Chemical and Biological Properties of the Lake Blue Clay

Rasma Tretjakova, Samanta Marija Misiņa, Jevgenijs Lukašenoks
Rezekne Academy of Technologies, Faculty of Engineering,
Research Center Chemical, Biology and Biotechnology
Address: Atbrivosanas aleja 115, Rezekne, LV-4601, Latvia

Abstract. In this paper the chemical and biological properties of the lake blue clay are explored. A blue clay bed layer was found under the sapropel layer in the lake Pluons (area 4.8 km², Ludza county, Latvia). It has been determined that the lake Pluons blue clay has a colloid composition, which contains Na, Mg, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Al, Ag, Ba. In samples Candida albicans, Pseudomona aeruginosa, Staphylococcus aureus and a total number of aerobic mesophile bacterium have been defined. In microbiological analyses the presence of Candida albicans, Pseudomonas aeruginosa, Staphylococcus aureus has not been stated. The number of mesophyll aerobic microorganisms is <1 CFU/0.1 g. Based on feasibility analysis Latgale lake blue clay has a high potential for its use in cosmetics and medicine.

Keywords: blue clay, chemical properties, biological properties.

I. INTRODUCTION
There are 2256 lakes in Latvia with a total area of 1001 km², which stands for 1.5% of the territory of Latvia. Sapropel is found in nearly all these lakes. The State Geology Office of Latvia states that there are more than 750 million m³ of lake sapropel resources. A sufficient number of researches on sapropel in Latvia, its composition, qualities and possibilities of application, for instance, using sapropel in manufacturing solid soaps, manufacturing glues and composite materials, using sapropel as sorbent in heavy metal manufacturing and impact of sapropel humus substance on hydroponics [1] has been done. It has been proved that sapropel of the lakes of Latvia is not polluted with heavy metals.

A blue clay bed layer has been found under the sapropel layer in the lake Pluons (area 4.8 km², Ludza county) [2]. There has been a research on the possible applications of the clay of Latvia [3, 4]. There is no any other data about the amount of blue clay bed in the lakes of Latvia due to the insufficient number of research works. Also, there are no scientific researches into blue clay composition, qualities and possibilities of its application. Lake blue clays are gained not from pits, but from freshwater waterbody depths, which are not influenced by anthropogenic pollution, that is why it is considered to be ecologically clean product, the research into which would open wide possibilities in usage of local product in cosmetology, medicine and other fields. The composition and qualities of lake blue clays and their usage possibilities in Europe are not sufficiently studied.

There are about 1000 lakes in Latgale region, in which the resources of blue clay have not been studied yet, therefore, carrying out the research and scientifically justifying the usage of blue clay as a local resource, will create a beneficial environment for manufacturing new high value-added products and services.

The aim of this research is to determine chemical and biological properties of Lake Pluons blue clay.

II. MATERIALS AND METHODS
Blue clay samples were inspected and collected from the lake Pluons. A blue clay bed layer has been found under the sapropel layer in the lake Pluons. Blue clay has been found in two places at depths of 4-12 m. Bed layer is estimated to be about 2 m thick. For gathering clays the device made after the sample collection analogue device (“Eijkelkamp” type) with working camera of 2 l volume was used. Samples are placed into sterile, airtight plastic package and transported to the laboratory for analysis.

Research into organoleptic quality - odour is defined with sensory method, colour - visual method, consistency - sensory, visual method. The moisture of sediments was determined after drying at 105 °C. Define in samples pH (LVS ISO 10390:2006), Ca, Na, K, Mg, Fe, Al, Mn, Zn, Co, Cr, Si, Cu, Ni, Zn, Cd, Pb, Hg. Metal concentrations were determined by use of flame atomic absorption spectroscopy (Perkin Elmer 503). The reliability and accuracy of the analytical results were checked using blank and references samples. Metal content data is provided for dry matter of sample. Two replicates were done for...
each sample. The mean values and standard deviation (SD) calculated.


The chemical composition average values, standard deviation and organoleptic qualities of the Plusons lake blue clay and sapropel are presented in table I.

