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Acid Rain and Its Effects on the Lakes of Fars County in Iran

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Abstract One of the main environmental issue these days is acid rain and its effects on the human and environment. Acid rain effects are more dominant in countries such as United States, Canada, and Europe due to acidic nature of soils in some parts of their lands as well as heavy pollution resulted from vast industrial activities which are conducted through these countries. Contrary to these facts, Iran situation regarding acid rain is totally different and in spite of high pollution in cities and industrial areas, the water of lakes and streams are not acidic. Data collected in this research show that the pH and alkalinity of the lake water and soils are almost high. Some of the lakes in Fars County are dried and the rest are not in normal situation. Lakes of Barmshoor, Droodzan, and Haftbarm have pH around 7.93 -8.07 and alkalinity around 186 to 220 mg/L $CaCO_3$. The soils around the lakes have pH in the range of 7.69-7.89 and alkalinity 208-235 mg/L $CaCO_3$. Therefore both the soil and the water have high alkaline buffer capacity to resist acid rain because; most part of the Fars County consist of calcite, dolomite and some alkaline salts. Pollution load indexes for Al, Zn and Cu for both lake water and related soils are close to one (1.063-1.54) which means no considerable metal pollutions are created by acid rain in Fars County. In fact, high pH and alkalinity of the water and soil make metal salts mostly insoluble and limit the availability of the free metals. The pH changes of rain water show gradual increase of pH during raining. If the sample of rain water is left alone, its pH decreases by residence time.

Keywords Acid Rain, Soil Alkalinity, Lakes Acidity, Pollution Load Index

1. Introduction

Acid rain describes any form of precipitation with high levels of nitric and sulfuric acid. It can also occur in the form of snow, fog, and tiny bits of dry material that settle to Earth[1-4].

Most acid rain falls because of human activities. The biggest cause of acid rain is the burning of fossil fuels by coal-burning power plants, industries and automobiles. Free CO_2, and gases resulted from human burn fossil fuels such as sulfur dioxide, SO_2, and nitrogen oxides, NO_x are released into the air. These chemical gases react with water, oxygen and some other compound to form a weak solution of carbonic, sulfuric and nitric acid. These acidic particles may spread by wind across the atmosphere and over hundreds of miles. When acid rain precipitate on the Earth, it enters in water streams, lakes and other form of water systems and may sinks into the soil[5,6].

Acid rain have many natural and ecological effects[7]. However its impacts on lakes, water streams and wetlands are greater than others. The main adverse effect of acid rain is that it can wash away the soil aluminium into lakes, and streams. As a result, dissolved aluminium cation, makes lake water and stream toxic and dangerous for crayfish, clams, fish and other aquatic animals[8-10].

Increasing amounts of acids can "mobilize" aluminium ions which are normally present in an insoluble non-toxic form of aluminium hydroxide. It appears that when the soil pH dips to 5 or lower, aluminium ions are dissolved into the water and become toxic to plants[11]. Aluminium ions cause a stunting of the root growth and prevent the roots from taking up calcium. The result may be the overall slowing of the growth of the entire tree[12].

Lower soil pH and aluminium mobilization can reduce populations of soil microorganisms[13]. Soil bacteria have the job of breaking down the dead and decaying leaves and other debris on the forest floor. The effect of this action is to release nutrients such as calcium, magnesium, phosphate, nitrate, and others. Low pH and high aluminium ion concentrations inhibit this process. Higher amounts of acids can mobilize other toxic metals from the insoluble to the soluble ion forms in the same fashion as aluminium. The toxic metals include lead, mercury, zinc, copper, cadmium, chromium, manganese, and vanadium[14,15].

These may all contribute to slow the growth of a tree. In addition, these combination of toxic metals may also adversely affect the growth of soil bacteria, mosses, algae, fungi, and earthworms.

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That soil may neutralize some or all of the acidity of the acid rainwater. This ability is called buffering capacity, and without it, soils become more acidic[16-18]. Differences in soil buffering capacity are an important reason why some areas that receive acid rain show a lot of damage, while other areas that receive about the same amount of acid rain do not appear to be harmed at all.

Researches about acid rain in Iran especially Fars County are very limited in spite of high pollution in cities and industrial centers. Therefore, this study regarding acid rain, lakes of Fars County and soil alkalinity, in fact is the starting steps to illustrate how these factors may affect the environment of Iran. In previous studies, measurements were very simple, superficial and several pH measurements or alkalinity were used as criteria for showing acid rain reality. However this research is more complex and has gone further to show acid rain reality in detail for Fars County.

