

Role of hot springs' hydrochemistry in Balneotherapy, Case Study: Fotoyeh and sanguyeh springs, western Hormozgan

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Abstract

Introduction: Hydrochemical properties of waters used in balneotherapy are very important, as they play a key role in success or failure of this kind of treatment. There are 30 mineral and hot spas in Hormozgan Province, Southern Iran, which are traditionally used for treating diseases. In this study, hydrochemical properties of Fotoyeh and Sanguyeh Springs, in western Hormozgan Province, are discussed and analyzed.

Methods: The mentioned springs' water was sampled four times during different seasons of 2012. Physicochemical factors including EC, pH, and temperature were measured using portable devices at the sampling point; whereas primary and secondary ions were measured using ICP, titration, atomic absorption spectroscopy and photoelectric flame photometer in laboratory. Radon concentration also was measured by Rad7, an active radon detector, at the sampling location.

Results: Measurements showed that the average total of minerals in Fotoyeh and Sanguyeh springs is 5741 and 24037 mg/l and their mean electrical conductivities (EC) were 9626 and 42550 $\mu\text{s}/\text{cm}$, respectively. Sodium cations, chloride and sulfate anions are the most frequent primary ions of these springs. Concentration of some rare and secondary elements and heavy metals in the mentioned springs varies from 0.1 ppb to 10 ppb and radon concentration in Sanguyeh and Fotoyeh Springs was 76.51 and 159.98 kBq/m^3 , respectively.

Conclusion: Water in Sanguyeh and Fotoyeh Springs is of sodium-chloride type with high concentration of sulfate for treating rheumatism, lymphatism, Rickets, gynecological diseases and localized swelling. Since concentration of some rare elements and heavy metals such as copper, plumb, and antimony is high in these springs, drinking, vapping or injecting them in the framework of balneotherapy is not recommended. Likewise, regarding high radon concentration in the Fotoyeh Spring, frequent and long-term uses seem unhelpful.

Key words: Balneotherapy – Hydrochemistry - Hot Springs - Radon Gas - Fotoyeh

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Introduction:

Using mineral and hot water springs for treatment purposes has a very long history as the first time human being started to use this treatment is unknown, so far. It seems that people who lived around hot water springs had found unique properties of these waters after frequent experiments; however, it seems that Antyllus, an ancient Greek physician (circa 200 AD), was the first physician who wrote a pamphlet about advantages of some mineral waters and prescribed them for treating certain diseases (1). A physician named Polin (1979) for the first time tried to treat gout, sciatica and nervous pains using hot and mineral waters (through bathing, drinking, inhaling, etc.) (2).

Ancient geographical and historical writings had pointed to several famous mineral and hot springs in Iran and other Muslim lands and their health benefits for certain diseases such as gout, mange, vitiligo and colic. Likewise, it has been recognized that such springs can heal abscesses, wounds and bone fractures (3).

Thanks to its unique geological properties including proximity to the folded Zagros Zone, containing numerous salt domes, there are several hot springs in Hormozgan Province, Iran. Thirty mineral springs have been identified in the Hormozgan Province, out of which 20 ones are hot springs.

The root of Balneotherapy is the Latin word *balneum*, which means bath. It is an experimental and traditional treatment in which patients immersing their body in cold and/or hot mineral waters in order to treat some diseases (6-8). This type of treatment is very popular in treating skin diseases; perhaps, because such diseases are very prevalent in the developing countries and at the same time it is a less expensive treatment in contrast to other dermatologic methods. This treatment may be ineffective to treat diseases, however it has no side effects, as well (8). Although using pools containing hot and mineral water is the most popular way to use such waters, there are other methods including drinking, injecting, using gas, vapor, controlled shower, etc.

Balneotherapy is used for treating significant skin diseases such as eczema, warts, psoriasis, vitiligo, and erythroderma, but it is mostly used to treat psoriasis and relevant problems (8). Many

successful cases of treating diseases using mineral and hot waters across the world, which some of them are reported as follows.

Pinton et al. (1995) demonstrated that 20-minute showering with 35° Celsius mineral water and drinking 1 liter mineral water containing selenium compounds every day has been resulted in improvement of half of 92 patients of the their study (10). Cobota et al. (1997) published results of a study in which the effect of balneotherapy in treating atopic dermatitis (a skin condition which is often accompanied with allergic symptoms such as rhinorrhea and sneezing and is exacerbated with staphylococcus) has been explained. They demonstrated that using hot acidic mineral water (42°C) bath for ten minutes two times a day during a two-month period will treat dermatitis and will remove staphylococcus bacteria from the skin of 76 percent of 70 patients in their study (11).

