

Detection of Toxic Materials at Death Valley and Death Spring, a New Ecosystem in Tashan District, Southern Iran.

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Abstract

Death Valley and its stream form a unique landscape in the Tashan district of southern Iran. The water from the headstream of Death Spring to 100 meters downstream and the air around it are lethally dangerous and cause death. The color of the stream beds changes to five different colors. In this study, sampling of sediment and water took place in two seasons and at five stations. Historical information about the area was also collected and analyzed. The heavy metal concentrations in the water and sediment were high; in successive order from high to low, they were $Fe > Al > Ag > Pb > Zn > Mn > As > Cu > Cr > Ni > Cd > Co > Sb$. The toxic gas is H_2S , and the treated concentration of this gas rises up to 410 ppm making the surrounding air toxic as well. The Gas emission has Geological origin. At the source of Death spring the Sulfur compounds in the water, soil, and sediment do not allow the growth of any macroscopic plants or animals. The current study aimed to identify the eco-touristic capacities and mortal danger in this valley, and to carry out environmental action plans, such as installing warning plates and notes to protect people and animals, so that all can benefit from the clean air and mineral water of 7 clean springs at the higher regions of Death Spring and enjoy the pleasant landscape of this area without being injured by the lethal gas of Death Valley. Other wonders of this area are also introduced.

1. Introduction

In the southeast of Khuzestan and part of the Zagros Mountain range, there is a deep valley. The area of this valley and its spring was named Death Valley in the year 2012 because of the deaths of five people in recent decades. The lethal agent and water characteristics of Death Valley had been introduced in a short paper. In the current paper, the chemistry of the water running at Death Spring, the chemistry of the sediment are described in more detail.

"Heavy metals are serious pollutants due to their toxicity, persistence in natural conditions and ability to be incorporated into food chains" (Szefer et al. 1997; Klavins M et al. 2000; Armitage et al. 2007; Sakan et al. 2009). "heavy metals have a substantial toxicity to living creatures" (Gaetke et al. 2003; Quartacci et al. 2005). "Heavy metals are natural ingredients of the Earth crust. A number of these elements are biologically essential at trace levels present in natural water, air, dusts, soils and sediments, and play an essential role in human life" (Mokhtar et al. 1991, Juvanovic et al. 1995) "Opencast mining activities have a serious environmental impact on soils and water streams, having generated millions of tons of sulfide-rich tailings" (Bhattacharya et al. 2006). If these metals are phyto available, some toxic metals are potentially accumulated in some plants and may pose a threat to humans and grazing animals. Some soils contain high concentrations of metals from geochemical sources" (Adriano DC. 1986), "while others are contaminated by metals from anthropogenic activity such as phosphate fertilizer application, industrial wastewater effluents derived from the mining process, and wastewater sludge's" (Williams et al. 1976; Shallari et al. 1998). The earlier studies have described that "riparian wetland has a large capability to store heavy metals" (Du Laing G et al. 2009; Prokisch J et al. 2009). "Sulfur springs are characterized by alkaline pH, sulfur reduced species and high anomalous contents of silica,

fluoride, bromide, boron, ammonium, and sodium" (Marques, 1999, Calado, 1993). Nicholson (1993) suggests that "the majority of mineral waters, including thermal waters, have a meteoric origin. Assessment of soil contamination with heavy metals can be determined by estimating the bioavailable fraction of toxic metals. Metal mobility in soils has generally been assessed using a chemical approach based upon selective extractions" (Morel et al. 1984; Wenzel et al. 1999).

1.2 The study area

Iran's Death Valley is located beside the Khuzestan Plain on one side and the Zagros mountains on the other. The geography of the area comprises huge mountains and vast, deep valleys. The research was carried out in Death Valley situated at $50^{\circ} 12' 11''$ east longitude and $30^{\circ} 54' 23''$ north latitude, with an altitude of 970 meters above sea level in southern Iran. Death Valley is located in the 15 Km of northern part of Behbahan city (Figs. 1, 2, 3, 4). The current study evaluated the metal element content and the toxicity of the water and sediments of Death Valley in the Tashan region of southern Iran. Furthermore, a preliminary assessment of the environmental risks associated with the heavy metal pollution in the water and sediments of the studied area was carried out.

Figure 1

Location map of the studied area and sampling points.