2. Experimental

2.1. Soil and Water Sampling

Water samples were collected from middle of lakes. Bottles of pet, sterilized with 60 ppm chlorine were used for water samples. Soil samples were taken from area around lakes located in 2 km from the lake. Soil samples were taken within 30 cm dept. The method of composite sample, i.e., a single sample consisting of the composite of several randomly selected soil cores were used in these experiments. Samples were taken to laboratory no more than 6 hr delay.

2.2. Drying, Crashing and Sieving

The soil samples were air dried, and the large stone and gravel were removed before crashing process. Thorough mixing requires that the sample be crushed and ground to particles of uniform size. After drying the sample, clods and large aggregates were crushed and mixed. Then the crushed material was further ground to pass 2 mm sieve. The purpose of grinding is to reduce heterogeneity and to provide maximum surface area for physical and chemical reactions. For crashing, pestle and mortal were used.

2.3. water and Soil pH Measurement

All pH measurements carried out by Metrohm 827 pH meter. The pH meter was calibrated over 7 to 9 range using the standard buffer of 7 and 9. weigh 5 g of sieved and dried soil into a 100 ml beaker. Add 5 mL distilled or deionized water to the sample. Stir vigorously for 15 seconds and let stand for 30 minutes. Then place electrodes in the slurry, swirl carefully, and read the pH immediately. Ensure that the electrode tips are in the slurry and not in the overlying solution.

2.4. Determination of Al, Cu and Zn in Soil

The instruction of Lindsay and Norvell, (1978) DTPA (diethylenetriaminepentaacetic acid) or DTPA extraction method[19] was used for measurement of these metals in soil samples.

2.4.1. Diethylenetriaminepentaacetic Acid (DTPA) Solution

Weigh 19.67 g DTPA, with constant stirring, dissolve in 1 liter of distilled water. Weigh separately 149.2 g TEA (triethanol amine) and 14.7 g $CaCl_2.2H_2O$, and dissolve in 1 liter of distilled water. Pour under constant stirring the DTPA solution to the TEA-$CaCl_2.2H_2O$ mixture. After the DTPA has dissolved completely, dilute the solution to 9 liters. Adjust the pH to 7.3 with 1:1 HCl (approximately 42 ml required), and make up the volume to 10 liters with distilled water.

2.4.2. Standard Solutions of Fe, Zn, Cu and Mn

Stock standard solutions containing 1000 mg/l of the metals.

2.4.3. Preparation of Soil Extract

1. Weigh 5 g of air-dried soil (<2 mm) in a 100 ml polyethylene centrifuge tube, add 20 ml DTPA solution, and shake for 30 minutes on a mechanical shaker.
2. Centrifuge, and decant into a sample bottle fitted with funnel and filter paper.
3. If needed, dilute the extract so that the reading is in the linear working range of the atomic absorption spectrophotometer.

2.4.4. Procedure

1. Prepare an intermediate standard solution by pipetting 10 ml from the 1000 µg/ml Stock solution of the analyte into a 200 ml volumetric flask, and dilute to the volume with DTPA solution.
2. Prepare standard solutions in the working range, like 0, 1, 2, 5, 10 µg/ml of the trace metal. Always dilute with the DTPA solution.
3. Now follow the step by step procedure given in the instruction manual to optimize the working condition of the instrument.
4. Measure the signals from the series of working standards of known concentration, and plot the analytical signals (the instrument or detector response) as a function of analyte concentration.

2.5. Pollution Load Index (PLI)

Pollution load index (PLI), for a particular site, has been evaluated following the method proposed by Tomilson et al. (1980). This parameter is expressed as: $PLI = (CF_1 x\ CF_2 x\ CF_3\ x \ldots\ldots\ldots x\ CF)^{1/n}$ where, n is the number of metals (4 in the present study) and CF is the contamination factor. The contamination factor can be calculated from the following relation:

$$CF = \frac{\text{Metal concentration in the sediments}}{\text{Background value of the metal}}$$

3. Results and Discussion

In Fars county, there are eight main lakes located at different regions. Unfortunately, due to drought, five of the lakes are dried. Lakes of Droodzan, Haftbarm and Barmshor have some water left but they are gradually subjected to water decreasing process. Measurement of water pH for these lakes shows that their waters are alkaline as is shown in Table 1. The pH of the soil slurries are also alkaline Table 2. These facts strongly confirm that the buffer capacity of the soils with respect to acid rain is high.

Table 1. The pH of selected lakes are alkaline

	Sample location	Temperature	pH
1	Droodzan	25	8.00
2	Barmshor	25	7.93
3	Haftbarm	25	8.07

Table 2. The pH of selected soils at 25℃ are alkaline

	Sample location	Time	PH
1	Droodzan	20 min	7.89
2	Barmshore	20 min	7.73
3	Haftbarm	20 min	7.69

In fact, the alkaline nature of the soil can neutralize all acid rains. Contacting time of the soil samples with water changes the alkalinity of slurry (more contacting time more alkaline is the soil extract), therefore the measurement of alkalinity or pH determination needs careful attention. Most parts of Fras County consist of calcite and dolomite rocks therefore, the soils are alkaline. On the other hand, Fars County is a dry region and evapotranspiration of plants is high. This process helps to dryness and carbonate can concentrate. In this case accumulation of gypsum and sodium salts may occur. All these events help to enhance the alkalinity of the soils.

