Textural, Mineralogical and Geochemical Assessment of the Pikrolimni Lake Sediments (Kilkis District, Northern Greece) and Suitability for Use in Pelotherapy

Emilia Sofianska*, Constadinos Athanassoulis, Dimitrios Tarenides, Nikolaos Xirokostas, Maria Gkagka

1Hellenic Survey of Geology and Mineral Exploration, 1 Sp. Loui St., 13677, Acharnes, Athens, Greece.

esofianska@igme.gr, athanc@igme.gr, dtar@igme.gr, nxirokostas@igme.gr, marietta@igme.gr

Abstract

Pelotherapy is the application of thermal muds (peloids) for recovering muscle, bone and skin pathologies. Specific criteria were established for the evaluation of the therapeutic suitability of peloids. Critical factors ruling the quality of the solid phase of peloids include granulometry, mineralogy, and physical-chemical properties. The aim of the present study was to investigate the textural, mineralogical and geochemical characteristics of the Pikrolimni Lake sediments (PLS), Kilkis district (N. Greece) in order to assess their suitability for application as raw material into mud therapy technologies. Representative PLS samples were collected and analyzed by means of different techniques at the analytical laboratories of the Hellenic Survey of Geology and Mineral Exploration (HSGME). Results showed that, texturally, the PLS were classified as sandy loam sediments. X-ray diffraction (XRD) study revealed that the PLS consist mainly of quartz, clay minerals (kaolinite, montmorillonite, illite), and muscovite, with minor feldspar and calcite. X-ray fluorescence (XFR) analysis showed that PLS samples have higher SiO₂ and lower Al₂O₃ contents compared to the average shale composition. Among the analyzed, by means of inductively coupled plasma mass spectrometry (ICP-MS) technique, potentially toxic elements only As and Pb contents were found significantly higher than those of the average shale. Based on the calculated mean values of enrichment factor (EF) and geo-accumulation index (Igeo) PLS displayed minor enrichment and moderate contamination by Pb and As, respectively. In conclusion, an improvement of the grain size composition of PLS by means of a sieving process is needed. Besides, the study of the concentration and behavior of toxic
elements in peloids formed by the mixing of the processed PLS with salty thermominerwater is proposed.