### III. RESULTS AND DISCUSSION

It was determined that the lake Plusons blue clay has a colloid composition, grey colour, sludge odour, plastic, soft, smooth consistency which contains Na, Mg, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Al, Ag, Ba. Grey and blue colour indicates the presence of Fe (II) compounds [5]. Comparing the chemical composition of the blue clay and sapropel of Plusons lake shows that they are similar only in pH. pH of the Plusons lake blue clay is 7.74. French clays pH varied from 7.64 to 10.23 [6]. Clayey soils used traditionally for cosmetic purposes in South Africa the pH of the analysed samples ranged from 4.53 to 9.57 [7]. The pH of the clay soils used for cleansing can also influence their cleansing activity. According to [8, 9, 10] suitable skin cleansers must have pH near neutral or similar to that of the skin (4.5 to 5.5).

In comparison with sapropel there is significantly more Na, Mg, Al, Ca and Ba and less heavy metals such as Cd, Zn, Cu. EU directives forbid the presence of heavy metals in perfumery cosmetics, but there are no detailed requirements for sapropel and clay. Sanitary norms of Russia, Ukraine and Kazakhstan developed for health resorts and rehabilitation centres, determine that the concentration of heavy metals in therapeutic mud shall not exceed the local natural background soil concentrations that are characteristic of mud deposit region. Requirements for therapeutic mud properties and particularly sapropel type sediments have been developed only in Belarus. According to the requirements of Belarus, heavy metals in the lake Plusons blue clay do not exceed the permissible norms.

The most widely studied are French clays, which are obtained from quarries in the deepest layers of the lithosphere. In comparison with French green clays [24] the Plusona lake clay has a higher concentration of Ca and Mn, on average the same amount of Ba, but the content of other chemical elements is lower. There is significantly less Co, Ni, Cu, Zn, Pb, Al, element. Traditionally considered as toxic are As, Sb, Cd, Co, Cu, Pb, Ni, Zn, Hg, Se, Te, Ti, Ba, other less dangerous elements are Li, Rb, Sr, Cr, Mo, V, Zr[6]. Clays with high cation (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ and H$^+$) exchange capacity have been reported to ensure cleansing through absorption of toxins, bacteria and unwanted substances from the skin during topical application [6].

Clay control of contamination by microorganisms is also extremely important, given that they can be the origin of diseases or can damage the product when it

### Table I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Result</th>
<th>SD</th>
<th>Sapropel</th>
<th>SD</th>
<th>MAC Belarus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>-</td>
<td>grey</td>
<td>0.67</td>
<td>90.53</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>Odour</td>
<td>-</td>
<td>black-grey</td>
<td>0.20</td>
<td>7.51</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>Consistency</td>
<td>-</td>
<td>plastic, soft, smooth</td>
<td>70</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Moisture</td>
<td>%</td>
<td>80.16</td>
<td>0.67</td>
<td>90.53</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>Dry matter</td>
<td>%</td>
<td>19.84</td>
<td>0.67</td>
<td>9.47</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>7.74</td>
<td>0.20</td>
<td>7.51</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>mg/kg</td>
<td>135</td>
<td>14</td>
<td>70</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>4267</td>
<td>135</td>
<td>1053</td>
<td>114</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg</td>
<td>53</td>
<td>7</td>
<td>169</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>328174</td>
<td>583</td>
<td>10805</td>
<td>303</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>6418</td>
<td>114</td>
<td>11550</td>
<td>116</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td>2.57</td>
<td>0.04</td>
<td>3.76</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>959</td>
<td>38</td>
<td>369</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td>1.09</td>
<td>0.03</td>
<td>9.04</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td>2.5</td>
<td>0.1</td>
<td>5.9</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>3.2</td>
<td>0.2</td>
<td>&lt; 9</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>17.0</td>
<td>4.0</td>
<td>45.2</td>
<td>3.6</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>&lt;0.1</td>
<td></td>
<td>0.6</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td>4.8</td>
<td>0.2</td>
<td>2.2</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td>917</td>
<td>56</td>
<td>2780</td>
<td>102</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>mg/kg</td>
<td>&lt;0.05</td>
<td>-</td>
<td>&lt;0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>mg/kg</td>
<td>422</td>
<td>24</td>
<td>359</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>%</td>
<td>7.01</td>
<td>0.79</td>
<td>25.41</td>
<td>8.4</td>
<td>-</td>
</tr>
</tbody>
</table>