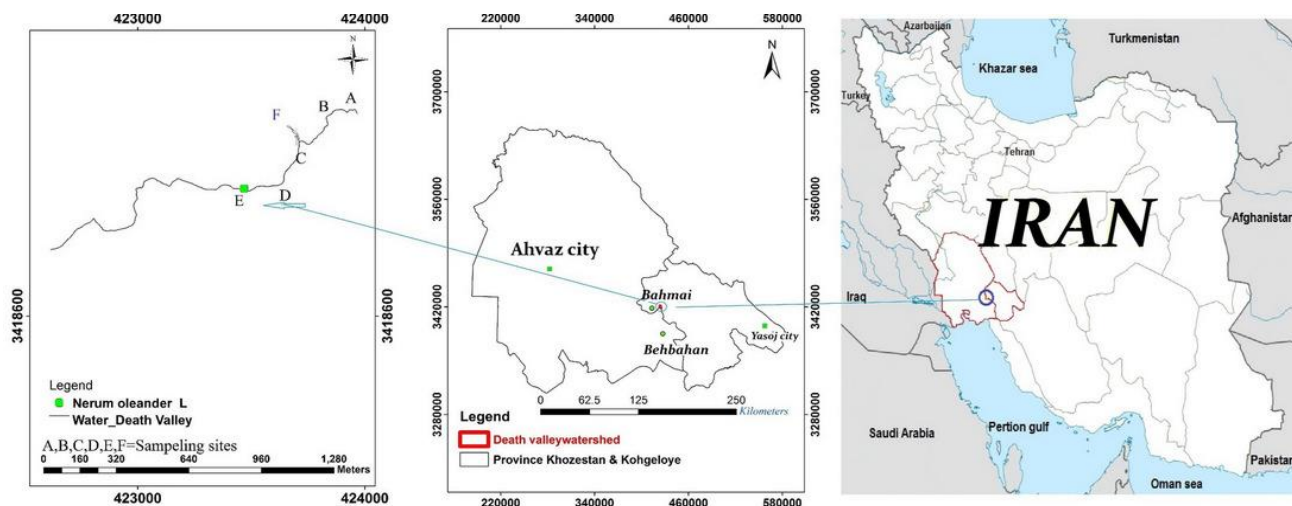


Figure 2

Different color of water in the Death Valley stream, from above to below , A- point of water inject from spring, B-from 10 meter to 200 meter of upstream, C- from 200 m to 300 m, D- from 300 m to 1500 m , E- from 1500 m and more, respectively, F-. the huge and tall mountains with vast and profound valleys, Death Valley in Zagros Mountains.



Figure 3

Detection of poisonous Gas by Gas sensor(MSA) and Gas Filter and Mask.



Figure 4

Healing property of hot spring. photo is Reza Fatemi Motlagh. 2012.



2. Materials and methods

The nearest village to Death Valley is located 5 km south of Death Valley. It is populated by 60 families, their jobs is agriculture or ranching. The investigation on this spring and valley started with a questionnaire completed by local residents.

Water and sediment samples were collected from 5 sampling stations in two stages and two seasons. The pH, EC concentration in water were measured. The H_2S and temperatures of air and water were analyzed locally. Other substances and metals element (Fe, Al, Ag, Pb, Zn, Mn, As, Cu, Cr, Ni, Cd, Co, and Sb)(Table 2, 3, 4, Fig. 5, 6, 7, 8) were analyzed at laboratories in Behbahan and Tehran.

Maps and images were prepared using ArcGIS® 10 (Fig. 1, A, B, C, D, E, F, stations). A Canon camera was used to take pictures (Figs. 2-A, B, C, D, E, F).

To detect the nature of the toxic gas, MSA gas sensors were used. During sampling at Death Spring, oxygen capsules or anti-gas masks were used (Fig. 3).