**Keywords:** Pikrolimni, sediments assessments, toxic elements, pelotherapy

**Περίληψη**

Πηλοθεραπεία είναι η χρήση θερμών πηλών («πηλοειδών»), με σκοπό τη θεραπεία παθήσεων του μυϊκού συστήματος, του δέρματος και των οστών του ανθρώπου. Τα «πηλοειδή» είναι είτε φυσικά, είτε δημιουργούνται τεχνητά με την ανάμειξη λεπτόκοκκων, αργιλοίχων ιζημάτων (πηλών) με ολατούχα θερμομεταλλικά νερά. Η πηλοθεταπεία σήμερα έχει εξελιχθεί σημαντικά, έτσι ώστε να εφαρμόζεται πλέον σε εξαιρετικά τέτοιες παθήσεων. Επομένως, για την εκτίμηση της καταλληλότητας των «πηλοειδίων» για θεραπευτική χρήση, έχουν καθιερωθεί κριτήρια που αφορούν τα συστατικά τους. Για αυτό απαιτείται ο καθορισμός προδιαγραφών και τυποποίηση των χαρακτηριστικών των υλικών που θα εφαρμοστούν στην πηλοθεραπεία. Για τους πηλούς, που είναι η στερεή φάση των «πηλοειδίων», ιδιαίτερης σημασίας είναι η κοκκομετρική τους σύσταση, η ορυκτολογική σύνθεσή τους και οι συστατικές φυσικο-χημικές τους ιδιότητες. Η παρούσα έρευνα αναφέρεται στη μελέτη της κοκκομετρίας, της ορυκτολογίας και της γεωχημείας των ιζημάτων της Πικρολίμνης στην περιοχή του Κιλκίς (Β. Ελλάδα), σε μια προσπάθεια να εκτιμηθεί η καταλληλότητά τους για χρήση, ως πρώτης ύλης, στην τεχνολογία της πηλοθεραπείας. Για το σκοπό αυτό έγινε συλλογή αντιπροσωπευτικών δειγμάτων από το βυθό της Πικρολίμνης, τα οποία αναλύθηκαν με διαφορετικές μεθόδους στα Εργαστήρια της Ελληνικής Αρχής Γεωλογικών και Μεταλλευτικών Ερευνών (ΕΑΓΜΕ). Από την κοκκομετρική ανάλυση των δειγμάτων προέκυψε ότι αυτά αποτελούνται από υψηλά ποσοστά άμμου (73,10%) και ιλύος (23,62%), με πολύ χαμηλό ποσοστό αργίλου (3,27%). Η μελέτη της ορυκτολογικής σύστασης με τη χρήση ακτίνων Χ (XRD), έδειξε ότι τα ιζήματα αποτελούνται από υψηλά ποσοστά χαλαζία (59,3%), αργιλικά ορυκτά (καολινίτης, μοντμοριλλονίτη, ιλλίτη) (19,7%), μοσχοβίτη (12,0%), αλβίτη (8,0%) και ασβεστίτη (1,0%). Χημικές αναλύσεις με φασματομετρία ακτίνων – X (XRF) έδειξαν ότι τα ιζήματα έχουν πολύ υψηλότερα ποσοστά σε SiO\(_2\) (66,97%) και πολύ χαμηλότερα σε Al\(_2\)O\(_3\) (10,72%) σε σύγκριση με τη μέση σύσταση πρότυπου σχιστόλιθου. Ιδιαίτερης σημασίας για τη χρήση ιζημάτων στην πηλοθεραπεία είναι η περιεκτικότητα τους σε ορισμένα υγιεινά ιχνοστοιχεία όπως τα As, Co, Cr, Cu, Ni, Pb και Zn, τα οποία είναι τοξικά, μπορούν να απορροφηθούν από το δέρμα και πιθανά να δημιουργήσουν προβλήματα υγείας στον άνθρωπο. Από την
ανάλυση των στοιχείων αυτών με Φασματομετρία Μάζας Επαγωγικά Συζευγεμένου Πλάσματος (ICP-MS: Inductively Coupled Plasma – Mass spectrometry), προέκυψε ότι στα ιζήματα τα στοιχεία As και Pb είναι σε υψηλότερες συγκεντρώσεις σε σχέση με τη μέση σύσταση πρότυπου σχιστόλιθου. Από τον υπολογισμό των δεικτών εμπλουτισμού (EF: enrichment factor) και γεωσυσσώρευσης (Igeo: geo-accumulation index), προέκυψε ότι τα ιζήματα της Πικρολίμνης παρουσιάζουν αντίστοιχα, ελάχιστο εμπλουτισμό και μέτρια ρύπανση στα στοιχεία As και Pb. Συμπερασματικά, από τα αποτελέσματα της έρευνας προέκυψε ότι απαιτείται η εφαρμογή κάποιας επεξεργασίας (π.χ. κοσκίνισμα για αφαίρεση αδρόκοκκου κλάσματος) στα ιζήματα για να βελτιωθεί η κοκκομετρική, ορυκτολογική και χημική τους σύσταση για να γίνει δυνατή η χρήση τους στην πηλοθεραπεία. Η παρουσία, σε αυξημένη ποσότητα, των τοξικών στοιχείων As και Pb στα ιζήματα θα μπορούσε να θεωρηθεί σχετικά μικρής σημασίας, γιατί ανάλογης σύνθεσης πηλοί χρησιμοποιούνται σε άλλες περιπτώσεις στην πηλοθεραπεία. Προτείνεται, μετά την επεξεργασία των ιζημάτων, η ανάμειξη με θερμομεταλλικό νερό και η δημιουργία «πηλοειδούς» στο οποίο να ερευνηθεί η συγκέντρωση και η γενικότερη συμπεριφορά των τοξικών στοιχείων.

