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The Detection of Toxic Boron in Groundwater and Sludge in Bethlehem Area

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Abstract

Bethlehem is located in the Eastern Basin of the Mountain Aquifer. This part of the Aquifer is hydrologically important as one of the main sources of water supply in the southern part of the West Bank. This analytical study is carried out to determine the permissible amounts of boron in water samples from the Bethlehem area during the wet and dry seasons of 2014-2015. Boron (B) is a dark brown/black element which occurs naturally in fresh and saline waters. It can also result from pollution occurring from sewage or industrial discharges. The excessive use of boron in the industrial production of detergents and glass products increase boron concentration in wastewater. Boron is an essential nutrient for plants at low concentrations, but it is toxic to plants above 0.5 – 2.0mg/L. The Curcumin method is used for the detection of boron in drinking water by spectrophotometer at wavelength of 540 nm. The results show that the average concentration of boron in wells was the same (0.00333 mg/L) during the summer and winter seasons. The average concentration of boron in springs during the winter season was 0.00422 mg/L and it was 0.00556 mg/L during the dry season. The detection of boron in the sludge samples of Wadi Nar was conducted by the spectrophotometric method of Azomethine – H at a wavelength for 420 nm. The average concentration of boron in the sludge samples during the dry season was 1.523 mg/L and 1.135 mg/L for the wet season. Finally, the results of the analysis of the samples taken from wells and springs show that boron concentration was within the acceptable limits according to WHO standards of 2011.

Keywords: Bethlehem, boron, springs, wells, wastewater, sludge.

1. Introduction

Boron (B) is a natural dark brown/black element; it is widely found in sedimentary rocks and sediments especially in clay marine sediments. (Khayat et al., 2006). A high boron concentration of 4.5 mg B/L in seawater ensures that marine clays or sediments are rich in boron rather than other elements. Boron, as a natural element, is slowly released into the environment by natural weathering processes. Boron's mobility depends on soil acidity and rainfall because of its affinity to leach. (Keren and Mezuman, 1981). As a result, boron toxicity is more problematic in arid climates rather than temperate climates. Boron is widely used in detergent manufacturing as a major component because it is an excellent bleaching and cheap agent. As a result, it increases boron contents in sewage. However, wastewater with high boron concentration is not easily removed during standard sewage treatment processes. (Moss and Nagpal, 2003).

Boron is used in the industry as boric acid and sodium salts of boron primarily borax, or disodium tetraboratedecahydrate in a variety of products. It is widely used in the manufacture of glass and housing materials such as fiber-glass insulation and porcelain varnish, ceramic glazes and metal alloys. It is a major ingredient in many cleaning products, and is typically used in cleansers, cosmetics, detergents and laundry additives. It is also used in the manufacture of agrochemicals, insecticides and fertilizers in which boron is an essential element for plant growth. Boron compounds are also used as fertilizers and pesticides especially in areas with low boron constituents and high precipitation; boron fertilizers are added to increase the B content of soil fluids. Boric acid, borates, and perborates have been used in mild antiseptics and in the pharmaceutical industry. The U.S. Environmental Protection Agency (EPA) also identifies boron neutron capture therapy in cancer treatment (EPA, 2008).

The EPA classifies boron as a Group D element, meaning that there is inadequate or no evidence that boron is carcinogenic for humans or animals. Boric acid or sodium tetraborate in the diet causes growth retardation in mammals but low dietary levels protect against fluorosis and bone demineralization and may indirectly influence calcium, phosphorus, magnesium and cholecalciferol (Vitamin D3) metabolism. Long-term exposure may produce negative reproductive impacts on human health (WHO, 1998). The EPA limitations showed variation in the permissible concentration among adults and infants.

The EPA does not regulate boron in water, but it does monitor it in foods, and the Occupational Safety and Health Administration (OSHA) sets standards for workplace exposure especially in the industrial branch. The WHO (1998) suggests that the concentrations of boron for human consumption should not exceed 0.3 mg/l. as a guideline value.

The Bethlehem area has an arid to semi-arid climate with an increasing aridity towards the eastern slopes of the Jerusalem desert. The eastern basin of the Mountain Aquifer, in which the Bethlehem area is located, is the

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principal source of water in the southern part of the West Bank. The mismanagement of wastewater, especially over the highly permeable areas of limestone overlying the West Bank aquifer, endangers the quality of the groundwater. The hydrology of Bethlehem area is affected by the presence of fissures, fractures, joints and karstification in addition to the rock porosity and permeability. (Rofe and Raffety, 1963).