2.1 Sampling and sample preparation

In Death Valley the water depth is shallow with an average depth of 0.25 m. Thus, water samples were collected from 0.15 m below the surface and prepared according to the criteria and procedures explained in standard method books published by the WHO in 2017. The methods explained by ZHANG Honggang et al., 2010, were used to prepare water and sediment samples and analyze heavy metals and other metals concentrations. As described as following procedure: The water samples after collecting stored in 500 ml crystal bottles pre-cleaned with deionized water and rinsed with the sample to be collected from different sites. The water samples were filtered through 0.45 μm Millipore filters and acidified to $\text{pH} < 2$ using concentrated nitric acid and then stored in the dark at 4°C . The concentrations of heavy metals were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The sediments samples used in this study were collected at each site for 0 to 10 cm depth and the exact location was recorded with Meter. All of soil samples were air-dried at room temperature immediately after collection and sieved through a 2-mm nylon sieve to remove coarse debris. For each sample, 30 g sub-sample of soils was ground with an agate mortar until all particles passed a 100-mesh nylon sieve. A 0.1000 g sub-sample of dried and homogenized soil was accurately weighed and digested with 2 ml HNO_3 , 1 ml HClO_4 and 5 ml HF at a temperature of $90 \pm 190^{\circ}\text{C}$ for 16 h. The residue was then dissolved in 2 ml of 4 mole/L HCl and diluted to 10 ml with deionized water and analyzed for a number of heavy metals (Fe, Al, Ag, Pb, Zn, Mn, As, Cu, Cr, Ni, Cd, Co and Sb) by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The single plant (Nerum oleander L.) that has seen in down of the waterway was sampled in the Death Valley. For this plant, the roots, and the aboveground parts stored in the zipped polyethylene bags, respectively. The samples were washed thoroughly with tap water and rinsed with deionized water, then dried at 70°C for 24 h in an oven. After the measurement of dry weights, the samples were ground into fine powder in an agate mortar. Precise weigh samples (0.2000 g) were used to prepare the solution of digestion reaction. A mixture of concentrated HNO_3 (2 ml) at 65% and H_2O_2 (1 ml) at 30% was used for digestion reaction. After cooling to the room temperature, the residue was diluted with deionized water to 10 ml and analyzed for metals by ICP-AES.

For quality control analysis, standard reference soil material (GBW07401, GSS-1) and plant material (GBW08513) from the National Research Center for Standards in Iran were used to verify the accuracy of metal analysis. The recovery rates of heavy metals in the standard reference material were around 91-97%. Reagent blanks were also employed to detect potential contamination during the digestion and analytical procedure.

2.3 Time and points of sampling

Water and sediment samples were collected during two time periods (Table 1) from the water source or head of Death Spring (A station), 10 meters downstream (B station), 200 m downstream (C station), 700 m downstream (D station), and 1500 m downstream (E station) (Fig. 1).

3. Result and discussion

The results indicated significant correlations between iron and aluminum and sediments and the samples of water from the spring. The average concentrations of metals, anions, and cations in the water are summarized in Table 3. Also total concentrations of these element and WHO[®] standards for Fe, Al, Pb, Zn, Mn, As, Cu, Cr, Ni, Cd, Co, and Sb in river water from Death Valley are presented in Table 2, Figure 5, 6, 7, and 8. The concentrations of Al, Fe, Pb, As, and Sb were higher than the threshold established by the WHO. The concentration of aluminum was higher than the other elements. The Pb, As, Sb, and Al concentrations were not at a safe level for aquatic life.

The average concentrations of heavy metals, and other elements such as anions, and cations in the sediment were far higher than those in the water (Tables 2, 4, and 5; Fig. 5, 6, 7, and 8) This evidence showed the enrichment of metals in the sediment. The metal concentrations in sediment were higher than the standard thresholds for these elements, established by the WHO. However, the amounts of Fe and Al were significantly higher than the values of contaminants in sediment.

3.1 The metals elements distribution among water and sediment

The distribution of metals among sample site in sediment was higher than in water from different sample stations. (Tables 2 and 4). The correlations of metals in the water and sediment analyzed in the current study were significant.

The detection and measurement of gas showed that the concentration of H₂S at Death Spring is as high as 410 ppm during the hot days of summer. At the summer because of decreasing of water flow and less precipitation and high evaporation of water the concentration of gas will increase. By investigating the possible route of pipeline that may cross at the Death Valley district, our observation showed that the origin of Gas is not artificial, is not from Gas Reservoir or from leakage of artificial pipeline. The reason for the increase in the concentration of the elements and their origin also the existing H₂S gas has a geological origin.

