Physicochemical Nature and Therapeutic Potential of Thermal Springs: An Overview

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Abstract
In this article physicochemical characteristics and therapeutic potentials of world’s renowned thermal springs including Manghopir (Pakistan), Shrgalijuut (Mongolia), Ranong (Thailand), Kusatsu (Japan), Southern/Nothern part of Limpopo (South Africa), Arkansas (USA), Selangor Malaysia and Ikogosi (Nigeria) were reviewed and compared. Thermal springs were characterized by flame photometry, graphite furnace atomic absorption spectroscopy, ion chromatography, inductively coupled plasma atomic emission spectroscopy, X-ray fluorescent spectrometry, atomic absorption spectroscopy and titrations (argentometric, acidometric & complexometric). They are classified on the basis of pH, temperature and mineral contents. The common mineral contents in these springs include 0.67-621.99 mg/L sodium, 0.67-189 mg/L potassium, 2.06-84 mg/L calcium, 0.00-56 mg/L magnesium, 0.12-12 mg/L fluorides, 0.00-982.62 mg/L chlorides, 0.15-442 mg/L sulphates and 4.3-494 mg/L bicarbonates. Their temperatures were found in the range of 26.0-90.50 °C with the pH 2.0-9.7 and TDS value of 104.74-2188 mg/L. The mineral concentration in most thermal springs is highly ideal for the treatment of numerous diseases including atopic dermatitis, cardiovascular diseases, inflammatory arthritis, ankylosing spondylitis, osteoarthritis, chronic rhinosinusitis, chronic bronchitis/asthma, obesity, wounds healing and cardiovascular diseases. For curative purposes, the body is soaked in thermal waters or water may be used in the form of drinking/inhaling.

Keywords: Thermal Springs, Soaking/bathing, Nutrient’s intake, Disease’s Treatment

Introduction
Thermal springs release the hot water whose temperature is considerably higher as compared to that of ground water. They are generally emerged along the deep faults and fissures of earth from which the ground water is releases into the surface. Disintegration of radioactive elements, exothermic reactions and geothermal energy cause the high temperature of thermal springs. These springs are comprise of high concentration of dissolved solids and variety of minerals like alkali metals, alkaline earth metals, carbonates, bicarbonates, sulphates, trace elements and gases [1]. There are reports that thermal spring water is highly effective in the treatment of various diseases e.g., atopic dermatitis, cardiovascular diseases, inflammatory arthritis, ankylosing spondylitis, rheumatic disease, asthma and rhino sinusitis. Moreover, it is commonly believed that soaking in hot spring helps overcoming joint pains and strained muscles [2, 3]. Absorption of minerals through soaking is fractional and the amount absorbed into the body is concentration dependent [4]. The hot mineral water contains over 80 essential nutrients and minerals which are highly important for about 7000 enzymatic processes necessary for human body’s
metabolism. Many elements found in such waters possess therapeutic properties. Balneology which involves the use of natural thermal mineral water in order to treat a number of diseases, has a long history [5]. Animals are believed to discover the medicinal properties of thermal springs; they used this water to cure their feet wounds or to maintain their body temperature and hence, mankind began to explore the therapeutic properties of hot springs. In 1986, thermal springs were declared as an alternative treatment option to obtain good physical and mental health. Thus medical hydrology has been accepted as complementary medicine and an emerging new discipline by World Health Organization [6].

Though the thermal springs are natural sources of important nutrients and minerals for balneotherapy, however, reported studies also suggest that they may also contain toxic elements such as arsenic and mercury so care should be exercised regarding appropriate and precise use of thermal springs [7]. The presence of metal contents in balanced amounts is compulsory as their exceeding concentration in water may also lead to environmental issues [8-11].