The sewage network serves 40.4 % of the total population in the Bethlehem Governorate which had 210484 inhabitants in 2014 while cesspits and open channels serve wastewater collection for the remainder. (PCBS, 2009a; PCBS, 2017; PWA, 2009). Direct disposal of wastewater into the environment can pollute the soil, surface water and groundwater. Increased modernization and the use of chemicals add more dangerous materials to the wastewater and increase the potential for environmental damage. As the population increases, the wastewater will also increase with more hazardous materials harming the environment (PCBS, 2009b). The lack of a sewage treatment plant in the Bethlehem area will increase the negative influence and create real problems for public health. Groundwater will be polluted as a result of seepage. Although wastewater in Bethlehem is collected through the municipality sewage networks, it is discharged as raw sewage into the Wadi Nar where it flows unprotected through the neighboring agricultural lands. In addition to this improper disposal of wastewater, there are also solid waste products such as glass, electrical conductors, and other commercial products which are rich in boron. The frequent disposal of sewage water from the Israeli settlements into Palestinian areas has a serious impact on human health by polluting the environment especially groundwater. A checkup survey is conducted to determine whether the concentrations of boron in waste water and in the local aquifer are within the permissible WHO guidelines.

2. Study Area

The study area is the Bethlehem governorate which lies in the Eastern Basin of the Mountain Aquifer. Bethlehem governorate is between 158 and 198 East and between 98 and 128 North on the Palestinian Grid. According to (ARIJ, 2010b) the governorate has a total area of approximately 659.1 km². Conferring to Palestinian Meteorological Department, the average annual rainfall for the Bethlehem governorate is 518.4 mm/yr. The average annual rainfall for Bethlehem during 1900 to 2006 from Cremisan Monastery of coordinates 166.4 East to 126 North and at an elevation of 820 m is 574.7 mm/yr. More than 80 % of the rainfall is received during the winter season that is from December to May (Zeitoun, 2011). Bethlehem contributes to the arid and semi-arid climate with an increase in aridity towards the Eastern Slopes in the Jerusalem desert (Rofe and Raffety, 1963).

2.1. Soil Type

In the Bethlehem area Cenomanian, Turonian and Senonian stages of the Upper Cretaceous Period are represented by limestones, dolomites, marls and, at the top of the sequence, chalk with chert layers and bands of nodular chert.

Bare rocks cover some of the area and the soil types include Lithosols, Brown Lithosols and LoessialArid Brown soils, Brown Rendzinas and Pale Rendzinas, Terra Rossas, Brown Rendzinas and Pale Rendzinas and Brown Lithosols and Loessial Serozems. The major soil types in the study area are Brown Lithosols and Loessial Arid Brown soils and Brown Rendzinas and Pale Rendzinas (Rofe and Raffety, 1963). The major soil types are shown in Figure (1).

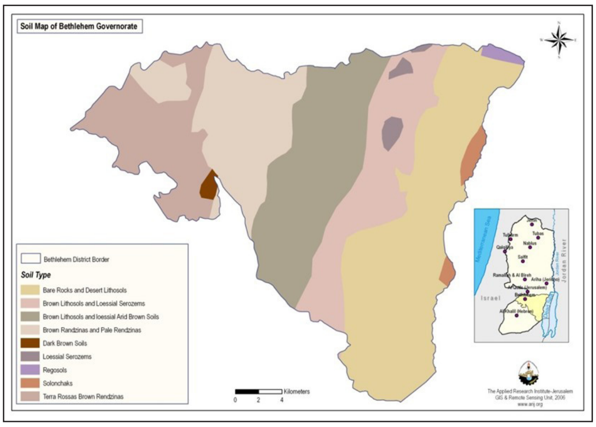

Figure 1. Soil map of Bethlehem governorate. (ARIJ, 1997)

2.2. Land-use

The total area of the Bethlehem Governorate is 659.1 km². The land-use map shows that most of the agricultural areas, forests, permanent crops, seasonal crops and plastic houses are located to the west of the Bethlehem region. Agricultural irrigation is provided by local village springs.

Agricultural land makes up 621.748 km², which is 94.3 % of the 659.1 km² of the Bethlehem Governorate. The Palestinian built-up areas cover 9.715 km² with a percent of 1.47 % of the total area of the Bethlehem Governorate (ARIJ, 2010b). The main activities are shown in the land-use map of Figure (2).

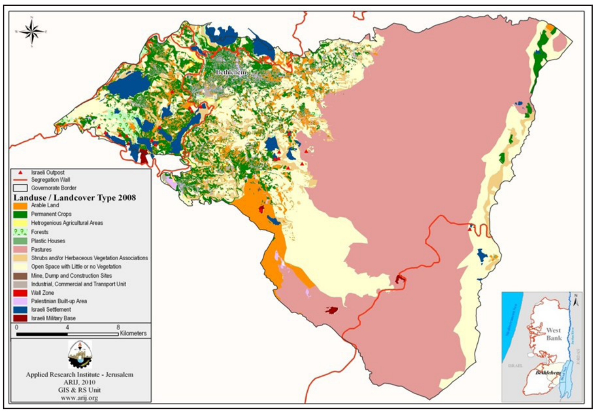

Figure 2. Landuse map of Bethlehem Governorate. (ARIJ, 2010b)

2.3. Water Resources

Discharge from springs and bore-hole well extraction from the eastern basin of the Mountain Aquifer provide the water supply for the Bethlehem Governorate. Of the three wells in this study Beit Fajjar is owned by the Water Supply and Sewerage Authority (WSSA), while "PWA 3" and "PWA 11" are owned by the Palestinian Water Authority (PWA) (PWA, 2015). Other wells in the area are owned by the occupational controller Mekorot.