MAC (Maximum Allowable Concentration)
is stored. Results of the microbiological testing with Plusons lake blue clays show that the presence of *Candida albicans*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* is not stated. The number of mesophyll aerobic microorganisms varied <1 to 3.6 X 10 CFU/0.1 g (Table II). It [11] must be mentioned that since clays can be contaminated during processing and storing by *Bacillus anthracis*, *Clostridium tetani* and *Clostridium welchii*, in this study the above mentioned microorganisms were not determined in the clay samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of aerobic mesozofile bacterium</td>
<td>LVS EN ISO 21149 : 2009</td>
<td>&lt;1 to 3.6 X 10 CFU/0.1 g (Tryptic soy agar)</td>
</tr>
<tr>
<td><em>Candida albicans</em></td>
<td>LVS EN ISO 18416: 2009</td>
<td>Has not been stated 0.1 g (Sabouraud dextrose agar)</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>LVS EN ISO 22717:2009</td>
<td>Has not been stated 0.1 g (Cetrimid agar)</td>
</tr>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td>LVS EN ISO 22718:2009</td>
<td>Has not been stated 0.1 g (Baird-Parker agar)</td>
</tr>
</tbody>
</table>

Both animals and people have used clay for therapeutic purposes since prehistoric time. There has already been proved the effectiveness of clay in cosmetology and in medicine [12, 13,14].

In pharmaceutical formulations, spas and beauty therapy, clay minerals are used for therapeutic purposes and their beneficial effect on human health. In pharmaceutical and clinical applications these minerals are used as active principles (gastrointestinal protectors, antacids anti diarrhoeaics, dermatological protectors, cosmetics) and excipients (inert bases, delivery systems, lubricants, emulsifiers) [15].

In SPA procedures and for maintaining skin health clay is used due to its sorption and calorific properties. In spas and beauty therapy clay minerals are used in geotherapy, pelotherapy and paramuds, to treat dermatological diseases, alleviate the pain of chronic rheumatic inflammations, arthritis, locomotor system diseases and injuries, moisturise the skin, and combat compact lipodystrophies and cellulite [15, 16]. The exchange of ions between the clay mixture and the skin can enable absorption of unwanted substances from the skin by the clay; hence ensuring skin cleansing action [7]. In dermatology clays are used in wound healing and in treatment of various irritations of the skin, different skin conditions, as well as they are recommended for inflammatory processes such as boils, acne, ulcers, etc. [17, 18]. In cosmetic industry clay is used in creams, lotions, body and face masks, shampoos, sunscreen products, toothpastes, powders, emulsions, bathroom salts, antiperspirants, lipsticks and eye shadows [19, 20, 6]. Clays are widely used in protective creams. Although such creams differ in composition according to the particular class of hazard against which protection is desired (dust, water, grease, sun, etc.). Clays are also used in sunscreen products, designed to provide sun protection by either scattering or absorbing radiant energy [19].

The usage of clay as UV filters is based on the layered structure of their particles and large specific surface and as a result, these particles effectively cover a certain area of skin and are able to absorb and reflect ultraviolet radiation [21]. Different types of clay minerals have different capacities to retain UV radiation. Comparing kaolinite, montmorillonite, illite and mixed-layer clay minerals, the lowest UV protection ability is in kaolinite, but the highest in clay minerals containing mainly illite clay minerals [21]. Clay mineral UV transmittance ability is affected by the parameters of clay mineral particles. Increasing the amount of clay in cream, UV transmittance decreases, thus increasing protection against UV radiation [21].