Aragane et al. (2001) indicated that balneotherapy is useful for treating scleroderma (12) and Stact et al. (2002) also demonstrated that balneotherapy affects migration and stimulation of human langerhans cells (13). Balneotherapy has also general effects such as improving thyroid function (14), lipid metabolism (14,15), cardiovascular system function (15), respiratory system (14), nickel and cobalt disposal, diabetes mellitus (14,16), stomatologic diseases (17), stomach ulcer (18-20), rheumatoid arthritis (21,22) and arthritis (22).

The first scientific dispersed studies about Iranian mineral and hot springs started by foreign tourists and scientists in the second half of 19th century and they were continued in a more scientific and precise form since 1927 (4); however, many Iranian mineral and hot springs and their physical, chemical and medical properties have not studied so far. Regarding health benefits of this national wealth hence its undeniable economic value in medical tourism, conducting regular and extensive studies in this regard seem necessary.

Methods:

Sanguyeh and Fotoyeh Springs, in villages with the similar names, are located 30 km and 48 km from northern Bastak City in western Hormozgan Province and are used by both natives and

passengers from other provinces throughout the whole year. The climate of the area is warm and semiarid and its height above sea level is 520 m. Lack of any hydrochemical information about the mentioned springs, their proximity to residential areas, large number of visitors, their proximity to salt domes and the potential risk of radioactive anomalies that may influence them were amongst the most important reasons to select the mentioned springs in this study.

Faryab hot springs of Sangueh and Fotoyeh were sampled through four phases during various seasons of 2012 (winter 2011 to fall 2012) and a single phase in fall 2012. Initially sterile bottles were filled with spring's water and then they were emptied and this process repeated two times; then samples were prepared by soaking the whole bottle under the water where the spring rises. The prepared samples were sieved using filter papers, with a size of 0.45 μm , in order to remove any possible particulate. Two separate sterile polyethylene bottles were used in any attempt of sampling during all five stages; one was used for assessing anions and after adding several drops of Merck nitric acid for declining its pH to less than 2 (in order to prevent possible oxidation, absorption and precipitation reactions of some cations and also to minimize or prevent growth of bacteria) the other one was used for assessing cations and finally all bottles were sent to laboratory. All physicochemical factors including EC, pH, and temperature were measured by a portable multimeter (model: WTW-Multi 340i) at the sampling location. Chemical analysis of samples prepared through first four phases was conducted in Amdel Lab, Australia, and Geological Survey of Iran (GSI) lab; whereas chemical analysis of the sample prepared in the fifth phase was conducted in the regional water laboratory in Hormozgan Province. Inductively couple plasma (ICP) was used for measuring primary cations, secondary and rare metallic and non-metallic elements (Ag, As, Co, Hg, Cu, Pb, Zn, Mg, Se, U, etc.) and secondary anions; whereas titration, atomic absorption spectroscopy and flame photometer, according to Kegli and Andrews instruction (1998) (25), as the most popular and accurate methods of measuring water samples, were used to measure primary anions (sulfate, chloride, bicarbonate and carbonate). ICP

is among the emission spectroscopy methods in which atom formation is carried out using the plasma synthesized by an inert gas, which is often argon. ICP is used for analyzing elements except Argon. Sample is directed by argon gas (which flows in the central quartz tube with a pressure of 1 l/min) upwards the tubes containing hot plasma. The sample can enter the torch in the form of warm steam or very fine powder. After evaporation, under influence of energy, the environment's electrons and ions are converted into their constituting atoms and finally are excited in the very warm environment of plasma. Rays emitted from the elements after passing a monochromator reach a photodetector, used for measuring its intensity. Therefore, it will be possible to determine and measure concentration of the element in question. Measurement accuracy regarding analysis of the iterative samples is about 3.8%. Anion-cation balance was used to make sure about accuracy of the analyses, according to which the total difference between concentration of anions and cations varied from 0.55 to maximum 3.36. With regard to the high importance of the carcinogenic Radon (^{222}Rn) and the possibility of its presence in the mentioned springs (because of the relationship between springs and salt domes), its concentration was measured by RAD7 radon monitor in each phase of sampling at the sampling location. Measurement accuracy of RAD7 is 1 Bq/m³ and it was calibrated before sampling phase in the Industrial University of Kerman laboratory.