Keeping in view the use of thermal springs for curative purposes, the physicochemical characteristics and therapeutic potentials of thermal springs of World’s renowned thermal springs e.g., Manghopir (Pakistan) [12], Shrargalijuut (Mongolia) [13], Ranong (Thailand) [14], Kusatsu (Japan) [15], North and Southern Part of Limpopo (South Africa) [7, 16], Arkansas (USA) [17], Selangor (Malaysia) [18] and Ikogosi (Nigeria) [19] are reviewed in this article. Table 1 displays the brief geology, sampling and methodology of the investigated springs.

### Table 1. Brief geology, sampling and methodology of the investigated springs.

| Springs          | Sampling                                                                 | Methodology                                                                 | Geographic location and geology                                      | References |
|------------------|---------------------------------------------------------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------------|------------|
| Manghopir (Pakistan) | 26 samples collected from different sites (closed bath and open bath)  | Titrations (Argentometric, acidimetric & complexometric) for Cl, HCO₃, Alkalinity, Gravimetric analysis for Ca, Mg & TDS, Flame photometer for Na & K | About 1.3 km from north Karachi at the base of Haller mountains range 35p/11 Lat. 24.59° and 67.06° above sea level | [12]       |
| Shrargalijuut (Mongolia) | 23 samples collected from the said spring | Digital instruments for pH, Temp and conductivity, Na and K by inductively coupled plasma optical spectrometry, Ca and Mg by Trilon-Bitratrin method, Argentometric, Acidimetric titrations for HCO₃, Cl, SO₄ | About 60 km north-east of Bayankhongor city, spring covers the banks of the river between the peaks Myangan Ugalzat Uul (3483m) and shrargalijuut Uul (3137m) in the Gobi region | [13]       |
| Ranong (Thailand) | Samples collected from two hot spring Rashwni (father well) & Porn rang | TDS by titration K, Ca, Mg, Na, F, Cl, SO₄, HCO₃ by chromatographic technique, Fe, Mn Pb by graphite furnace atomic absorption spectrometry | 2 km east of Ronong town, porn-rang, hotspring located in Nga national park and far larger than rashwani hot string | [14]       |
| Kusatsu Onsen (Japan) | Samples collected from 6 major hot springs in the Kusatsu hot springs | Flame emission spectroscopy (FE), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ion chromatography | Located at the eastern foot of Kasatsu-Shirane volcano are all strongly acidic | [15]       |
| Limpopo North & South (Africa) | 5 samples (southern part) 8 samples (from northern part) | Chemical analysis conducted by institute of water, climate and soil (ARC, Pretoria ) | Includes various lithologies, Goud plaats-Hot river Gnessi suite and Beit Bridge complex. Surface geology indicated as quartzite, shall and red sandy sand stone, 50 miles distance from little rock and 75 miles east of the Oklahoma line. 500 feet above sea level and lies at the easterly base of the mountain complex Ouachita range | [7, 16]    |
| Arkansas (USA) | Sample were collected from all the hot spring area | Gravimetric analysis was done for all ions | Western part of the Peninsular Malaysia along the main range Granite Batholith | [17]       |
| Selangor (Malaysia) | Samples were collected from 11 hot springs | Energy dispersive X-ray Flourescent spectrometry (EDXRF) for Na,K,Cu,S, and ion chromatography for SO₄ and Cl | Its under lain by a group of slightly migmatised to non-migmatised para-schists and meta-gneous rocks (quartized quartz and granulites). | [18]       |
| Ikogosi (Nigeria) | Samples collected from (OOzing point of warm and cold springs and their mixing point) | TDS by gravimetric analysis, Na, K, Mg, Ca by Alpha 4 Atomic Absorption Spectrometer other ions analysed by standard procedures | | [19]       |
Numerous studies involving the patients and Murine models were also reviewed for the treatment of diseases including atopic dermatitis [20-22], psoriasis [23-25], rosacea [26], diabetes [27, 28], rheumatoid arthritis [29], ankylosing spondylitis [30], osteoarthritis [31-33], chronic rhinosinusitis [34], chronic bronchitis/asthma [35, 36], obesity [37], wound healing [3] and cardiovascular diseases [38, 39]. Other literature consulted include that of physical and chemical nature [2, 4-7, 14, 16, 40-50], geological influence on chemical composition [7, 16, 51], classification of thermal springs [6, 40], ways of using the thermal mineral water for curative purposes [52-57] and therapeutic potential of thermal springs [58-65].