Δέκατος κλειδί: Πικρολίμνη, ανάλυση ιζημάτων, τοξικά στοιχεία, πηλοθεραπεία

1. Introduction

Mud therapy (pelotherapy) has been used since ancient periods for medical or cosmetic purposes (e.g., Veniale et al., 2007). Peloids consist of fine-grained sediments (muds) produced by different geological processes. Their mixture with salty thermo-mineral water, followed by a maturation process, results in a positive and beneficial effect on human organism and thus they could often be used for mud baths and cataplasms. The feasibility of using mud in spas received much attention over the past few decades (e.g., Carretero et al., 2006; Veniale et al., 2007; Karakaya et al., 2010). However, not all muds can be used for mud therapy, whereas natural occurrences of suitable thermal muds are becoming exhausted. Nowadays, pelotherapy is being more and more focused on specific human pathologies and treatments. Such innovative health applications need certification of the peloids suitability (e.g., Veniale et al., 2007). Thus, for the evaluation of the therapeutic suitability of peloids, a detailed assessment of some of their properties is needed. Specifically, for the solid phase of peloids critical factors controlling its quality include grain size composition, mineralogy and some physico-chemical properties. Of particular concern is the concentration of some potentially toxic elements in the muds, such as As, Cd, Cr, Cu, Ni, Zn, and Pb. The abundance of these elements in peloids must be very carefully controlled because of their potentially hazardous
effects on health, due to their toxicity and possible absorption through the skin (Veniale et al., 2007; Tateo et al., 2009; Carretero et al., 2010; Karakaya et al., 2010; Rebelo et al., 2011). Not only the total toxic element content of the muds but also the mobility, bioavailability, and potential mobility of the constituents in the final products applied to mud therapy should be taken into consideration (Adamis and Williams, 2005; Tateo, 2009).

The present study refers on the assessment of some characteristics of the PLS, at an effort to determine their suitability for potential application as raw material in mud therapy technologies. The objectives of the study are: a) the texture, mineralogy and geochemistry of representative Pikrolimni Lake sediment (PLS) samples b) the levels of potentially toxic elements enrichment and contamination of PLS using the enrichment factor (EF) and the index of geo-accumulation (Igeo), respectively. This study may contribute new knowledge to natural peloids characterization and their quality criteria related to therapeutic purposes.

2. Study area

Pikrolimni is a small, nearly rounded lake, approximately 2.43 km in length and 2.35 km in wide, covering an extent of 3.772 km² (Fig. 1). It is a shallow depression not exceeding 1.5m in depth. The broader area is a cultivated land covered by alluvial sediments and belongs to the Kilkis district.
3. Materials and methods.

Three locations of the Pikrolimni Lake bottom sediments were chosen for sampling (Fig.1). At each location a composite sample was prepared by mixing of at least 10 subsamples collected from a surface $5 \times 5$ m of the lake bottom. This sampling procedure was intended to obtain a more representative average sample from each site. Samples were homogenized, air-dried for 7 days and stored in polyethylene bags for further analytical work. Portions of the sediment samples were used for grain size, mineralogical and geochemical analyses. The grain size composition analysis was performed according to the Standard Test Method for Particle-Size Analysis of Soils ASTM D 422-63 and ASTM 2217-85 (ASTM, 2000).

The mineralogical composition of the sediments was determined by optical microscopy and X-ray powder diffraction (XRD) using a X’Pert PRO X ray diffractometer equipped with Cu Kα radiation. Operating conditions were 40 kV accelerating voltage, 30 mA current and tracing space was in the range of 2 to 70 2θ for bulk samples and 2 to 35 2θ for the clay fraction. Diffraction patterns were identified with the X’Pert High Score program.

Two types of XRD analyses were made:

a) on the bulk powdered samples to determine the clay and non-clay minerals present, and

b) on the separated clay fraction (<2 μm) using oriented, glycolated and heated sample mounts for the identification of clay minerals.

Semi quantitative mineralogical composition of the PLS was found by analysis of the XRD patterns using the X’Pert PRO program.

The chemical composition of PLS samples (major and some minor elements) was determined by X-ray fluorescence analysis (XRF), using the S4 PIONEER equipment of the BRUKER AXS. The concentrations of potentially toxic elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) using the PE SCIEX ELAN 6100 equipment. All the analytical work was conducted at the Laboratories of the Hellenic Survey of Geology and Mineral Exploration (HSGME). Chemical results were compared with the composition of the average shale (Li, 2000) and muds used for medical purposes (Mihelčić et al., 2012).

