Comparative study between summer and winter of selected Heavy elements in water, sediment and two species of aquatic plants collection from Al-Gharraf River near Al- Gharraf oil field- Thi-Qar province – Iraq

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Abstract

The present study was deal with Concentration of some Heavy elements (Cd, Pb, Ni, Zn) in water, sediment and two species of plant (Phragmites australis and Ceratophyllum demersum). in water, sediment and two species of aquatic plants collection from Al-Gharraf River, samples were collected of three stations in Al-Gharraf River to investigate the possibility of pollution in this area with these elements. three station (Al-Fajr districts, Qal'at Sukkar districts and Al-Rifa'I districts) were chosen to execute this study during the period from winter and summer 2019. Some physical and chemical variable of this river in water (water Temp., pH, Salinity, DO, BOD5) were measured in the study area, also total organic carbon was measured and the result expressed as a percentage. The high water temperature was recorded (17.00°C in winter to 26.33°C in summer), pH (7.44 to 7.73) and salinity (0.66 to 1.66)pppt, DO(7.06 to 3.07), BOD5 (4.34 to 2.91). Also, all the Heavy elements recorded a significant increase in water and Ceratophyllum demersum plant samples in the winter higher than summer and in the sediments and Phragmites australis plant the rise in the winter was only in the elements nickel and zinc, but in cadmium and lead were concentration low or do not make a big difference in the winter compared to the summer. Where there is a positive relationship between the increase in concentrations of Heavy elements in the samples studied and increase in the amount of rain, speed of runoff and the rise in water level in the river in winter due to the volume of rising smoke as a result of pollution which descends during the rainfall and erosion of the edges of the river and lack of control over the domestic sewage that has been brought into the river. As well as probable cause to exist Al-Gharraf oil field that newly established and located north of Fajr city, was considered a control station and opposite to the Qal'at Sukkar city and south of Al-Rifai city we can be observed through the results which show a gradual rise in the second and third stations and the third station was higher than stations 1 and 2.

Keywords: Heavy elements, Water, Sediment, Phragmites australis, Ceratophyllum demersum, Al-Gharraf River and Al-Gharraf oil field
Introduction

Generally, the human environment is defined as a biosphere that includes the land cover, atmosphere, water, and many types of organisms. The biosphere is large and complex, but it is divide into many units per to the relation between living beings and arranges environments such as earth, water, and air [1]. Pollution is defined as any change (sudden or gradual) in the environment and its compositions from the side the chemical, physical and bioproperties [2]. The main subject of pollutants for river water are suspended solids, Heavy elements, oils and greases, oxygen requirement and organic compound [3]. The healthy aquatic environment has a balance of plant and animal life represented by great species diversity. Pollution creates a disturbance in this balance, resulting in a reduction in the variety of individuals and the dominance of the remaining living organisms alive [4]. Over the past decade, although there has been increasing attention to persistent organic pollutants and greenhouse gases resulting from fuel combustion and global warming, toxic Heavy elements in the aquatic environment remains an enduring risk. The continued flow of metals into the water by industrial activities, domestic practices and mining have ensured that the levels of Pollutants continue to be a problem Anthropogenic emissions of Heavy elements exceed the fluxes from natural sources [5]. The investigation of the existence and concentration of Heavy elements in water, sediment and aquatic plants is fundamental to the study of the water pollution by these types of pollutants [6].

Heavy elements are dangerous pollutants of aquatic environment because of their persistence, toxicity in low concentration, and their ability to inserted into food chains and fixed by aquatic organisms such as fish [7]. Heavy elements appear in the aquatic environment naturally and in trace concentrations and varied according to the type of sediment [8]. These metals have strong affinities for sediment, so the sediment can serve as a marker of time history and extension of pollutant inflow in a specific locale [9]. Because there is no any Comprehensive study about the present study area. so the present study deal with the measurement of four heavy elements (Cd, Pd, Ni and Zn ) in water, sediments and plants in Al-Garraf river near oil field to use the result of the present study as a baseline to compare with the result of the future studies in this field.

Study Area

Three areas were Selected on Al- Gharraf River to execution the current study as in Fig (1). To determine the probability of pollution of the area by Heavy elements (HMs), and the problem of pollution spread the result of human activity because of the presence of Al- Gharraf oil field was selected part of the Al- Gharraf river Which extends from Al-Fajr city through Qalat Sukkar city and up to Al- Rifai district Where this area is located near this oil field where is the distance about 10 km north of the Al- Rifai district and this area have been divided into three sections:
Station (1): - North at the Al- Fajr district and Selected is a control station, which is far from the oil field area 23 km.