3.2 The reason for changing the color

As mentioned above the chemical component of water and sediment samples were measured from the water source or head of Death Spring, 10 meters, 200 m 700 m and 1500 m downstream. The colors of the water are in accordance with the change in water chemistry and the color of the bed of the valley. For example during the time because of calcium compounds deposits in deb and sediments the bed color of stream is totally milky white(Fig. 4). The composition of water and sediment in Death Valley stream changes within two kilometers path of its flow the patterns of change are interpreted as follows:

- The black color of the bed is related to the sulfide compounds of the metals, in particular, the iron and silver sulfide deposits (Ag₂S, FeS and Fe₂S₃).
- The milky white color of the bed is related to the sulfide compounds of metals, especially aluminum sulfide (Al₂S₃) deposits, calcium sulfate (CaSO₄), or calcium carbonate(CaCO₃). Because these milky stones were found everywhere, these compounds were also found to be abundant.
- The green color of the water is related to the (Fe₂O₃) ferric oxide and iron fraction in the water sulfur oxides (SO₂) and the iron oxide (FeO and).
- The blue color is the sulfate-containing water, such as copper sulfate (Cu₂O).

The major sources for the heavy metals and other contaminations in the stream are emitted from groundwater that passes beneath the mountain. The natural and toxic emissions transported by

effluents are considered to be responsible for the increasing metals concentrations found in the sediment and water at the central part of the area. Iron was detected in the most polluted area. The concentration of this metal was 6457 ppm. The concentration of aluminum (Al) was up to 3490 ppm and for silver (Ag) was 170 ppm.

Figure 5

A Pareto chart plots the distribution of the metal elements in order of frequency, with a cumulative line (red line) on a secondary axis as a percentage of the total.

