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Research paper

# Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses

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ABSTRACT

The present study was conducted to characterize the river sediment and the final peloid from San Diego de los Baños Thermal Center (Pinar del Rio, Cuba), based on its original sedimentary geochemistry and composition, in order to establish the physicochemical and geochemical properties for its inorganic quality assessment in therapeutic uses. The original sediment was extracted from the estuary of San Diego River, and then maturated with thermal waters, yielding a peloid with known anti-inflammatory and dermatological properties. A comparative study of total content and geochemical speciation of seven transition metals (Cr, Cu, Fe, Ni, Mn, Pb and Zn) in the sediments was performed using a sequential extraction procedure and Inductively Couple Plasma Emission (ICP) techniques, as well as hydrogeochemical modeling to predict and correlate species under the physicochemical conditions measured for the river and peloid sediments. The results showed that the main differences originated from maturation process are closely related to the changes in electric conductivity (EC) and redox potential (Eh). These variations are reflected in the composition of major elements, and at a lesser extent, in the total content of the transition metals. Most of the elements studied in this investigation appeared in the less mobile fractions, which suggested low availability in the sediments, under the studied conditions. In the case of Mn, species are mainly located in the most leachable fractions, which together with its relatively high content, indicates a need for regular monitoring of this element in the peloids used in the Thermal Center. The findings were useful to predict the behavior of these transition metals regarding solubility, potential motility and availability in the river and final peloid sediments, and led to classify the San Diego de los Baños peloid as mud or fangi. It was concluded that most of the metals are strongly retained in the peloid through the maturation process, as many factors contribute to the low mobility, such as the nearly neutral pH, the presence of organic matter, redox conditions, and the presence of carbonates and salts. The sediments were finally characterized regarding possible contamination, according to USEPA and background criteria, and were considered as non-polluted/non-contaminated except for Mn, which showed a moderate contamination factor. The results from the present work show the relevance of physicochemical and elemental characterization to peloid classification and quality assessment. Moreover, it evidences the importance of performing geochemical speciation using both experimental and theoretical techniques, for proper assessment of mobility and distribution mechanisms of soluble and solid mineral species present in these sediments.



## 1. Introduction

Thermal muds (peloids) are hydrothermal or hydrothermalized sediments produced by primary or secondary mixing of clay (geo) materials with salty thermo-mineral waters, accompanied by organic materials produced by the biological–metabolic activity of

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micro-organisms growing through years in the so-called "natural maturation process" (Veniale et al., 2007). The final product is a sediment containing micro-organisms and organic and inorganic compounds with biological activity that allow its application for treatment of different pathologies, usually related with stimulatory, antiphlogistic and analgesic actions (Veniale, 1997; Martin-Díaz, 1998; Carretero, 2001; Nappi, 2001; Tateo et al., 2005). The therapeutic use of peloids is called *Pelotherapy*, and it constitutes a typical procedure of medical hydrology for the treatment of the osteoarticular system, cutaneous diseases among others.

Nowadays, the new frontier of pelotherapy (healthy therapies focused on wellness and relaxing) is impacting two main hindrances: (i) natural occurrences of thermal muds are going exhausted; and (ii) focused treatments of specific pathologies need the formulation of peloids possessing suitable properties. Therefore, many spa-centers currently prepare the thermal muds by "maturation" of sedimentary clays mixed with thermo-mineral waters, as shown in Fig. 1 (Veniale et al., 2007). The maturation process can be very complex since it is necessary to initially modify the water–sediment paste environment to create the appropriate conditions for developing a new-growth of micro-flora and fauna, as well as their metabolic products. The final product will depend not only on the conditions used in the maturation process (pH, Eh, temperature, light exposure, hydrologic regime) but also on the initial composition of water and sediment, such as biogenic elements and organic matter, as well as on the maturation time and the specific procedure. All these variables have a decisive effect in the chemical and biologic reactions that can occur during maturation, defining the properties of the final peloid (Carretero et al., 2010).

During the last decades, several investigations have been done to get insights on the reactions occurring during the "maturation" process of the sediments (Veniale et al., 1999, 2004), which has evidenced the need for "certification" of the quality and suitability of peloids devised for specific therapies (Nicolini et al., 2004; Setti et al., 2004). Important reactions related with the maturation process have been associated with changes in the redox environment, which causes ions and other compounds to be released and incorporated into the original sediment. In particular, mobile and/or exchangeable toxic elements (e.g. Fe, Mn, Cu, Zn, Pb, Cr, As, Cd, Hg), are of special concern, since they can be scavenged by the skin sweat (Summa and Tateo, 1998; Summa et al., 2005; Tateo and Summa, 2007). These metals have therefore become important discussion issues in the "certification" of the quality of sediments for therapeutic uses (Nicolini et al., 2004; Setti et al., 2004). However, there are few comprehensive studies related to the presence and availability of these metals in sediments after maturation process, despite being a key knowledge to understand the possible beneficial and/or dangerous effects to human health (Carretero, 2001; Wilson, 2003). In particular, there is a need for studies related to the geochemical composition of peloids used in balneotherapy due to the risk of heavy metals in peloids, the changes in the maturation process, the interaction between metals and other components of the peloid matrix, and with the human biomembranes, with possible re-adsorption through the skin (Mihelčić et al., 2012).