During the past 25 years, ~70% of newly discovered drugs introduced in the USA have been derived from natural products [22]. Vast application of French green clay in medicine has already been proved [14, 23]. A wide range and variety of minerals are used in the pharmaceutical industry as active ingredients. Such minerals may be administered either orally as antacids, gastrointestinal protectors, anti diarrhoeaics, osmotic oral laxatives, homeostatics, direct emetics, antianemtics and mineral supplements, or parenterally as antianemtics and homeostatics. They may also be used topically as antisepsics, disinfectants, dermatological protectors, anti-inflammatories, local anesthetics, keratolytic reducers and decongestive eye drops [19]. The absorptive properties of clay minerals are well documented for healing skin and gastrointestinal ailments. Sarkisyanst et al. [24] studied the sorption characteristics of blue clay in relation to ions of heavy metals, the possibility of the introduction of this class of sorbents in bioprevention environmentally related chronic pathological processes were studied. Clay adheres to the gastric and intestinal mucous membrane and protect them and can absorb toxins, bacteria and even viruses. They do, however, have the disadvantage that they also eliminate enzymes and other necessary nutritive elements, which makes their prolonged use inadvisable [17, 25].

Clay therapeutic effects are divided by its colour, although scientific research on such categories is not available. Yellowish clay is used in some spas to
prevent bacterial infection on the skin; reddish clays are used for cleansing the skin, and bluish clays against the development of acne. Similarly, greenish coloured clays are applied to reduce the amount of oil on the skin; and black clays for general body nourishment [26]. Similar information, but much more extended, can be found on cosmetic facial clay mask packages. There has also been the research on the use of nano-clays in medicine delivery systems [27].

Clay could provide an alternative treatment against numerous human bacterial infections. Clay has antibacterial properties. For example, the silver and quaternary ammonium surfactant-modified clays showed suitable inhibition properties over E. coli [28]. Three types of clays (white clay, gray clay and yellow clay) have an antibacterial effect against Staphylococcus aureus that was isolated from skin infection and have no effect against Pseudomonas aeruginosa that was isolated from patient with urinary tract infection. Pink mineral clay explained an antibacterial effect against Pseudomonas aeruginosa, and has low effect against Staphylococcus aureus. Results indicated that mineral clay provide an alternative treatment against numerous human bacterial infections [29].

French green clays have recently been shown to heal Buruli ulcer, a necrotic or ‘flesh-eating’ infection caused by Mycobacterium ulcerans. A clear distinction must be made between ‘healing clays’ and those we have identified as antibacterial clays. The highly adsorptive properties of many clays may contribute to healing a variety of ailments, although they are not antibacterial. The two French green clays used to treat Buruli ulcer, while similar in mineralogy, crystal size, and major element chemistry, have opposite effects on the bacterial populations tested [14]. Moreover, antimicrobial testing of the two clays on a broad-spectrum of bacterial pathogens showed that one clay promotes bacterial growth, while another kills bacteria or significantly inhibits bacterial growth [23]. One specific mineral demonstrated bactericidal activity against pathogenic Escherichia coli, extended-spectrum β-lactamase E. coli, Salmonella enterica serovar Typhimurium, Pseudomonas aeruginosa and Mycobacterium marinum, and a combined bacteriostatic/bactericidal effect against Staphylococcus aureus, penicillin-resistant S. aureus, methicillin-resistant S. aureus and Mycobacterium smegmatis, whereas another mineral with similar structure and bulk crystal chemistry, had no effect on or enhanced bacterial growth [30]. The reasons for the difference in antibacterial properties thus far show that the bactericidal mechanism is not physical (e.g., an attraction between clay and bacteria) but by a chemical transfer or reaction (pH and oxidation) [14]. The biological effects of clay minerals are influenced by their mineral composition and particle size [31].

Discovery that natural geological minerals harbour antibacterial properties should provide impetus for exploring terrestrial sources for the presence of novel therapeutic compounds. Combining the availability of natural bioactive resources with powerful combinatorial chemistry optimization methodologies could result in the development of new antibacterial agents to fight existing antibiotic-resistant infections and diseases for which there are no known therapeutic agents [30].