Station (2): - At the Qalqat Sukkar city, which is located along to oil field.

Station (3): - In the Al- Rifai district south of the Al- Gharraf oil field, which is the distance about 10 km from the oil field.

Samples Collection

1- Water samples were collected from three stations in a region in the winter to summer 2019 from the center of the river and at a depth of approximately 30 cm below the water surface, from the first station to the third station. The samples were collected using plastic bottles (Polyethylene), 5 liters per sample, three random replicates at each station for physical analysis, and heavy metal tests. Adding a few drops of concentrated nitric acid equivalent to 2 ml per liter of the sample as a stabilizer for the conservation of Heavy elements in water, the samples were examined for each season.

2- Samples of sediment were collected by using the Van Veen Grab Sampler sediment from the center of the river and stored in nylon bags marked in a cooled box [10].
3- Samples of aquatic plants were collected by hand after being washed in river water to get rid of the suspended materials and were kept in plastic bags until they reached the laboratory.

**Methods of extraction:**

- **Extract Heavy elements from water**

  Heavy elements were extracted from the water in the following way [11].

- **Extract Heavy elements from sediment**

  Heavy elements were extracted from the sediment in the following way [12].

- **Extract Heavy elements from Phragmites australis and Ceratophyllin Demersum**

  Heavy elements were extracted in plants depending on the method [13].

**Results and Discussion**

1- **Heavy elements in Water Samples**

   The analysis of Heavy elements the samples show a gradual increase starting from the first station in Al-Fajr district and passing through the second station at Qal'at Sukkar district which is adjacent to Al-Gharraf oil field and ending with the third station in Al-Rifa'I district which lies south of the oil field and in both seasons (winter and summer 2019) apparently in a table (1). Water is exposed to a lot of sources of pollution, including industrial designs resulting from various industries such as oil refineries and gas associated with oil extraction, paper industry, fertilizers, spinning, weaving, rubber and petrochemical industries [14]. In 2004, Aziz explained that the sources heavy elements in the aquatic environment are due to the heavy sewage discharged into the river without [15]. We also note in a table (1) that show concentrations in the winter of 2019 are higher than those recorded in the summer of 2019, the waste from cities or agricultural land and It is considered from sources that are difficult to treat Most of them reach to rivers through Rainfall or melting of snow [16].

2- **Heavy elements in Sediment Samples**

   In the sediments, the concentrations were also gradually increasing from the first station through the second station and ending with the third station apparently in a table (2) and this situation is similar to that in water samples seasons (summer and winter 2019), except Cd and Ni in the first station is higher than the second station in summer 2019, when comparing the metals concentrations between the summer 2019 and winter 2019 we notice a decrease in the concentrations of Cd and Pb in winter 2019 as opposed to that of Ni and Zn the concentration in winter 2019 higher than in summer 2019.