**Physical and chemical nature of thermal springs**

The physicochemical properties of world’s eight renowned thermal springs are given in Table 2. The temperature and pH lies in the ranges of 26-90.50 °C and 2.0-9.7, respectively; the total dissolved solids lie between 104.74 and 2188 mg/L, but most thermal springs contain their values less than 400 mg/L. Common cations present in thermal water include K⁺, Na⁺, Mg²⁺ and Ca²⁺. The magnesium (Mg), calcium (Ca), potassium (K) and sodium (Na) contents lie in the ranges of 0.00-56 mg/L, 2.06-84 mg/L, 0.67-189 mg/L and 0.67-621.99 mg/L, respectively. Anions present in hot springs include Cl⁻, SO₄²⁻ and HCO₃⁻ with their concentrations in the ranges of 0.00-982.62 mg/L, 0.15-442 mg/L, and 4.3-494 mg/L, respectively. Most of the thermal springs do not have fluoride ions; however, some thermal springs contain the F⁻ ions in range of 0.00-11 mg/L. Fluorides are present in less amount than Cl⁻, SO₄²⁻ and HCO₃⁻ in most of the thermal springs. Trace elements found in hot/thermal springs include majorly zinc (Zn), iron (Fe), strontium (Sr), lithium (Li), selenium (Se), bromide (Br) and iodide (I) ions. The gases such as H₂S, NH₃, He, Ne and Rn are also reported in hot/thermal springs [2, 4-7, 14, 16, 40-50].

**Table 2. Physical and chemical properties of world’s eight renowned thermal springs regions.**

|                        | Mongolir (Pakistan) [12] | Shgraljiiu (Mongolia) [13] | Ranong (Thailand) [14] | Kusatsus (Japan) [15] | Southern Part [7] | Northern Part [16] | Arkansas (USA) [17] | Selangor (Malaysia) [18] | Ikogos Nigeria (Nigeria) [19] |
|------------------------|--------------------------|-----------------------------|------------------------|-----------------------|-------------------|-------------------|----------------------|--------------------------|-----------------------------|
| Temp°C                 | 47                       | 50-90.50                    | 61-65.3                | 60-67                 | 40-60             | 26-67.5           | 32-62                | 36.7-67.9                | 35.20-37.0                  |
| pH                    | 7.2-7.6                  | 8.2-9.7                     | 7.56-7.74              | 2                     | 6-9               | 7.35-9.70         | 4.52-7.70            | 7.14-8.98                | 6.1-7                       |
| TDS (mg/L)            | 2180-2188                | -                           | 210-230                | -                     | <450              | 104.74-1385       | >400                 | 225-376                  | 170-514                     |
| Sodium (mg/L)         | 544-555                  | 62.5-105                    | 10.2-13.8              | 53.7                  | 21.98-151.6       | 10.59-621.99      | 4                    | 33.68-81.91              | 0.67-0.71                   |
| Potassium (mg/L)      | 21-25                    | 1.3-1.9                     | 150-189                | 16                    | 2.9-6.13          | 0.99-21.79        | 1.5                  | 1.47-56.81               | 0.67-0.84                   |
| Calcium (mg/L)        | 80-84                    | 1.8-7.2                     | 18.7-20.6              | 72                    | 13-36.13          | 1.31-79.37        | 45                   | 2.44-19.77               | 2.06-2.67                   |
| Magnesium (mg/L)      | 56                       | 0.4-0.5                     | 0.36-0.51              | 39                    | 1.8-6.44          | 0.00-27.60        | 4.8                  | 4.22-4.32                |                             |
| Fluoride (mg/L)       | -                        | 0.00-1.37                   | 0.12-0.89              | 12                    | 0.95-11           | 0.18-6.50         | 0.2                  | _                       | _                           |
| Chloride (mg/L)       | 584-599                  | 13-26                       | 18.3-23.2              | 343                   | 2.21-138.5        | 19.43-982.62      | 1.8                  | 7.06-20.66               | 0.0-0.004                   |
| Sulphate (mg/L)       | 437-442                  | 25-66                       | 8.1-12.1               | 611                   | 2.16-92.82        | 2.98-226.00       | 8                    | 0.15-1.51                | 30.81                       |
| Bicarbonate (mg/L)    | 395-494                  | 97-170                      | 4.3-5.7                | -                     | 102-213.5         | -                  | 165                  | _                       | 35-51.5                     |