In general, there are four main reasons why Fars county soils are alkaline: 1- Fars county is one of region with dray climate, 250 mm rain fall per year, and a high evapotranspiration of plants occurs. 2- The region is mountainous, and consists of numerous valleys. 3- The soils of Fars county consist of calcareous precipitate of tertiary period mostly of calcite and dolomite. 4- Fars county regions are mostly deserts and they are not green therefore, decay process of vegetation that causes acidic environments is not significant.

The acidity of the rain in unpolluted and polluted regions, such as Shiraz city, Asaluyeh and Dashteargen were determined to see if we have acid rain at all. We choose Shiraz City and Asaluyeh where numerous flares are active and is considered as a most polluted area in the Fars county. As is shown in Table 3 , the pH of rain water in polluted area such as Shiraz and Asaluyeh are 5.8 and 5.5 respectively. However, the pH of the rain water in unpolluted area such as Dashteargen is around 6.7. The pH compatibility with pollution of the area is pretty good. Of course this fact is not so straightforward, because wind direction and strength is very important therefore, transportation of polluted air could occur and different oxides travel miles away from the origin.

Table 3. Rain pH at the start of raining in selected area

	Raining Location	pH	Time
1	Shiraz	5.8	Start of raining
2	Dashteargen	6.75	Start of raining
3	Asaluyeh	5.5	Start of raining

The pH of the rain water with respect to the time was determined. Time variation effects on the pH of acid rain can be considered in two ways: one, pH variation with respect to the time period of raining, second pH variation with respect to residence time of the rain water after collection. Even though, at the time of raining the pH of the rain water is clearly acidic, however, the pH changes can occur both during raining and after collection. Raining process itself cleans the atmosphere in which raining is going on therefore, by the time the oxides and polluted rain will decrease and the pH of the rain increases. But residence time has another effect on the rain pH. The pH of the rain gradually will decrease after collection because rain water has an opportunity to react with unreacted SO_2 and NO_x and become more acidic. However in this step, the presence (interference) or absence of CO_3H_2 is very critical in determination of the rain pH. Figure 1, shows relationship between raining time and pH.

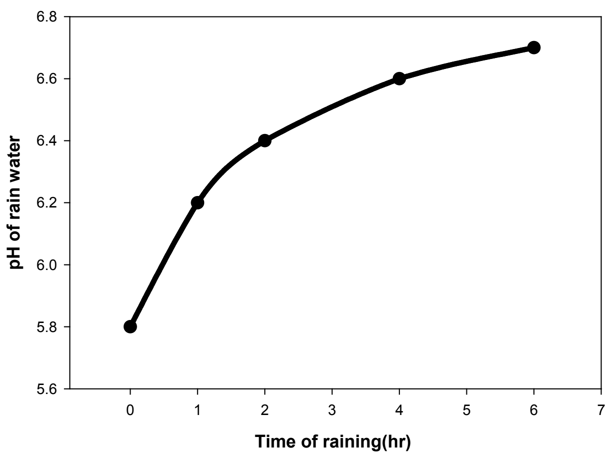

Figure 1. Variation in pH vs. raining duration in Shiraz city

Determination of variation in pH with respect to the raining duration was illustrated for unpolluted area such as Dashteargen. Since there is no pollution, the variation of acidity of the rain is not significant and slope of the line is almost zero, Figure 2.

The pH of the rain samples from polluted areas, after collection was subjected to change by the time. Acid rain collected in shiraz became more acidic by the time, probably because more SO_2 and NO_X reacted with water and the pH was diminished. However the effect of CO_2 in rain water is more complex, since there is always a dynamic equilibrium between CO_2 in air and in water. Therefore some one must carefully consider this mutual effect of CO_2 in acid rain. For this reason, research has to be under controlled condition and extra precaution is necessary otherwise the CO_2 concentration will be a non desirable variable and the source of errors in pH measurements.