   **Table (1):** The concentration of Heavy elements in water samples from Al- Gharraf river during the seasons winter- summer 2019 (μg / L)
| Season 2019 | Station | Mean   | SD     | Minimum | Maximum |
|------------|---------|--------|--------|---------|---------|
| Summary for Cd | St.1 | 0.002<sup>c</sup> | 0.0001 | 0.002 | 0.002 |
|             | St.2 | 0.003<sup>b</sup> | 0.0004 | 0.003 | 0.004 |
|             | St.3 | 0.008<sup>a</sup> | 0.0003 | 0.009 | 0.009 |
| LSD        |       | **0.00** |        |         |         |
| Winter For Cd | St.1 | 0.005<sup>b</sup> | 0.0001 | 0.005 | 0.006 |
|             | St.2 | 0.005<sup>b</sup> | 0.0001 | 0.006 | 0.006 |
|             | St.3 | 0.007<sup>a</sup> | 0.0002 | 0.006 | 0.007 |
| LSD        |       | **0.001** |       |         |         |
| Summary for Pb | St.1 | 8.26<sup>c</sup> | 0.15 | 8.10 | 8.40 |
|             | St.2 | 9.64<sup>b</sup> | 0.46 | 9.11 | 9.95 |
|             | St.3 | 14.40<sup>a</sup> | 0.45 | 13.90 | 14.80 |
| LSD        |       | **0.61** |       |         |         |
| Winter for Pb | St.1 | 8.63<sup>c</sup> | 0.25 | 8.40 | 8.90 |
|             | St.2 | 9.83<sup>b</sup> | 0.35 | 9.50 | 10.20 |
|             | St.3 | 10.56<sup>a</sup> | 0.32 | 10.20 | 10.80 |
| LSD        |       | **0.49** |       |         |         |
| Summary for Ni | St.1 | 3.86<sup>c</sup> | 0.15 | 3.70 | 4.00 |
|             | St.2 | 4.30<sup>b</sup> | 0.10 | 4.20 | 4.40 |
|             | St.3 | 5.23<sup>a</sup> | 0.06 | 5.19 | 5.30 |
| LSD        |       | **0.17** |       |         |         |
| Winter for Ni | St.1 | 6.36<sup>c</sup> | 0.07 | 6.29 | 6.44 |
|             | St.2 | 7.49<sup>b</sup> | 0.05 | 7.43 | 7.53 |
|             | St.3 | 7.92<sup>a</sup> | 0.05 | 7.88 | 7.98 |
| LSD        |       | **0.1** |       |         |         |
| Summary For Zn | St.1 | 22.40<sup>c</sup> | 0.65 | 21.80 | 23.10 |
|             | St.2 | 27.40<sup>b</sup> | 1.55 | 25.80 | 28.90 |
|             | St.3 | 35.46<sup>a</sup> | 0.60 | 34.90 | 36.10 |
| LSD        |       | **1.63** |       |         |         |
| Winter For Zn | St.1 | 48.36<sup>c</sup> | 1.02 | 47.20 | 49.10 |
|             | St.2 | 52.53<sup>b</sup> | 1.001 | 51.40 | 53.30 |
|             | St.3 | 73.00<sup>a</sup> | 3.14 | 69.60 | 75.80 |
| LSD        |       | **3.15** |       |         |         |
Table (2):- The concentration of Heavy elements in Sediment samples from Al- Gharraf river during the seasons winter- summer 2019 ($\mu$g /g) D.W

| Season 2019 | Station | Mean | SD  | Minimum | Maximum |
|-------------|---------|------|-----|---------|---------|
| Summary for Cd | St.1 | 0.01<sup>b</sup> | 0.002 | 0.02 | 0.02 |
|              | St.2 | 0.02<sup>a</sup> | 0.002 | 0.02 | 0.02 |
|              | St.3 | 0.02<sup>a</sup> | 0.001 | 0.02 | 0.02 |
| LSD         |      | 0.005 |     |         |         |
| Winter for Cd | St.1 | 0.013<sup>c</sup> | 0.0004 | 0.01 | 0.01 |
|              | St.2 | 0.015<sup>b</sup> | 0.0002 | 0.01 | 0.02 |
|              | St.3 | 0.016<sup>a</sup> | 0.0001 | 0.02 | 0.02 |
| LSD         |      | 0.001 |     |         |         |
| Summary for Pb | St.1 | 2.20<sup>c</sup> | 0.02 | 2.19 | 2.23 |
|              | St.2 | 2.53<sup>b</sup> | 0.13 | 2.40 | 2.66 |
|              | St.3 | 3.16<sup>a</sup> | 0.15 | 3.00 | 3.30 |
| LSD         |      | 0.187 |     |         |         |
| Winter for Pb | St.1 | 2.06<sup>b</sup> | 0.06 | 2.00 | 2.12 |
|              | St.2 | 2.09<sup>b</sup> | 0.02 | 2.07 | 2.11 |
|              | St.3 | 2.19<sup>a</sup> | 0.02 | 2.17 | 2.21 |
| LSD         |      | 0.05  |     |         |         |
| Summary for Ni | St.1 | 60.50<sup>b</sup> | 1.05 | 59.30 | 61.30 |
|              | St.2 | 60.30<sup>b</sup> | 1.96 | 58.10 | 61.90 |
|              | St.3 | 66.40<sup>a</sup> | 2.74 | 63.30 | 68.50 |
| LSD         |      | 3.23  |     |         |         |
| Winter for Ni | St.1 | 75.66<sup>b</sup> | 1.26 | 74.30 | 76.80 |
|              | St.2 | 86.06<sup>a</sup> | 1.10 | 84.90 | 87.10 |
|              | St.3 | 86.76<sup>a</sup> | 0.61 | 86.10 | 87.30 |
| LSD         |      | 1.63  |     |         |         |
| Summary for Zn | St.1 | 45.53<sup>c</sup> | 1.70 | 43.90 | 47.30 |
|              | St.2 | 48.23<sup>b</sup> | 1.17 | 46.90 | 49.10 |
|              | St.3 | 59.50<sup>a</sup> | 1.01 | 58.60 | 60.60 |
| LSD         |      | 2.10  |     |         |         |
| Winter for Zn | St.1 | 69.30<sup>c</sup> | 1.20 | 68.10 | 70.50 |
|              | St.2 | 73.90<sup>b</sup> | 1.20 | 72.70 | 75.10 |
|              | St.3 | 86.40<sup>a</sup> | 1.60 | 84.90 | 88.10 |
| LSD         |      | 2.13  |     |         |         |
3- Heavy elements in plants Samples (*Phragmites australis* and *Ceratophyllum demersum*)