Temp°C = Temperature
**Geological influence on chemical composition**

The origin of hot springs is owed to the local presence of deep geological structures such as faults, folds, fractures, and dykes providing means of circulation to depth and return of heated water to surface. The amount of dissolved salts, nutrients and trace elements found in thermal waters are dependent on regional differences in climate, geology, soil and vegetation [7]. The less saline water comes out from crystalline rocks whereas the saline water is found to be associated with sedimentary rocks [16]. The physico-chemical nature of hot water depends on mixing with fresh precipitation, rock or water interaction in deep formations, residence time of hot water in migration pathway, migration depth, composition of infiltrating solution etc [51].

**Classification of thermal springs**

Thermal springs are classified on the basis of temperature, pH and dry waste [6, 40].

1. There are three types of thermal springs according to temperature:
   (i) Hypothermal springs: The temperature ranges from 20 to 30°C in these thermal springs.
   (ii) Thermal springs: The temperature of these thermal springs is in the range of 30 to 50°C.
   (iii) Hyper-thermal springs: The temperature of these thermal springs is above 50°C.

2. The thermal water is classified on the basis of pH into six classes:
   (i) Alkaline springs $9 \leq \text{pH}$
   (ii) Weak alkaline springs $7.5 \leq \text{pH} < 9$
   (iii) Neutral springs $6 \leq \text{pH} < 7.5$
   (iv) Weak acid springs $4 \leq \text{pH} < 6$
   (v) Acid springs $2 \leq \text{pH} < 4$
   (vi) Strong acid springs $\text{pH} < 2$

3. Hot springs may be classified into following three categories depending upon their dry waste material:
   (i) Minerals from 1-1.5 g/L
   (ii) Middle minerals from 0.2-1.0 g/L
   (iii) Oligo minerals less than 0.2 g/L

**Ways of using the thermal mineral water for curative purposes**

For the therapeutic purposes, the thermal/hot mineral waters can be used internally or externally. The important ways of using the thermal/hot minerals waters are as follows:

**Balneotherapy**

The immersion of the body (except head) or body parts into the water for the treatment and cure of diseases is called bathing or soaking [52]. The minerals and other substances in the water are transferred to the skin and blood streams through the process of osmosis [53]. The osmotic pressure, mineral concentration, pH, the nature/amount of mineral contents [54], fat/water solubility due to structure of membrane and fluid condition of the individual [55] affect the osmotic transfer and the movement of minerals into the body. Medical balneotherapists have noted that even small amounts of therapeutic minerals absorbed into the body through skin have a significant therapeutic value [56].

**Hydropenia (mineral water drinking cure)**

Ingestion of mineral water is another treatment method which aimed at modification of metabolic activities, gastrointestinal, renal and urodynamic functions. The mineral water can also be taken as a substitute for drinking and supplementation of minerals.