The anthropogenic impact on the PLS was estimated using the enrichment factor (EF). The $EF$ method normalizes the measured potentially toxic elements contents with
respect to a reference element. Elements, such as Fe (Kartal et al., 2006; Li and Feng, 2012) and Al (Lu et al., 2009) are most commonly referenced when calculating the EF of soil or sediment heavy metal pollution, because they are slightly affected or remained unaffected. In this study, Fe was used as the reference element for normalization, because standard deviation of Fe is less than that of Al (Table 2). The EF was calculated according to the following equation:

\[ EF = \frac{M_x \times Fe_x}{M_b \times Fe_b} \]  

where \( M_x \) and \( Fe_x \) are the sediment sample concentrations of an individual metal and Fe, respectively, while \( M_b \) and \( Fe_b \) are their concentration in a suitable background or baseline reference material (Abrahim and Parker, 2008). In this study the concentration of trace elements in average shale were used as natural geochemical background values.

Seven contamination categories have been recognized on the basis of the enrichment factor (Guo et al., 2014):
- \( EF \leq 1 \); denotes deficiency to no enrichment,
- \( EF = 1-3 \); minor enrichment,
- \( EF = 3-5 \); moderate enrichment,
- \( EF = 5-10 \); moderately severe enrichment,
- \( EF = 10-25 \); severe enrichment,
- \( EF = 25-50 \); very severe enrichment, and
- \( EF > 50 \); extremely severe enrichment.

The levels of metal contamination of the PLS were calculated using the geoaccumulation index (Igeo), as proposed by Müller (1969). This index is given by the following equation:

\[ I_{geo} = \log_2 \frac{C_n}{1.5B_n} \]  

where \( C_n \) is the concentration of the element in the analysed samples, and \( B_n \) is the local geochemical background of the element, i.e., the mean concentration of element in the sediments in the broader area found by previous investigation. The factor 1.5 is introduced to minimize the effect of possible natural variation in the background values which may be attributed to lithologic variations in sediments, and to detect very small anthropogenic influences (Wei and Yang, 2010). Given that the geochemical background of the elements in the study area is not known, the average shale composition for each element was used for \( I_{geo} \) calculations.
Müller (1969) proposed the descriptive classes listed in Table 1 for increasing $I_{geo}$ values (Table.1).

Table 1: Descriptive classes of sediment contamination based on $I_{geo}$ values (Müller, 1969).

<table>
<thead>
<tr>
<th>$I_{geo}$ value</th>
<th>$I_{geo}$ class</th>
<th>Designation of sediment quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;5</td>
<td>6</td>
<td>extremely contaminated</td>
</tr>
<tr>
<td>4-5</td>
<td>5</td>
<td>strongly to extremely contaminated</td>
</tr>
<tr>
<td>3-4</td>
<td>4</td>
<td>strongly contaminated</td>
</tr>
<tr>
<td>2-3</td>
<td>3</td>
<td>moderately to strongly contaminated</td>
</tr>
<tr>
<td>1-2</td>
<td>2</td>
<td>moderately contaminated</td>
</tr>
<tr>
<td>0-1</td>
<td>1</td>
<td>uncontaminated to moderately contaminated</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>uncontaminated</td>
</tr>
</tbody>
</table>

4. Results and discussion

Grain size analyses showed that the PLS samples are composed of 71.0% (69.5%-73.1%) sand, 23.9% (23.1%-24.9%) silt and 5.1% (3.3-7.4%) clay. The percentages of sand, silt and clay fractions were plotted on the triangular discrimination diagram of United States Department of Agriculture (USDA) triangle (Fig. 2). They are dominated by the sand and silt fractions. The PLS are classified as sandy loam sediments (Garcia-Gaines and Frankeinstein, 2015). Therefore, a sieving process is necessary to reduce the coarse-grain fractions and to improve their grain size quality for application in pelotherapy.