In the table (3) and (4) all concentrations of Heavy elements in plants showed a gradual increase, as in water and sediment, where the lowest concentration of metals was recorded in the first station followed by the second station and the highest concentration was recorded in the third station in both seasons (summer and winter 2019), except for Zn, its concentration in the second station was higher than the third station by a very small amount. This confirms that the increased activity in Al-Gharraf oil field of human activities and oil operations has a significant impact in increasing concentrations of Heavy elements in the waters of the Al-Gharraf river. Because of the rainwater and during the fall and in large quantities during this year has washed all the pollutants on the surface of the soil and carry it to the course of sewage water, and increase the speed of this water inside the Sewage channels led to carry a lot of pollutants from within these channels and throwing it to the river.

**Table (3)**: The concentration of Heavy elements in *Phragmites australis* samples from Al-Gharraf river during the seasons winter - summer 2019 (μg/g) D.W

| Season 2019 | Station | Mean | SD | Minimum | Maximum |
|-------------|---------|------|----|---------|---------|
| **Summary for Cd** | St.1 | 0.057^c | 0.002 | 0.06 | 0.06 |
|             | St.2 | 0.067^b | 0.001 | 0.07 | 0.07 |
|             | St.3 | 0.071^a | 0.001 | 0.07 | 0.07 |
| **LSD** | 0.001 |      |    |       |         |
| **Winter For Cd** | St.1 | 0.056^c | 0.002 | 0.05 | 0.06 |
|             | St.2 | 0.061^b | 0.002 | 0.06 | 0.06 |
|             | St.3 | 0.072^a | 0.001 | 0.07 | 0.07 |
| **LSD** | 0.002 |      |    |       |         |
| **Summary for Pb** | St.1 | 0.21^c | 0.01 | 0.20 | 0.23 |
|             | St.2 | 0.30^b | 0.01 | 0.29 | 0.31 |
|             | St.3 | 0.35^a | 0.02 | 0.33 | 0.37 |
| **LSD** | 0.04 |      |    |       |         |
| **Winter for Pb** | St.1 | 0.24^b | 0.01 | 0.23 | 0.26 |
|             | St.2 | 0.29^a | 0.004 | 0.29 | 0.30 |
|             | St.3 | 0.31^a | 0.009 | 0.30 | 0.32 |
| **LSD** | 0.025 |      |    |       |         |
| **Summary For Ni** | St.1 | 0.012^b | 0.002 | 0.01 | 0.01 |
|             | St.2 | 0.020^a | 0.001 | 0.02 | 0.02 |
|             | St.3 | 0.024^a | 0.002 | 0.02 | 0.03 |
| **LSD** | 0.005 |      |    |       |         |
| **Winter For Ni** | St.1 | 0.22^a | 0.009 | 0.22 | 0.24 |
|             | St.2 | 0.21^a | 0.17 | 0.03 | 0.37 |
|             | St.3 | 0.32^a | 0.05 | 0.28 | 0.39 |
| **LSD** | 0.16 |      |    |       |         |
| Summary For Zn   | Station | Mean   | SD    | Minimum | Maximum |
|-----------------|---------|--------|-------|---------|---------|
|                 | St.1    | 8.92   | 0.07  | 8.85    | 8.99    |
|                 | St.2    | 9.40   | 0.17  | 9.20    | 9.50    |
|                 | St.3    | 12.93  | 0.47  | 12.40   | 13.30   |
| LSD             | 0.5     |        |       | 0.5     |         |
| Winter for Zn   | St.1    | 15.48  | 0.09  | 14.53   | 15.60   |
|                 | St.2    | 16.25  | 0.57  | 15.90   | 16.92   |
|                 | St.3    | 16.11  | 0.61  | 15.41   | 16.56   |
| LSD             | 0.80    |        |       | 0.80    |         |