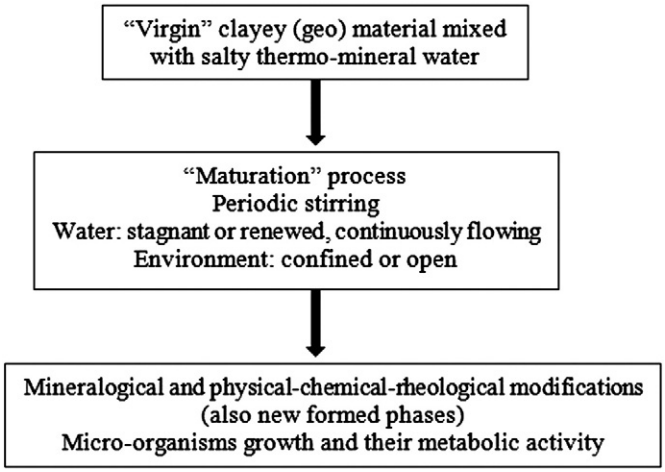


**Fig. 1.** The cycle for the preparation (maturation) of thermal mud (Veniale et al., 2007).

The potential effect of metals in peloids can be assessed by total content determination and by speciation. Depending on chemical and geological conditions, metallic elements can be partitioned into different chemical forms that are associated with a variety of organic and inorganic phases (Pagnanelli et al., 2004; Clozel et al., 2006; Arain et al., 2007). Thus, speciation analysis of metallic elements might provide useful information regarding the potential mobility and bioavailability of a particular element, which consequently can offer a more realistic estimation of its effects (Yang et al., 2009).

In Cuba, there is still a great reserve of natural peloids, used in pelotherapy. However, in the case of San Diego de los Baños peloid, the original sediment is extracted directly from the estuary of San Diego River, and enriched later with inorganic and organic components, as well as with the microbiota of calcic sulfated, fluoric, radionic and sulfurous mesothermal waters (33 °C) of San Diego de los Baños Thermal Center. Our group has systematically study these waters, which show low Eh values (−226 to −270 mV) and their EC values oscillate between 1480 and 2200 μS/cm (Fagundo et al., 2007). The maturation process of the sediment is done using a static, open method for 15 days, and under different environmental conditions. The peloid produced in this way is routinely used in the form of mud-bath or mud-patch to alleviate inflammatory (osteoarthritis, rheumatoid arthritis, bursitis) and dermatological (eczemas, psoriasis, cutaneous seborrhea and mycosis) processes, as an analgesic, in male and female infertility treatments, and as a cosmetic product (acne, keloids). In a previous study, we characterized the organic content of the original sediments and resultant peloids by chromatographic techniques, and found that there is relationship between these compounds and the potential therapeutic action of the thermal mud (Suárez et al., 2011). These organic compounds are present as a result of the organic matter decomposition and the rich biological activity in the peloid. The presence of bioglea in San Diego de los Baños has been well documented, and it is composed in the higher percent of cyanobacteria as the *Leptothrix subtilissima*, and in the lower percent by diatoms (Ex. *Navicula* sp.) (Pérez Loyola et al., 2003). On the other hand, the sanitary safety of the peloid is guaranteed by verifying or limiting the presence of total coliforms, *Escherichia coli*, fecal streptococcus, *Pseudomona aeruginosa*, *Staphylococcus aureus*, *Clostridium perfringens* and *Salmonella* (NC, 1998).

The present study aims to characterize further the complex systems that compose the San Diego de los Baños peloid, in order to establish the physicochemical properties, geoavailability and inorganic content quality related to its therapeutic uses, and based on its original sedimentary geochemistry and composition. Total concentration and chemical speciation of Cr, Cu, Fe, Ni, Mn, Pb and Zn, will be determined in the different phases, by Inductively Couple Plasma Emission (ICP) techniques, which will lead to a partial assessment of the maturation process to determine the influence of this procedure in the incorporation, leaking or mobility of metals in the sediment.

## 2. Materials and methods

### 2.1. Field methodology

Samples of the original river sediment (RSD) were collected directly from the estuary of San Diego River, while peloid sediment (PSD) samples were collected from the maturation pool in San Diego de los Baños Thermal Center, located in Pinar del Rio, Cuba. In both cases, a composite sample was prepared from the different collected fractions. After sampling, sediment samples were sealed in clean polyethylene