**Inhalation**

Mineral waters and some other natural gases present in thermal/hot springs (mainly radon) are used via the respiratory tract. It has beneficial effects on the respiratory functions and mucosa of respiratory tract. After inhalation substances get absorbed and induce systemic effects [57].
**Table 3. Studies reported on therapeutical potential of thermal springs.**

| Subject | Water Classification | Pathology | Mode of Therapy | Treatment Duration | Results | References |
|---------|----------------------|-----------|----------------|-------------------|---------|------------|
| Murine model | Na-HCO₃ | Balneotherapy | 5 mins daily for one week | Effective and safe | [20] |
| 70 patients | Acidic plus Mn 1.4 mg/L, 10.3 mg/L | Atopic dermatitis | Balneotherapy | Useful for controlling the skin symptoms of acute flares of AD | [21] |
| 104 children | Na and Mg rich water | Balneotherapy | Once daily (20 min) for 2 weeks | Effective for mild to moderate AD | [22] |
| Murine model (Oxazolone induced mice) | Sulphurous mineral water | Psoriasis | Balneotherapy | Somatostatin plasma concentration was increased. Significant reduction in PASI score | [23] |
| 71 adult patients with PASI score greater than 10 | Sodium and magnesium rich water | Psoriasis | Balneotherapy | Minor therapeutic effects with saline spa water alone, and no beneficial effect of bathing to enhance phototherapy | [24] |
| Patients with mild to severe psoriasis | Selenium rich water | Psoriasis | Immersion and drinking | Improvement in psoriatic plaques | [25] |
| Patients | Na, Ca, sulphate bicarbonate and fluoride | Psoriasis | Balneotherapy | Significant down regulation of TNF α, IL-1α and VEGF gene expression. Benefits observed in rosacea and psoriasis | [26] |
| Murine Model (alloxan induced diabetic rats) | Sulphurous and alkaline water Andrade junior | Diabetes | Ingestion | Reversed the hyperglycemic state and improved SOD synthesis. Beneficial effects for diabetics | [27] |
| 35 patients (46-74 years old) | Rich in sodium chloride and sulfate | Rheumatoid arthritis | Mineral water baths and mud packs | Reduction blood glycaemia levels. Effective for type-2 diabetes. | [28] |
| 41 patients | Rich in sodium chloride and sulfate | Rheumatoid arthritis | Mineral water baths and mud packs | Temporary improvement in clinical indices | [29] |
| 14 patients | Rich in sodium chloride and sulfate | Rheumatoid arthritis | Mineral water baths and mud packs | Improvement in morning stiffness and significant reduction in the use of analgesics and NSAIDS | [30] |
| Murine model (Wistar rats) | Sulphurous rich water | Osteoarthritis | Balneotherapy | Reduced cartilage destruction and oxidative damage | [31] |
| 46 patients (57 to 85 years old) | Sodium-bicarbonate with fluoride and chloride ions | Osteoarthritis | Balneotherapy | Effective in advanced knee arthritis | [32] |
| Murine Model (Old female NMRI mice) | Na, K, Mg, bicarbonates sulphate and H₂S | Osteoarthritis | Balneotherapy | Found effective as anti-inflammatory and analgesic | [33] |
| 80 patients with CRS | Sulphurous mineral water with Na, Ca, Mg, chlorides, nitrates and H₂S | Chronic rhinosinusitis | Warm vapors inhalation and nasal irrigations | Significant reduction in Serum concentration of IgE, effective for CRS | [34] |
| 39 patients | Sodium-bromide-iodine | Chronic bronchitis / asthma | Inhalation | Reduces proportion of neutrophils in induced sputum, may have mild anti-inflammatory effect on the airways | [35] |
| Heavy smokers (50-75 years old) | Sulphurous mineral water | Chronic bronchitis / asthma | Inhalation | Reduction of NO shows anti-inflammatory effect | [36] |
| 50 women (average age 35) | Bonebole (klaipeda region) Na, Ca, Sulphate and bicarbonate | Obesity | Balneotherapy | Improvement in skin condition and reduction of hypodermic body fat content | [37] |
| Murine model (100 male rats) | Caltic-magnesic-sulphate mineral | Cardiovascular | Ingestion | Regulating the enzymes responsible for bile acid and cholesterol metabolism | [38] |
| 12 Hypercholesterolic patients | Bicarbonate-rich water | Cardiovascular | Ingestion | Decrease in basal TG and VLDL TG and VLDL cholesterol. Effective for hypercholesterolemia | [39] |
| Murine Model 9 Nude rats) | Carbonated with sodium (42°C) | Wound healing | Bathing at 42°C | Increase vessel density and reduced inflammatory cells of wound area | [3] |
Bicarbonate mineral water