Table (4):-The concentration of Heavy elements in *Ceratophyllum demersum* samples from Al-Gharraf river during the seasons winter - summer 2019 (μg /g) D.W

| Season 2019   | Station | Mean   | SD   | Minimum | Maximum |
|---------------|---------|--------|------|---------|---------|
| Summary for Cd| St.1    | 0.0167 | 0.001| 0.02    | 0.02    |
|               | St.2    | 0.0193 | 0.002| 0.02    | 0.02    |
|               | St.3    | 0.0220 | 0.003| 0.02    | 0.03    |
| LSD           | 0.004   |        |      | 0.004   |         |
| Winter for Cd | St.1    | 0.182  | 0.007| 0.18    | 0.19    |
|               | St.2    | 0.244  | 0.01 | 0.23    | 0.26    |
|               | St.3    | 0.292  | 0.007| 0.29    | 0.30    |
| LSD           | 0.01    |        |      | 0.01    |         |
| Summary for Pb| St.1    | 0.08   | 0.007| 0.07    | 0.09    |
|                | St.2    | 0.08   | 0.01 | 0.08    | 0.10    |
|                | St.3    | 0.08   | 0.01 | 0.08    | 0.10    |
| LSD           | 0.01    |        |      | 0.01    |         |
| Winter for Pb | St.1    | 0.36   | 0.02 | 0.35    | 0.39    |
|               | St.2    | 0.42   | 0.01 | 0.41    | 0.44    |
|               | St.3    | 0.45   | 0.006| 0.45    | 0.46    |
| LSD           | 0.04    |        |      | 0.04    |         |
| Summary for Ni| St.1    | 0.031  | 0.004| 0.03    | 0.04    |
|                | St.2    | 0.075  | 0.008| 0.07    | 0.08    |
|                | St.3    | 0.094  | 0.005| 0.09    | 0.10    |
| LSD           | 0.01    |        |      | 0.01    |         |
| Winter for Ni | St.1    | 0.13   | 0.01 | 0.12    | 0.15    |
|                | St.2    | 0.18   | 0.009| 0.17    | 0.19    |
|                | St.3    | 0.19   | 0.01 | 0.19    | 0.21    |
| LSD           | 0.03    |        |      | 0.03    |         |
| Summary For Zn| St.1    | 5.86   | 0.25 | 5.59    | 6.10    |
|                | St.2    | 6.13   | 0.20 | 5.90    | 6.30    |
|                | St.3    | 6.25   | 0.26 | 5.98    | 6.50    |
| LSD           | 0.41    |        |      | 0.41    |         |
| Winter for Zn | St.1    | 15.82  | 0.37 | 15.47   | 16.22   |
|                | St.2    | 19.21  | 0.37 | 18.79   | 19.47   |
You can also observe the high concentrations of zinc in all samples of the study, where the concentration was higher than the concentrations of other metals and this is due to several reasons. Plants take Heavy elements with Passive Transport (moving from high concentration to low concentration). Examples of negative elements are nickel and lead, while copper, zinc and others actively absorb active transport (Transfer against concentration) [17]. Concentrations (copper, lead and zinc) were also studied at 29 sites in some of the rivers on an island Fiji Japanese. It was found that the increase and distribution of these metals are related to the type of industrial waste produced from the various factories on this island as well as the activities of fishermen [18].

4- Physical and Chemical Characteristics

a- Water Temperature

In Table (5) we can show the high temperature was recorded in Summer 2019 for Stations 3 in air and lower temperature in Winter 2019 for water in Stations 1 and 2.

| Season | Station | Mean  | SD   | Minimum | Maximum |
|--------|---------|-------|------|---------|---------|
| Summery| St.1    | 25.00 | 4.00 | 21.00   | 29.00   |
|        | St.2    | 26.33 | 3.51 | 23.00   | 30.00   |
|        | St.3    | 26.33 | 2.08 | 24.00   | 28.00   |
| LSD    |         | 5.22  |      |         |         |
| Winter | St.1    | 17.00 | 3.60 | 13.00   | 20.00   |
|        | St.2    | 17.66 | 4.16 | 13.00   | 21.00   |
|        | St.3    | 18.66 | 4.16 | 14.00   | 22.00   |
| LSD    |         | 6.31  |      |         |         |

b- pH

Table (6) turbidity It was in both seasons (Summer and Winter 2019) at the station 1 higher than the station 2 and then go back to go up once again at station 3.