Optical microscope study showed the presence of quartz, muscovite, albite and carbonates detrital grains in PLS. Quantification of the XRD patterns revealed that the PLS are composed mainly of quartz (59.3%). Lesser amounts of clay minerals (19.7%), followed by muscovite (12.0%), albite (11.0%) and carbonates (1.0%) were found. The presence of quartz and albite in the PLS is not positive feature for mud application because they constitute abrasive minerals due to their hardness. The clay minerals present are mainly kaolinite, with minor montmorillonite, and illite (Fig. 3). The clay mineral content and type determine the desirable properties of a mud such as specific surface area, cation exchange capacity etc (Mihelčić et al., 2012; Quintela et al., 2012).
Table 2: Concentration of major and minor element oxides in the PLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLF1</td>
<td>63.44</td>
<td>12.60</td>
<td>4.42</td>
<td>0.08</td>
<td>3.44</td>
<td>3.25</td>
<td>2.78</td>
<td>2.02</td>
<td>0.47</td>
<td>0.12</td>
</tr>
<tr>
<td>PLF2</td>
<td>70.35</td>
<td>8.86</td>
<td>2.29</td>
<td>0.05</td>
<td>2.52</td>
<td>3.32</td>
<td>2.48</td>
<td>1.18</td>
<td>0.35</td>
<td>0.09</td>
</tr>
<tr>
<td>PLF3</td>
<td>67.11</td>
<td>10.70</td>
<td>3.51</td>
<td>0.07</td>
<td>2.93</td>
<td>3.29</td>
<td>2.59</td>
<td>1.61</td>
<td>0.41</td>
<td>0.11</td>
</tr>
<tr>
<td>Average</td>
<td>66.97</td>
<td>10.72</td>
<td>3.41</td>
<td>0.07</td>
<td>2.97</td>
<td>3.29</td>
<td>2.61</td>
<td>1.60</td>
<td>0.41</td>
<td>0.10</td>
</tr>
<tr>
<td>±SD$^3$</td>
<td>±3.46</td>
<td>±1.87</td>
<td>±1.07</td>
<td>±0.01</td>
<td>±0.46</td>
<td>±0.03</td>
<td>±0.15</td>
<td>±0.42</td>
<td>±0.06</td>
<td>±0.02</td>
</tr>
<tr>
<td>Aver.shale$^2$</td>
<td>58.39</td>
<td>15.12</td>
<td>6.75</td>
<td>0.11</td>
<td>2.49</td>
<td>3.09</td>
<td>1.29</td>
<td>3.21</td>
<td>0.77</td>
<td>0.16</td>
</tr>
</tbody>
</table>

$^1$ Total Iron as Fe$_2$O$_3$

$^2$ Average shale (Li, 2009)

$^3$ Standard deviation

Table 3. Summary statistics of the potentially toxic elements in the PLS and their quality characterization.

<table>
<thead>
<tr>
<th>Trace elements</th>
<th>Range (mg/kg)</th>
<th>Average (mg/kg)</th>
<th>Average shale</th>
<th>Morinje Bay</th>
<th>EF</th>
<th>Description of enrichment</th>
<th>Igeo</th>
<th>Description of contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>24-42</td>
<td>33.33</td>
<td>13</td>
<td>17</td>
<td>1.92</td>
<td>Minor enrichment</td>
<td>0.77</td>
<td>Moderate</td>
</tr>
<tr>
<td>Co</td>
<td>9-12</td>
<td>10.67</td>
<td>19</td>
<td>-</td>
<td>0.42</td>
<td>No enrichment</td>
<td>-1.42</td>
<td>Uncontaminated</td>
</tr>
<tr>
<td>Cr</td>
<td>80-92</td>
<td>85.67</td>
<td>90</td>
<td>122</td>
<td>0.71</td>
<td>No enrichment</td>
<td>-0.66</td>
<td>Uncontaminated</td>
</tr>
<tr>
<td>Cu</td>
<td>29-33</td>
<td>31.00</td>
<td>45</td>
<td>33</td>
<td>0.51</td>
<td>No enrichment</td>
<td>-1.12</td>
<td>Uncontaminated</td>
</tr>
<tr>
<td>Ni</td>
<td>46-52</td>
<td>49.00</td>
<td>50</td>
<td>62</td>
<td>0.73</td>
<td>No enrichment</td>
<td>-0.61</td>
<td>Uncontaminated</td>
</tr>
<tr>
<td>Pb</td>
<td>30-35</td>
<td>32.67</td>
<td>20</td>
<td>22</td>
<td>1.22</td>
<td>Minor enrichment</td>
<td>0.12</td>
<td>Moderate</td>
</tr>
<tr>
<td>Zn</td>
<td>85-110</td>
<td>95.33</td>
<td>95</td>
<td>76</td>
<td>0.75</td>
<td>No enrichment</td>
<td>-0.58</td>
<td>Uncontaminated</td>
</tr>
</tbody>
</table>
Results from the XRF analyses (Table 2) showed that the PLS samples displayed a great variation in their major and minor element composition. They have, on average, increased SiO$_2$ (66.97wt%) and much lower Al$_2$O$_3$ (10.72wt%) contents confirming the high quartz and low clays mineralogical composition found by the XRD analyses.