Bicarbonate natural mineral waters are alkaline with small amount of minerals having diuretic characteristics. The bicarbonate minerals have positive effects on digestive tract and play a vital role in the prevention of cardiovascular diseases [58].

Sulphorous mineral waters

Sulphurous mineral water is abundant in hydrogen sulphite (HSO\textsubscript{3}) and possesses the ability to cure internal organ disorders e.g., ischemia, adverse affects on kidney and nervous system and high blood pressure [58, 59]. Sulphurous mineral waters contain beneficial anti-pruritic and anti-inflammatory keratoplastic effects [60]. Its anti-fungal and bactericidal effects have enabled its applications in the treatment of tinea carports, infected leg ulcers, tinea versicolar, tinia capitis and tinia corporis. Sulphurous bathing has been considered useful for immunomediated conditions including atopic dermatitis and contact dermatitis psoriasis. It was recently concluded that the sulphurous minerals water can play a pivotal role in immune-regulation in the skin [61].

Salt mineral waters

Chlorides are often found in combination with sodium and are the main constituents of “salt mineral waters”. Such waters from mineral thermal springs are particularly valued and believed to improve the joint movements, muscle strengthening and improve/maintain functional mobility. Well known for its anti-inflammatory effects, it is also applied to treat successfully a variety of pathological conditions, such as issues of gastrointestinal system [61-65].

Calcic mineral waters

Calcium along with the bicarbonate content maintains an alkaline environment and helps in improving the acid-base balance in blood. The positive effects of calcium-rich mineral waters on bone mineralization have been verified [58].

Magnesia mineral waters

Such waters are characterized by the presence of magnesium as an essential ingredient. The presence of magnesium with sulphate, bicarbonate and calcium minerals in waters can induce the therapeutic activity in functional disorders of biliary tract. High range of magnesium is important for oddi sphincter relaxation and allows the bile flowing and also supports biliary ducts activity [58].

Conclusion

Thermal springs are the natural sources of many minerals depending on the geographical and geological conditions of the region and site. They are classified on the basis of pH, temperature and mineral contents. Presence of more than 80 essential nutrients and minerals in thermal springs enables them to possess therapeutic potential and makes them highly ideal for the treatment of numerous diseases including atopic dermatitis, psoriasis, rosacea, diabetes, rheumatoid arthritis, ankylosing spondylitis, osteoarthritis, chronic rhinosinusitis, chronic bronchitis/asthma, obesity, wounds healing and cardiovascular diseases. For curative purposes, the body is soaked in thermal waters or water may be used in the form of drinking/inhaling. The investigations on world's renowned thermal springs including Monghopir (Pakistan), Shargali Juul (Mongolia), Ranong (Thailand), Kusatsu (Japan), Southern/Northern part of Limpopo (South Africa), Selangor (Malaysia) and Ikogosi (Nigeria) contain 4-621 mg/L sodium, 0.99-189 mg/L potassium, 0.3-84 mg/L calcium, 0.00-56 mg/L magnesium, 0.00-11 mg/L fluorides, 0.00-982 mg/L chlorides, 0.00-442 mg/L sulphates and 10-494 mg/L bicarbonates. Their temperatures were found in the range of 32.0-90.5 °C with the pH 2.0-9.7 and TDS value of 104.74-1857 mg/L. Thermal springs classified on the basis of pH, temperature and mineral contents.

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