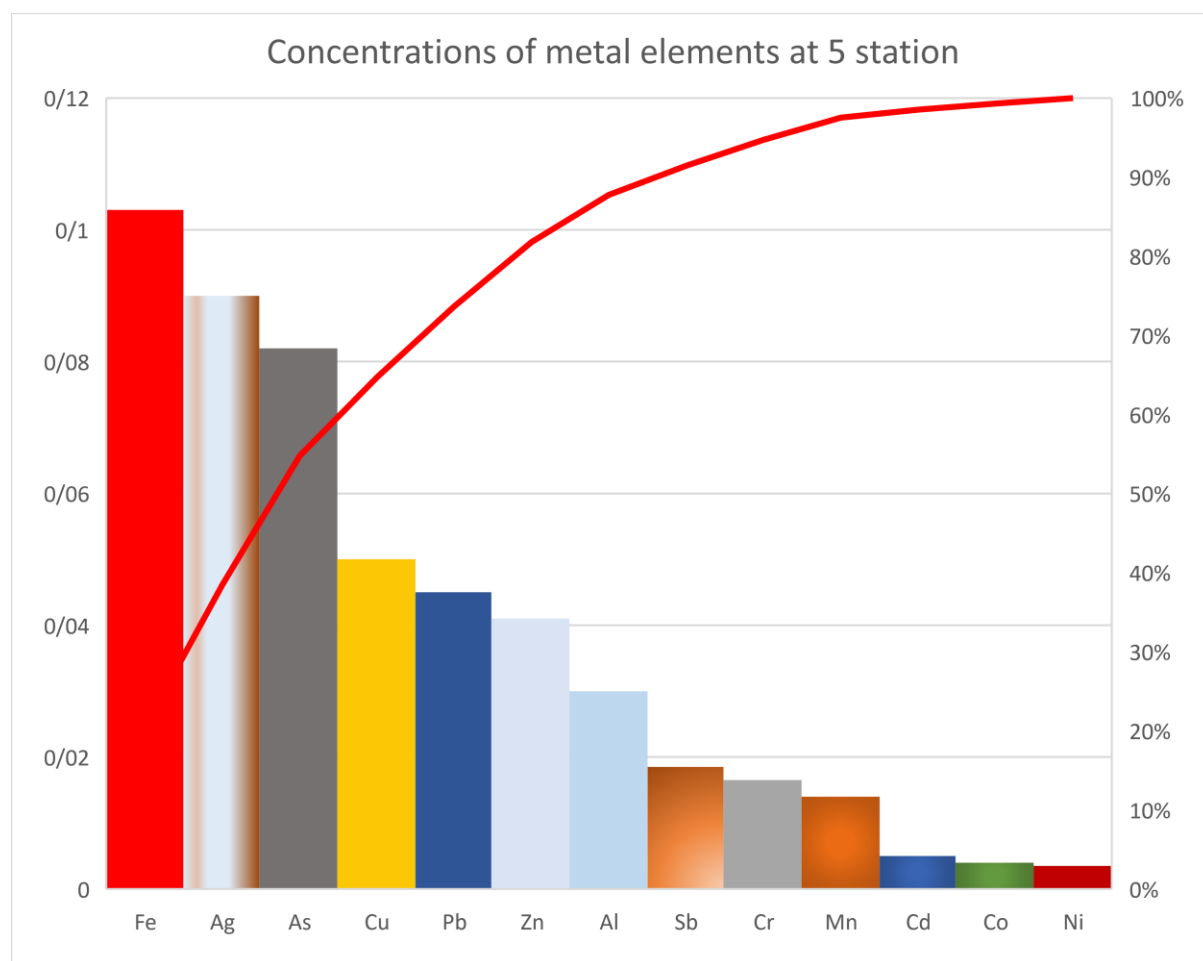


Figure 6

A: EC value at five sampling stations; B: A clustered column chart for comparing Chemical characters at 5 sampling station

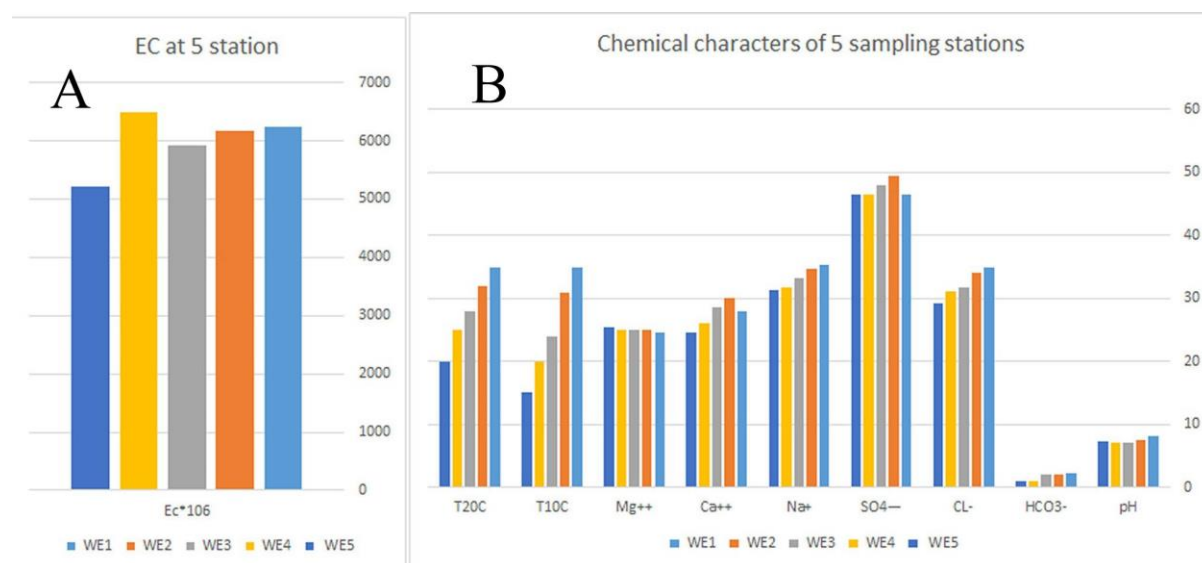


Figure 7

A: A line chart displays trends of Fe and Al over 5 sampling station in sediments; B: A cluster column chart to compare metal elements value across 5 sampling stations in sediments.