Results:

Measurements in the sampling location show that the average water temperatures in Sangueh and Fotoyeh Springs are 38.1° Celsius and 38.8° Celsius and are roughly fixed throughout the whole year. Sodium cation is the most frequent element in both springs (on average 1120 and 7098 mg/l in Fotoyeh and Sangueh Springs, respectively). Chloride and sulfate anions are the most frequent primary anions in both springs (on average 1858 and 1804 mg/l in Fotoyeh Spring and 10660 and 1800 mg/l in Sangueh Spring). The average total dissolved solids (TDS) in Fotoyeh and Sangueh Springs are 5741 and 24037 mg/l, respectively and

the mean electrical conductivity (EC) of the mentioned springs is 9626 and 42550 $\mu\text{S}/\text{cm}$.

Despite high concentration of dissolved solids, concentration of rare, secondary elements and

heavy metals measured in the mentioned springs was not very high and varied from less than 0.1 ppb to several dozen ppb (Tables 1 and 2).

Table 1. Concentration of some secondary, rare elements, and heavy metals in seasonal water samples in Fotoyeh Spring (measured by ICP method)

Element	Ag	Al	As	Au	B	Ba	Be	Bi	Cd	Co
Unit	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
FT1	< 0.05	0.002	< 0.5	< 0.05	412	8.44	0.06	< 0.05	< 0.05	0.48
FT2	< 0.05	< 0.001	< 0.5	< 0.05	1650	6.52	0.14	< 0.05	0.05	0.15
FT3	< 0.05	< 0.001	< 0.5	< 0.05	840	13.6	0.11	< 0.05	< 0.05	< 0.02
FT4	< 0.05	0.100	9.1	< 0.05	912	8.61	< 0.05	< 0.05	< 0.05	1.25
element	Cr	Cs	Cu	Fe	Hg	Li	Mn	Mo	Ni	P
Unit	mg/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
FT1	< 0.001	4.12	2.6	< 0.01	< 0.1	100	0.68	3.4	9.4	< 0.02
FT2	< 0.001	4.98	10.7	0.05	0.1	74.1	4.61	4.1	< 0.2	0.04
FT3	< 0.001	4.32	4.0	0.01	< 0.1	137	0.12	4.5	5.8	0.18
FT4	< 0.001	2.89	2.3	< 0.01	< 0.1	104	2.30	1.0	25.2	0.06
Element	Pb	S	Sb	Se	Si	Sn	Sr	Ti	V	Zn
Unit	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L	ug/L	ug/L
FT1	< 0.1	831	1.38	2.3	7340	< 0.05	15.4	< 0.01	8.8	8.3
FT2	2.0	833	2.79	1.3	7680	0.11	15.8	< 0.01	1.0	26.8
FT3	0.3	833	3.43	1.2	13500	0.18	13.4	< 0.01	7.3	2.8
FT4	0.4	632	2.59	5.7	3970	< 0.05	12.2	0.02	76.6	5.7

Table 2. Concentration of some secondary, rare elements, and heavy metals in seasonal water samples in Sangueh Spring (measured by ICP method)

Element	Ag	Al	As	Au	B	Ba	Be	Bi	Cd	Co
Unit	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
SN1	< 0.05	< 0.001	< 0.5	< 0.05	454	32.6	0.12	< 0.05	0.06	0.32
SN2	< 0.05	< 0.001	1.3	< 0.05	1060	57.5	0.29	< 0.05	0.08	2.25
SN3	0.06	< 0.001	1.1	< 0.05	1060	72.2	0.22	< 0.05	< 0.05	2.59
SN4	< 0.05	0.080	5.2	< 0.05	913	36.1	0.30	< 0.05	< 0.05	1.55
Element	Cr	Cs	Cu	Fe	Hg	Li	Mn	Mo	Ni	P
Unit	mg/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
SN1	< 0.001	10.6	1.8	< 0.01	< 0.1	300	0.84	2	7.1	< 0.02
SN2	< 0.001	14.7	18.2	< 0.01	< 0.1	328	12.3	0.4	3.4	0.04
SN3	< 0.001	12.1	5.4	0.01	< 0.1	302	1.91	0.8	7.6	0.57
SN4	< 0.001	9.26	1.4	< 0.01	< 0.1	243	3.46	0.3	25.3	0.04
Element	Pb	S	Sb	Se	Si	Sn	Sr	Ti	V	Zn
Unit	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L	ug/L	ug/L
SN1	0.2	742	0.8	2	6960	< 0.05	16.2	< 0.01	17.2	1.5
SN2	0.6	799	1.96	7.1	7700	0.07	20.1	< 0.01	< 0.2	37.7
SN3	0.6	784	2.45	5.8	11700	0.09	15.4	< 0.01	26.8	1.1
SN4	0.3	665	1.91	11.4	3560	0.63	14.2	0.01	68.4	2.8