Clay in Latvia is very widespread as a mineral resource and the extracted quantity is one of the largest in northern Europe. Its application and studies are mainly related to construction materials and production of various ceramic products [32]. The studies, which were carried out during the recent years on the expansion of application of the clay of Latvia and the creation of innovative products, are based on the application of new and improved ceramic materials in environmental technologies. [5] In the study [3] it was found that the majority of commercially available cosmetic clay masks in Latvia contain illite, which is the most common clay mineral in Latvia. In the field of geology clay is a size-based term for very fine-grained minerals with an estimated spherical diameter <2.0 μm and approximate density of 2.65 g/cm³. This size fraction commonly contains discrete clay minerals (smectite, illite, kaolinite) [33]. French green clays are dominated by 1Md illite and Fe-smectite also in the mineralogical aspect [23]. Despite the fact that the clay is one of the most popular and easily available minerals in Latvia, only 3.2% of the clay-containing cosmetic products are produced in Latvia. Most of clay-containing cosmetic products (40.8%) available in Latvia are produced in France [3]. Illite containing Latvian clays with fraction under 63 μm before and after the treatment can be used as sorbents in purifying facial masks, because their adsorption of oleic acid and squalene is comparable with commercial illite and chlorite containing facial masks. Illite containing clay fractions, obtained from untreated clays, can be used as UV filters in sunscreens and other cosmetic products with low SPF factors. The studies of clays available in Latvia do not provide any evidence of their antibacterial properties, but it is possible to improve the antibacterial properties of clay containing products by adding silver doped hydroxilapatite [5].

Clay is applied and used not only in pharmacy and cosmetics. Clays and clay minerals are used as well in environmental technology. Clay minerals can be used for the removal of organic pollutants from a water or by a filter [34, 35]. In order to remedy environmental damages caused by polluted gases the clays and clay minerals can be used as adsorbents in natural form or after specific modification [36]. Aflatoxins are toxic compounds found in grains and other food crops infested by Aspergillus fungi. Aflatoxins are
recognized carcinogens for animals and humans. Clay additives have been used to pelletize and improve the flow characteristics of animal feeds. Reduced aflatoxicosis in animals is an extra benefit of clay additives. Clay additive use has also been examined for reducing human aflatoxicosis [37].

However, clay minerals can also have an adverse effect on human health when they are inhaled over a very long period. In the lung, clay minerals can cause diverse pathologies such as cancer, mesothelioma, or pneumoconiosis, but the toxicity of these minerals is generally related to the presence of quartz or asbestos from mining operations. The pathogenicity of fibrous clay minerals (sepiolite and palygorskite) is related to the geological conditions of formation [15]. The studies of Bertolino et al. [38] on Mineralogy and geochemistry of bottom sediments from water reservoirs in the vicinity of Córdoba, Argentina: environmental and health constraints reveal alarming concentrations of trace metals (U, W, As). Regarding potentially toxic trace elements such as As, Cd, Hg, Pb, Te, Tl, Sb and Se, [39] simulated digestive processes with 14 different herbalist’s clays found on the Italian market and suggested for human internal use, and [40] carried out in vivo experiments on their mobility. The former observed that these trace elements are present in low concentrations after digestion, but pointed out that ingesting clays without knowledge of their composition may be dangerous. No information was available on the genotoxicity of clays or clay minerals [31].

In different places and different types of clay have different chemical, physical and biological composition; therefore its usage can be varied. The trace element contents in different clays are very variable [15, 41, 42]. Furthermore, the cosmetic ability of clays is not only influenced by their physicochemical properties. Other specific mineralogical and chemical properties also play vital roles in the cosmetic capabilities of clays [7]. Properties of Latvian illite clays for application in cosmetics depend on the amount of clay minerals, the presence of other non-clay minerals and particle size distribution [5]. Therefore, before the use of clay in the industry there has carefully been studied not only its chemical, physical and biological composition, but also specific mineralogical properties.

IV. CONCLUSION

Heavy metals in the lake Plusons blue clay do not exceed the permissible norms. The clay of the lake Plusons has high concentrations of Ca and Mn, which are valuable components for improving skin condition.

In microbial analysis the presence of Candida albicans, Pseudomonas aeruginosa, Staphilococcus aureus has not been stated.

Based on the performed chemical and biological analysis Latgale lake blue clay has a high potential for its use in cosmetics and medicine.

It is recommended to carry out further studies to get an in-depth understanding of the blue clay application possibilities in cosmetics, medicine or any other field. It is necessary to explore the lake blue clay mineral and granulometric composition and its anti-bacterial properties.

REFERENCES


