Table 2: Relationships between selected elements and aluminum in bottom sediments from Crucea area ($p < 0.001$).

| Element | Co | Cr | Cu | Ni | Pb | Sr | Th | U | V | Zn |
|------------------------------|------|------|------|------|---------|------|------|---------|------|---------|
| r (for 4 degrees of freedom) | 0.54 | 0.54 | 0.50 | 0.18 | (-)0.23 | 0.17 | 0.13 | (-)0.24 | 0.97 | (-)0.08 |

Table 3: The background level ($mg.g^{-1}$) for selected elements (Petrescu and Bilal, 2007).

| Element | Background level ($mg.g^{-1}$) | Element | Background level ($mg.g^{-1}$) |
|---------|----------------------------------|---------|----------------------------------|
| Cu | 13.63 | Pb | 0.36 |
| Th | 10.87 | Co | 14.36 |
| Sr | 107.66 | Ni | 19.30 |
| U | 5.39 | Cr | 73.58 |
| Zn | 66.38 | V | 97.44 |

Table 4: The geo-accumulation index in bottom sediments for selected elements.

| <i>Sample</i> | <i>Cu</i> | <i>Th</i> | <i>Sr</i> | <i>U</i> | <i>Zn</i> | <i>Pb</i> | <i>Co</i> | <i>Ni</i> | <i>Cr</i> | <i>V</i> |
|---------------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|----------|
| <i>S1</i> | 1.76 | 8.67 | -0.66 | 9.28 | 0.63 | 7.84 | -0.05 | 0.35 | -0.21 | -0.25 |
| <i>S3</i> | 1.31 | 5.76 | -0.60 | 6.37 | 0.39 | 8.42 | -0.10 | 0.67 | -0.34 | -0.32 |
| <i>S6</i> | 0.96 | 1.42 | -0.50 | 2.41 | 0.44 | 7.99 | -0.22 | 2.11 | 0.00 | -0.29 |
| <i>S9</i> | 1.50 | 1.52 | -0.55 | 2.37 | 0.56 | 8.70 | -0.13 | 0.80 | -0.31 | -0.29 |
| <i>S11</i> | 1.00 | 5.99 | -0.67 | 6.60 | 0.50 | 9.00 | 0.00 | 0.83 | -0.34 | -0.36 |
| <i>S16</i> | 1.63 | 7.19 | -0.60 | 7.82 | 0.70 | 9.44 | -0.29 | 0.75 | -0.23 | -0.31 |
| <i>S19</i> | 1.42 | 5.39 | -0.68 | 6.00 | 0.52 | 9.42 | -0.13 | 0.93 | -0.23 | -0.37 |
| <i>S23</i> | 0.99 | 4.30 | -0.67 | 4.95 | 0.39 | 8.02 | -0.52 | 0.54 | -0.43 | -0.47 |
| <i>S25</i> | 1.79 | 1.55 | -0.44 | 2.98 | 0.51 | 8.35 | -0.20 | 0.84 | -0.22 | -0.31 |
| <i>S27</i> | 1.37 | 0.78 | -0.49 | 1.68 | 0.32 | 6.12 | -0.27 | 0.58 | -0.34 | -0.27 |
| <i>S29</i> | 1.31 | 0.20 | -0.51 | 1.09 | 0.38 | 6.65 | -0.46 | 0.31 | -0.34 | -0.41 |
| <i>S32</i> | 1.49 | 0.87 | -0.43 | 2.61 | 0.39 | 7.37 | 0.00 | 0.60 | -0.25 | -0.28 |
| <i>S33</i> | 1.60 | 1.11 | -0.44 | 2.69 | 0.45 | 8.01 | -0.24 | 0.66 | -0.28 | -0.33 |
| <i>S35</i> | 1.66 | 5.62 | -0.48 | 6.28 | 0.52 | 8.73 | -0.26 | 0.69 | -0.32 | -0.28 |
| <i>S41</i> | 1.50 | 7.53 | -0.67 | 8.15 | 0.60 | 8.70 | 0.00 | 0.52 | -0.31 | -0.39 |
| <i>S43</i> | 1.32 | 7.42 | -0.69 | 8.04 | 0.56 | 8.64 | 0.00 | 0.57 | -0.33 | -0.46 |
| <i>S45</i> | 1.38 | 1.61 | -0.63 | 2.97 | 0.64 | 9.10 | -0.39 | 0.77 | -0.37 | -0.47 |