Measurements of the study showed that concentration of the dissolved radon in the mentioned springs varies from 53 to 104 kBq/m^3 in Sangueh Spring and varies from 125 to 253 kBq/m^3 in Fotoyeh Spring. Meanwhile, concentration variation range of Uranium in both springs is 0.53-2.13 and 1.99-2.52 g/l .

Conclusion:

Mineral waters temperature is one of their most important and tangible properties which is

important in several aspects including its medicinal property. Mineral waters temperature varies from environment temperature to boiling temperature. These waters are classified in terms of temperature degree as follows:

- Very hot waters: above 45°C
- Semi-warm waters: 28 to 35°C
- Temperate waters: 23 to 28°C
- Cold waters: under 23°C

Therefore, water of both Sangueh and Fotoyeh springs with 38.1 and 38.8 Celsius are classified as warm mineral waters. Water in Sangueh Spring is

salty and one can find brackish water in Fotoyeh Spring, which is not surprising regarding the measured TDS and EC values in this study (Fig. 1).

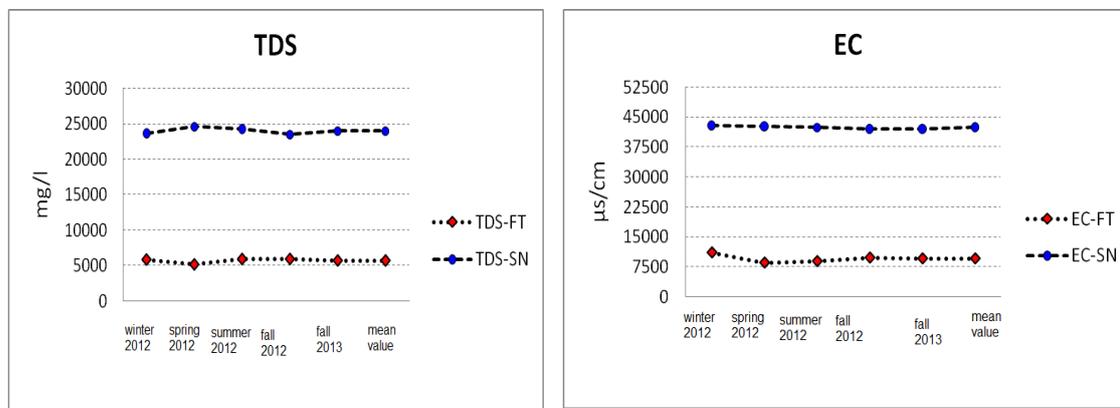


Figure 1. Variation of total dissolved minerals and water EC in Fotoyeh and Sangueh Springs