Normalization is a convenient method to show increasing or decreasing patterns of elements in relation to a reference material. In Fig. 4 the average oxide composition of PLS has been normalized to the average shale composition (Li, 2000), to display their relationship. The PLS have much higher Na$_2$O and higher SiO$_2$ and MnO than that of average shale. They also have a lower Al$_2$O$_3$, Fe$_2$O$_3$, K$_2$O, MnO, TiO$_2$ and P$_2$O$_5$ than the average shale. The concentration of CaO is comparable with that found in average shale. The study samples contain on average a lower percentage of K$_2$O due to their lower content of illite.
Fig. 3: XRD patterns of the PLS (Ill/Ms-Illite/Muscovite, Kln-Kaolinite, Mnt-Montmorillonite, Chl-Chlorite, Qtz-Quartz).

Fig. 4: Major element composition of PLS, normalized to the average shale composition.
The Na$_2$O/CaO ratio is <1, confirming the presence of the previously referred typical non-swelling 2:1 clay minerals (Karakaya et al., 2010; El-Hinnawi and Abayazed, 2012). Of particular concern in the use of a mud in pelotherapy is the concentration of some trace elements which are considered as hazardous (Tateo et al., 2009; Carretero et al., 2010; Rebelo et al., 2011). Among the analyzed potentially toxic elements (Table 3) Pb and As have average contents higher, while Co and Cu were found lower than the average shale (Fig. 5). Rebelo et al. (2011) have classified Pb and As in the first class of the hazardous elements which should be essentially absent from muds because they are known as human toxicans.

**Fig. 5:** Lg-lg relationship between the average concentration of trace elements in the PLS and: a) average shale concentration, b) Morinje Bay muds concentration.
The potentially toxic elements concentration of the PLS samples were also compared with the natural muds from the Morinje Bay (Croatia), which are used in pelotherapy (Mihelčić et al., 2012). Thus, among the potentially toxic elements the average contents of Pb, As and Zn are higher than those of Morinje Bay muds (Fig. 5). Rizo et al. (2013) referred also on comparable values of Pb (28 ppm) in natural muds from San Diego River, Cuba (Arsenic was not analyzed). Besides, Quintela et al. (2012) referred on peloid muds applied to pelotherapy which contain comparable levels of these heavy metals. These muds, however, were not compared to the PLS samples because they were elaborated before their application.

Iron normalized $EF$ values (Table 3) of Ni, Zn, Cr, Co, and Cu are <1 showing no enrichment and thus natural origin of these elements in PLS. Arsenic and Pb have $EF$ values in the range 1-3 denoting minor enrichment of PLS. In general, $EF$ values less than 1.5 were not considered significant, because such small enrichment may arise from differences in the composition of local sediment material (Zang and Liu, 2002).

The application of chemicals (fertilizer, pesticides and herbicides) on the cultivated area around the Pikrolimni Lake should contribute to the enrichment of As and Pb in the PLS (Alloway, 2012). Therefore, the source of As and Pb is considered mixed from natural and anthropogenic inputs (Guo et al., 2014). The calculated $I_{geo}$ values showed that the PLS samples displayed moderate contamination for Pb and As and no contamination for Ni, Zn, Cr, Co, and Cu (Table 3).

5. Conclusions

The PLS can be used as raw clay material for peloids only after sieving and improvement of their granulometry. Sieving process would also decrease the quartz content and consequently the $SiO_2$ in PLS.

The analyzed potentially toxic elements Ni, Zn, Cr, Co, and Cu are, generally, within normal ranges.

The detected slightly higher levels of As and Pb are probably of no significant concern for human health in case of mud application because similar concentrations were also encountered in other muds used for mud therapy.
A further investigation is needed to study the concentration of these metals in a derivative peloid formed after the mixture of PLS with thermo-metal water and to determine the mobility and bioavailability of the metals.

6. Acknowledgments

This paper was financially supported by HSGME. The authors appreciate the technical support and assistance from the staff of the Unit of Mineral Raw Materials Technology and Metallurgy of HSGME. Many thanks to the two anonymous reviewers for their critical and constructive comments which improved our manuscript.

7. References