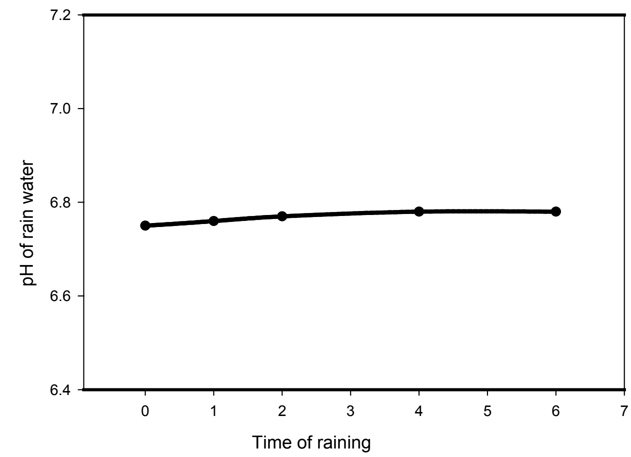

Figure 2. Determination of pH of the rain vs. raining duration

The concentrations of the selected cations, such as Al, Cd, Zn and Cu in the water of lakes were determined to see if pH of water had any kind of effects on the release of these cations. The concentration of these cations and their background concentrations are shown in Table 4.

The aluminium concentrations of the soil samples were determine to see if there is any correlation between the concentration of aluminium in soils and the pH of corresponding soils. The concentrations of Al in some cases were too low and the measured values did not show very clear compatibilities between Al concentration in soil and pH of that soil. Soils with lower pH should release more free aluminium. For instance, the pH of Droodzan soil is 7.89 and more alkaline than the other two lakes (Barmshore and Haftbarm) but the concentration of aluminium in Droodzan soil is 1.14 ppm more than the other two lakes of Barmshore and Haftbarm which are 0.66 ppm and 0.57 ppm respectively. This is contrary to this research assumption. The low concentration of aluminium may causes such an inconsistency and error.

Table 4. Concentration of Al, Zn, Cd, and Cu in water of selected lakes

Samples	Zn	Cu	Cd	Al
Drodzan	0.0017	0.0014	Nd	0.2290
Drodzan Background water	0.0012	0.0012	Nd	0.2165
Barmshore	0.0011	0.0003	Nd	0.0860
Barmshore Background water	0.0010	0.0003	Nd	0.0880
Haftbarm	0.0015	0.0007	Nd	0.0450
Haftbarm Background water	0.0012	0.0006	Nd	0.0422

The alkalinity of selected lakes were measured to determine buffer capacity of the water which can be used to neutralize acidity of acid rain. The alkalinities of Droodzan, Barmshore and Haftbarm are 220.0, 180.6 and 195.4 mg/l $CaCO_3$ respectively. The relationships between pH and alkalinities of selected lakes are show in Figure 3.

The last step for evaluating water acidity was determination of pollution load indexes for Al, Zn and Cu. The pollution Load Index (PLI), was developed by Thomilson et al[20]. Pollution load indexes for the selected lakes were calculated and are shown in Table 5. The pollution load indexes for these lakes are almost equal and close to 1. It means that there is no any water pollution of the lakes by Al, Zn or Cu.

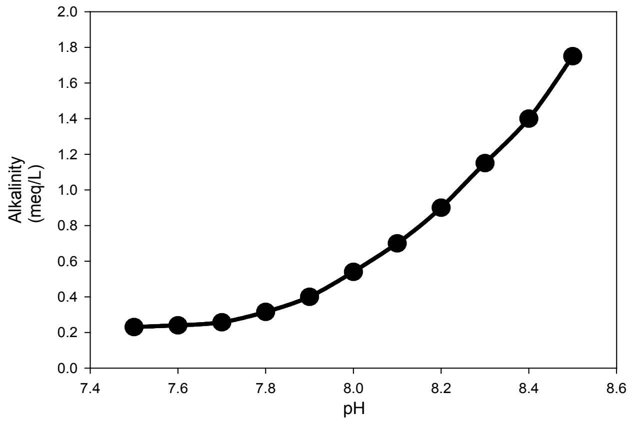

Figure 3. Relationship between pH and alkalinity of selected lake water

Table 5. pollution load indexes for related lakes

Pollution load indexes	Lakes
1.191	Droodzan
1.063	Barmshore
1.154	Haftbarm

4. Conclusions

The main conclusion derived from this research is that the lakes in Fars County are protected by the alkalinity of the soils in the region. Therefore, the acid rain can not be any kind of threat to environmental aspects of the lakes in the near future. In spit of this fact, the drought is going to affect drastically on the environmental issues of the lakes both economically and naturally.

However, in cities such as Shiraz and areas like Asaluyeh, the pollution is high and the pH of the rains are acidic; in Shiraz and Asaluyeh, pH of the rain is 5.8, and 5.5 respectively. This acidity could have a lot of destructive effects on constructions, factories and some how human health. Acidic fog at winter and spring can have more damages to trees and plants in mountain foots.

Measurement of soil's pollution load index regarding Al, Zn, and Cu confirms the high buffer capacity of alkaline soils in Fars County therefore the rain acidity will decrease drastically when it contacts with these alkaline soils.

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