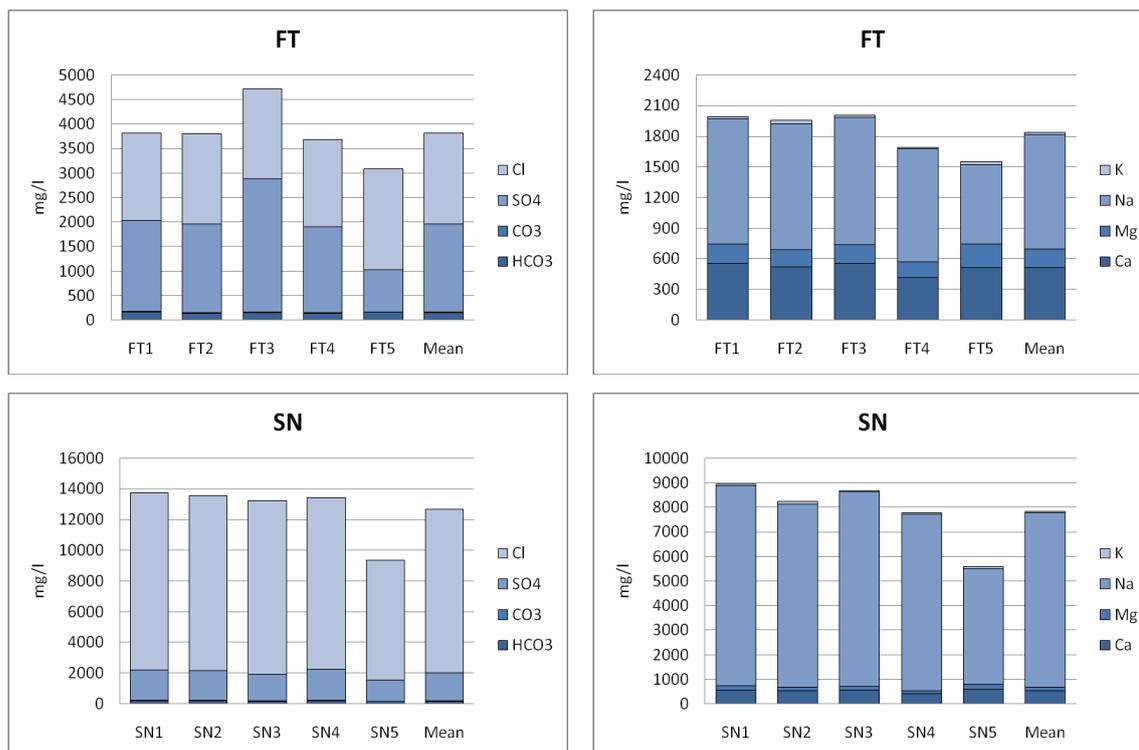


Figure 2. frequency of primary cations and anions in FT and SN springs (samples with codes of 1 to 5 represent winter 2012, spring 2012, summer 2012, fall 2012 and fall 2013)

Some references define waters proper for balneotherapy that whose total concentration of anions and cations is more than 1 gr/l (26,27).

Water in both springs is clear, colorless and without particulates and their mean pH varies in the neutral pH scale (7.40 and 6.94 for Fotoyeh and

Sangueh). Water of Fotoyeh Spring is odorless, whereas water in Sangueh Spring smells like hydrogen sulfide. Results of chemical analysis indicate that sodium is the most frequent cation in both springs and chloride and sulfate are the most frequent anions in both springs.

Figure 2 shows frequency variations of primary ions in the samples and figure 3 shows the Stiff hydrochemical diagram for such samples.

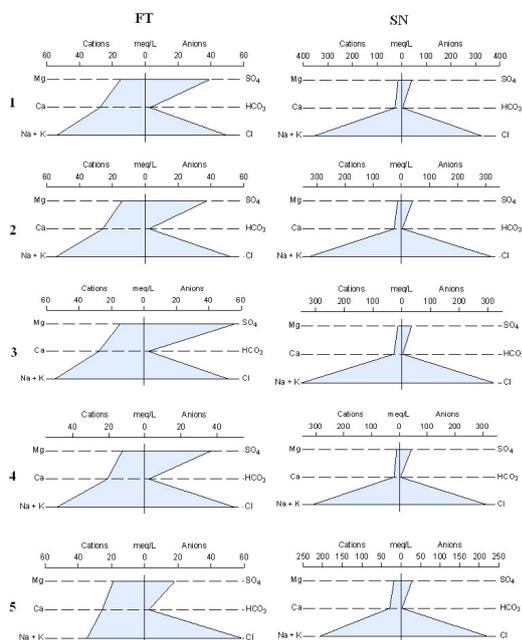


Figure 3. STIFF diagram of various water samples taken from FT and SN springs

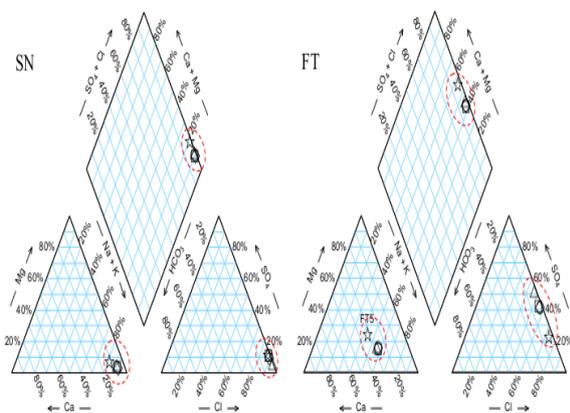


Figure 4. Location of water samples in FT and SN samples in the Piper Diagram

Piper hydrochemical diagram shows the position of water samples of both mentioned springs; according to which both Fotoyeh and Sanguyeh springs are of sodium-chloride type and you can find considerable amounts of sulfate in Fotoyeh (Figure 4).