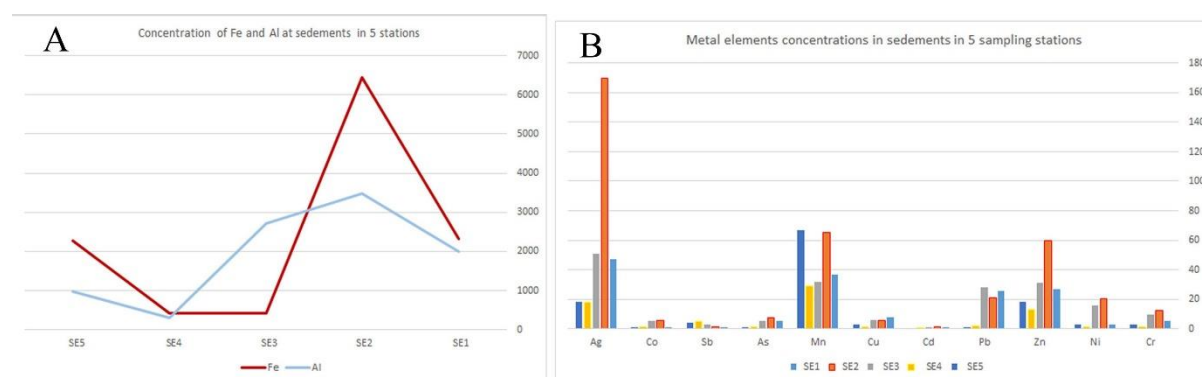


Figure 8

A: EC trends over 5 sampling stations in sediments; B: **Temperatures** and cations and anions at five sampling stations in sediments

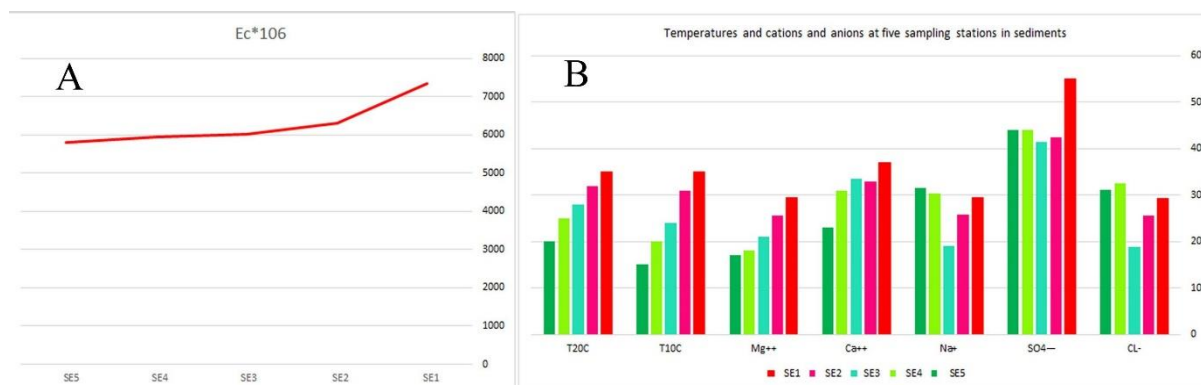


Table 1. Time and the air and water temperature in sampling points at Death spring.

Time periods	Date	Air degree	Spring water d ^o c	Air quality	Sampling quality
1	November 2012	15 °C	35 °C	Sunny	With mask and oxygen slander
2	April 2013	20 °C	35 °C	Sunny,	With mask and oxygen slander

Table 2. The average concentrations of *Heavy metals* in triple sampling of water from Stations at Death Valley (ppm).

W-STATIONS	Cr	Ni	Zn	Pb	Cd	Cu	Fe	Mn	As	Sb	Al	Co	Ag
Average WE ₁	0.0165	0.0035	0.041	0.045	0.005	0.05	0.103	0.014	0.082	0.0185	0.03	0.004	0.09
Average WE ₂	0.012	0.002	0.059	0.016	0.005	0.05	0.081	0.031	0.025	0.074	0.026	0.0015	0.008
Average WE ₃	0.0125	0.0025	0.047	0.016	0.005	0.05	0.067	0.013	0.63	0.64	0.5	0.001	0.008
Average WE ₄	0.01	0.004	0.116	0.024	0.002	0.05	0.472	0.067	0.078	0.059	1.692	0.002	0.068
Average WE ₅	0.08	0.008	0.211	0.046	0.003	0.05	0.259	0.032	0.088	0.053	3.26	0.001	0.074

Table 3. Average of anions and cations from triple sampling of water from Stations at Death Valley (meq/lit).

W-STATIONS	Ec*106	pH	CO ₃ —	HCO ₃ -	CL-	SO ₄ —	Na+	Ca++	Mg++	T ₁ °C	T ₂ °C
Average WE1	6230	8.12	0	2.25	34.9	46.5	35.25	28	24.5	35	35
Average WE2	6160	7.525	0	2	34.1	49.5	34.7	30	25	31	32
Average WE3	5925	7.14	0	2	31.8	48	33.15	28.5	25	24	28
Average WE4	6500	7.05	0	1	31.2	46.5	31.65	26	25	20	25
Average WE5	5220	7.31	0	1	29.2	46.5	31.35	24.5	25.5	15	20
Average WEf	1300	7.22	0	2	1.2	8	3.1	8.8	2.8		

Table 4. Average of heavy metals in triple sampling of sediment from Stations at Death Valley (ppm).