| Season | Station | Mean  | SD   | Minimum | Maximum |
|--------|---------|-------|------|---------|---------|
| Summery| St.1    | 7.45  | 0.03 | 7.42    | 7.49    |
|        | St.2    | 7.44  | 0.02 | 7.42    | 7.47    |
|        | St.3    | 7.48  | 0.04 | 7.44    | 7.53    |
| LSD    |         | 0.05  |      |         |         |
| Winter | St.1    | 7.73  | 0.06 | 7.68    | 7.80    |
|        | St.2    | 7.72  | 0.07 | 7.64    | 7.78    |
|        | St.3    | 7.72  | 0.10 | 7.62    | 7.82    |
| LSD    |         | 0.12  |      |         |         |
c- Salinity

In figure (7), Salinity in the summer of 2019 was much higher than in the winter 2019 and high Salinity was recorded in station 3 in summer 2019 it was 1.90 ppt.

| Season | Station | Mean | SD | Minimum | Maximum |
|--------|---------|------|----|---------|---------|
| Summery | St.1 | 1.13<sup>b</sup> | 0.05 | 1.10 | 1.20 |
|         | St.2 | 1.03<sup>b</sup> | 0.15 | 0.90 | 1.20 |
|         | St.3 | 1.66<sup>a</sup> | 0.25 | 1.40 | 1.90 |
| LSD     |     | 0.27 |    |    |        |
| Winter  | St.1 | 0.52<sup>b</sup> | 0.03 | 0.49 | 0.55 |
|         | St.2 | 0.65<sup>a</sup> | 0.03 | 0.62 | 0.69 |
|         | St.3 | 0.66<sup>a</sup> | 0.02 | 0.64 | 0.69 |
| LSD     |     | 0.05 |    |    |        |

d- DO

The highest mean concentrations were during the winter season, while the lowest mean values of DO were recorded during the summer season, Al-Gharraf river showed well oxygenated in the winter season. The increase in temperature will result in a decrease in the concentration of DO, as well as photosynthesis and aquatic organism’s respiration play an important role with fluctuations of DO concentration in water due to self-purification happen when the decomposing organisms use the DO to degrade the organic matter [19].

| Season | Station | Mean | SD | Minimum | Maximum |
|--------|---------|------|----|---------|---------|
| Summery | St.1 | 3.15<sup>b</sup> | 0.05 | 3.11 | 3.21 |
|         | St.2 | 3.07<sup>b</sup> | 0.09 | 2.98 | 3.17 |
|         | St.3 | 3.91<sup>a</sup> | 0.06 | 3.85 | 3.98 |
| LSD     |     | 0.11 |    |    |        |
| Winter  | St.1 | 6.83<sup>a</sup> | 0.07 | 6.77 | 6.92 |
|         | St.2 | 7.06<sup>a</sup> | 0.30 | 6.85 | 7.41 |
|         | St.3 | 7.06<sup>a</sup> | 0.07 | 6.98 | 7.11 |
| LSD     |     | 0.30 |    |    |        |
The results of the current study showed that the values of BOD$_5$ reached its highest concentration in winter 2019 compared with summer. This may be due to rainfall and large quantities in that period compared to previous years and high water levels and this result is identical [20]. The lowest value was recorded at Station 2 during the summer of 2019.

### Table (9) BOD$_5$ (mg/L)

| Season | Station | Mean  | SD  | Minimum | Maximum |
|--------|---------|-------|-----|---------|---------|
| Summery | St.1    | 2.92$^b$ | 0.01 | 2.91    | 2.94    |
|         | St.2    | 2.91$^b$ | 0.01 | 2.90    | 2.92    |
|         | St.3    | 3.24$^a$ | 0.05 | 3.19    | 3.30    |
| LSD     |         | 0.05   |      |         |         |
| Winter  | St.1    | 4.14$^b$ | 0.03 | 4.11    | 4.17    |
|         | St.2    | 4.33$^a$ | 0.07 | 4.25    | 4.39    |
|         | St.3    | 4.34$^a$ | 0.06 | 4.29    | 4.41    |
| LSD     |         | 0.08   |      |         |         |

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