It can be due to the relationship between underground water resources of this region and salt

domes of Hormoz series which mostly are composed of halite (NaCl) and gypsum (CaSO₄).

Chemical types of hot and mineral water have various health benefits. In a general classification hot and mineral waters are classified into bicarbonate, sulfated, sulfur, sodium - chloride, ferrous and radioactive waters (4). Each class has its own health benefits and when one decides to use them as a treatment, he/she needs to consider its geochemical type.

Sodium-chloride waters have both internal and external usages. Their external usages are recommended for treating rheumatism, lymphatism, rickets, gynecological diseases and localized swellings. They are also used as vapor, gurgle and nasal irrigation. Bathing in such waters dilate peripheral vasculature. Such waters are bile inducer and increase mouth and stomach secretions and gastric motility and sometimes acts as laxative. In general, chloride-sodium waters stimulate various activities of body and nourishment and treat swellings, even waters containing gas have sedative effects, facilitate respiration, stimulate pancreas actions and finally strengthen activities of digestive system. Katz et al. (2012) have discussed pervasively about the health benefits of such waters (29).

Cold sulfate calcic waters dispose body's waste materials such as urea, mineral salts and its warm type is sedative. Sodium-chloride and magnesium sulfate waters are laxative and bile inducing and if there is chloride-sodium along with the sulfate minerals in a spring, then we will have sulfate sodium-chloride waters (e.g. Fotoyeh Spring); such waters are sedative, anti-itch, laxative and bile-inducing.

Some studies (4,5) suggest that some known mineral and hot water springs such as Sarein, Khalkhal and Damavand's A'LA Spring are of bicarbonate type and their water is full of Ca and Mg, which are more than Na and K. it seems that most sodium-chloride mineral and hot water springs of Iran are located either in arid and semi-arid zones or are influenced by dissolvable rock units such as salt and gypsum. Both mentioned factors, arid climate and influence of rock units, were effective in formation of hydrochemical type of springs of this study.

Figure 5 indicates the mean quantities of Fotoyeh and Sanguyeh in contrast to Iranian well-known mineral and hot water springs.

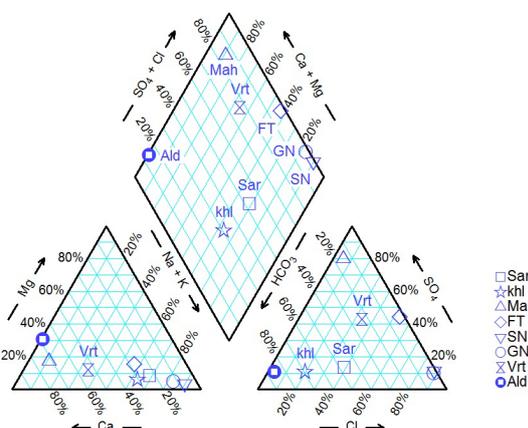


Figure 5. Location of SN and FT Springs in contrast to some famous hot water and mineral springs of Iran (Sarein (Sar); Khalkhal (Khl), Mahalat (Mah), Geno (Gn), Verton (Vrt), Aela of Damavand (Ald))

Assessment of some rare, primary elements and heavy metals in water of the studied springs (tables 1 and 2) suggest that the mean value of certain elements such as As, Bi, Ca, Ti and Hg is very trivial (below 0.1 ppb); whereas concentration of other elements such as Co, Cr, Cu, Mg, Mo, Ab, Ni, Pb, Zn, and Se varies from 0.1 to several dozen ppb. In general, there is not a significant difference between two springs in terms of concentration of the mentioned elements; it can be due to relatively similar lithology of their bedrocks. Although their concentration is very low, regarding toxicity of most of them, using water of these springs in balneotherapy is not recommended through drinking, vapping and injecting. It is necessary to note that trivial amounts of some of mentioned elements enter body through skin absorption, hence iterative and long-term use of such springs should be under supervision of an informed and expert doctor.