S-STATIONS	Cr	Ni	Zn	Pb	Cd	Cu	Fe	Mn	As	Sb	Al	Co	Ag
Average SE1	5	3	26.5	25.5	1	8	2333	36.5	5.5	1	1995	1	47
Average SE2	12.5	20.5	60	21	1	5.5	6457	65.5	7.5	1	3490	5.5	170
Average SE3	9.5	15.5	31	28	1	6	413.5	32	5.4	3	2725	5.5	51
Average SE4	1	1	13	2	0.085	1	428	29	1	5	312	1	18
Average SE5	3	3	18	1	0.09	3	2280	67	1	4	980	1	18

Table 5. mean anions and cations of two sampling station in sediment of Death Valley (meq/litr).

STATIONS	Ec*106	pH	CO ₃ —	HCO ₃ -	CL-	SO ₄ —	Na+	Ca++	Mg++	T ₁ °C	T ₂ °C
Average SE1	7340	7.62	0	3	29.3	55	29.35	37	29.5	35	35
Average SE2	6300	7.55	0	2	25.6	42.5	25.8	33	25.5	31	32
Average SE3	6010	7.345	0	1	18.9	41.5	19	33.5	21	24	28
Average SE4	5950	7.1	0	2.5	32.5	44	30.3	31	18	20	25
Average SE5	5800	7.05	0	2.5	31.2	44	31.5	23	17	15	20

4. Conclusion

Death Valley is a unique and mysterious ecosystem, its creation, and its attractions, one is reminded of the deaths in this valley with the true fountain of death on one side and hundreds of natural, eye-catching attractions and the healing property of hot spring, on the other side. The concentration of H₂S at Death Spring is as high as 410 ppm during the hot days of summer although during the other seasons this value is less than that, but for all the time the concentration of this gas is harmful for human and animals. The danger of death is more critical at near of spring the to 200 m of around it. "Previously, the ACGIH recommendation for an eight-

hour Time Weighted Average (TWA) exposure limit was a concentration of 10 parts per million and the 15-minute Short-Term Exposure Limit (STEL) was 15 ppm. The new recommendations for airborne H₂S exposure are a TWA of 1 ppm and an STEL of 5 ppm (Rick Wanek, 2011).

The results of this project may be guidelines for local and national environmental organizations to manage the tourism and ecotourism programs at this region. During this project expert from the environmental organization began visiting the habitat sections of the area, and prohibiting hunting is on the agenda. By introducing of this area to the local and central Environmental authorities, this habitat was recognized and documented as a national ecosystem and protected natural area. Because of the possibility that pollution will spread to nearby areas, especially along the direction of the water, this area poses a potential threat to local communities. Iran's Environmental Protection Agency (IREPA) placed an alert panel in this area, and hunting and non-authorized entrance to this area were banned.

5. Recommendation

For the optimum conservation, it is necessary to declare the area as a protected area. This region has a high potential for sustainable development.

In Death Valley, there should be a range of opportunities that can be organized by warning signs from the environmental organization. As a natural protected area, it is considered to be a global record, and all ecotourism laws and regulations must be applied in these protected areas. The river, as an active ecosystem, can create many Eco-touristic landscapes due to its natural characteristics. The national and international identification and registration of this ecosystem will add to the natural and cultural values of Iran, increase the attraction of tourism, entrepreneurship, and business prosperity, and will promote environmental education, business prosperity, and the social well-being of this region.

6. Acknowledgement

Exploring of Death Valley was the topic of the master's degree of Reza Fatemi Motlagh in the subject of Environmental Sciences. It is our pleasure and duty to acknowledge all of those who have been directly or indirectly involved in this project. We wish to acknowledge first of all to local people that eagerly helped us even in dead fully and dangerous condition especially we debt to the local sheared Mr Eshagh basti; Mr Fazlallah Jamashi; Mr Anbar Bahram Nejad; Mr Hamden Fardaei; Mr Korosh Fatemi. Thanks are due to Dr. Abolfazel Soltani and Dr. Mohamad Baghdadi for their advice and encouragement.

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