Measurement of Radon gas concentration (^{222}Rn) in Fotoyeh and Sanguyeh Springs suggest that concentration of this carcinogenic gas has changed considerably over years. Measured concentrations for Sanguyeh Spring vary from 53 to 104 kBq/m^3 (mean value: 76.51) and for Fotoyeh

Spring vary from 125 to 253 kBq/m^3 (mean value: 159.98) (Figure 6).

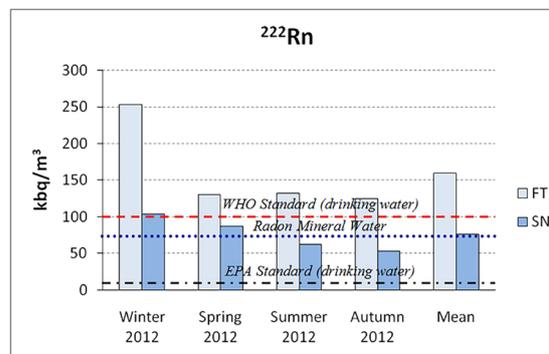


Figure 6. The measure concentrations of Radon (^{222}Rn) in various seasons of the years in FT and SN springs and comparing it with the current standards

For considering a mineral spring a Radon mineral water, its radon concentration should be more than 2 nCi/l (equal to 74 kBq/m^3) (31). Since the mean concentration of Radon in both springs of this study was more than what mentioned above, they are classified in the radon mineral springs.

The EPA standard for radon concentration in the internal air is 14 Bq/m^3 and its transmission coefficient from water to air is 10000:1 (32).

Therefore, regarding the results of this study, concentration of radon in the air, which is in contact with the Sanguyeh spring water, is estimated on average 7.65 Bq/m^3 and if the air is conditioned properly there will be no danger for visitors. For Fotoyeh Spring in which even a concentration of 253 Bq/m^3 has been reported (mean concentration of 159.9 Bq/m^3 in water and mean concentration of 15.99 Bq/m^3 in the air in contact with water), despite the fact that its pool is located lower than the natural ground level, which in turn makes air conditioning very difficult, there is no serious concern here because radon's concentration is lower than the suggested standards. It is necessary to note that EPA standard for the dissolved radon in the drinking water is 11.3 Bq/m^3 and WHO and potable water in Iran standards are 100 Bq/l [32, 33] and since water of the springs studied here is not used as the potable water (because of its low quality) there is no worry here.

Determining Radon risk in this spring depended on continuous and long-term measurement of radon

concentration in both air and water of pool which was not possible in this study.

Table 3. Concentrations of dissolved radon in water of some hot water springs and water resources of different parts of Iran and the world

	Variation range /average concentration of radon (Bq/l)	Reference
Fotoyeh	125-253	-
Sanguyeh	53-104	-
Sarein	907-1398	[35]
Sirch hot water spring in Kerman	42.5	[36]
Northwestern springs of Mashhad	30.2	[37]
hot water springs in Venezuela	1-560	[38]
El Castano in Venezuela	255-576	[38]
Rudas in Hungary	67-366	[39]
Gallert in Hungary	52-132	[39]
Kovasna in Romania	0.3-613	[39]
Springs and wells in Lebanon	0.91-49.6	[40]
Bakreshwar in India	34.5	[41]
Merino spring in Italy	2000	[42]
Drinkable and mineral waters in Austria	0.05-700	[38]
Drinkable water in Hungary	0.9-14.1	[38]

Table 3 summarizes the dissolved radon concentration in some hot water springs for comparing with the two springs of this study. Comparing these values shows that there are higher concentrations of radon in Sanguyeh and Fotoyeh springs in contrast to springs in Sarein and Kerman and it is due to the fact that the latter's water is supplied from igneous rocks. Since the springs of this study have been originated from the sedimentary rocks and have carbonate rocks [5], the higher concentration of dissolved radon in them can be attributed to the potential effect of salt domes in the region.

It is necessary to mention that the maximum allowable concentration of uranium in the underground and mineral waters, regarding to the WHO and DOE guidelines, is 10 to 20 ppb; its mean concentration in Sanguyeh and Fotoyeh Springs is 1.1 ppb and 2.2 ppb, respectively; hence these springs are not considered hazardous in this regard.

Although basic hydrochemical studies provide us with general information about status of the hot and mineral waters, it is recommended that people use this treatment after consulting with doctors and medical specialists. Also it is recommended that the medical specialists need to assess the quality of this treatment in terms of the scientific standards.

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