The majority of the springs are located in the western part of Bethlehem region as shown in Figure (3).

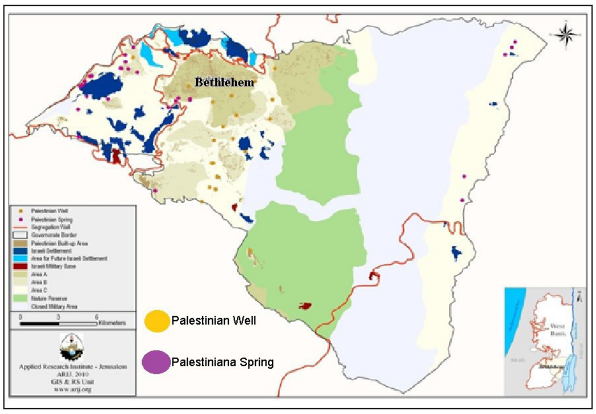

Figure 3. Water Resources map of Bethlehem Governorate modified after (ARIJ, 2010a).

Most of the villagers depend on local springs for irrigating their crops. As the network does not provide a regular supply, householders also have to make use of spring water for domestic requirements.

Although the main cities and refugee camps are connected to the sewage networks, there is no sewage treatment plant in the Bethlehem Governorate at all. Final discharge goes, without any primitive treatment, into open areas, agricultural land and into wadis such as the Wadi Nar. The sewage network serves about 40.4 % of the population the Bethlehem Governorate, while the remainder makes use of cesspits and open channels for wastewater collection (PWA, 2015).

3. Methodology

Implementation of the analysis for B concentration was completed for the wet and dry seasons of 2014-2015. The samples were collected at the end of May 2014 for the dry season and in January 2015 for the wet season. The survey was done for the available local wells and springs along the Bethlehem area as well as waste water and sludge from Wadi Nar in the wet and the dry seasons. Some more duplicate samples are also tested for the analysis and showed similar results.

In addition samples of waste water and sludge were collected from the Wadi Nar for both wet and dry seasons. The total number of samples for both seasons was about thirty samples for the study. In some cases, duplicate samples were collected for analysis and showed similar results.

3.1 Sludge Samples

The sludge samples were taken for a depth of 30cm from three different locations along 100 meter apart from the Wadi Nar stream. The standard chemical analysis for water was followed. Boron in soil is found in the crystalline structures of soil minerals. The detection of boron in soil is by the spectrophotometric method by Azomethine – H as a complex agent with the boric acid H_3BO_3 in aqueous media at a wavelength for 420 nm. Over a concentration range of 0.5 to 10 mg of B, Azomethine –H with H_3BO_3 forms a stable complex (APHA et al., 2005). A calibration curve is prepared with a linearity of 98.6 % for standards of boron in ppm as: 0.0ppm, 0.25ppm, 0.5ppm, 1.0ppm, 2.0ppm, 4.0ppm.The absorbance was: 0.00, 0.026, 0.67, 0.145, 0.298 and 0.648, respectively.

3.2 Water Samples

The concentration of boron in drinking water is no more than 1mg B/L and generally contains less than 0.1 mg B/L, and in seawater it is approximately 5mg/L. The standard chemical analysis for water was implemented. The Curcumin method is used for the detection of B in drinking water. The sample is acidified and evaporated in the presence of curcumin which is red in color, and rosocyanine is formed. The rosocyanine is compared with a standard curve by the spectrophotometric method at a wavelength of 540 nm (APHA et al., 2005). A calibration curve is prepared with a linearity of 99.6 % for standards of Boron in ppm as: 0.0ppm, 0.01ppm, 0.02ppm, 0.03ppm, 0.04ppm and absorbance was : 0.00, 0.046, 0.171, 0.237 and 0.330, respectively.

4. Results and Discussion

The experimental check on boron in the wet and dry seasons of the period 2014-2015 is successfully accomplished. The results show that almost all the samples are within the permissible limits although with a variety in concentration among soil and sewage samples. The results show that the average concentration of boron in wells for both the summer and winter seasons is the same at 0.00333 mg/L. The maximum concentration in both seasons was the same at 0.005 mg/L as shown in Table (1) and Figure (4).

Table 1. Boron concentration for well samples in the wet and dry season in 2014-2015. The wells coordinates are according to (Scarpa, 2006).

Boron in Wells – Bethlehem					
Name	**Location**	**Coordinates**	**Date**	**B mg/L**	**WHO 2011**
PWA 11	Teqou	169.30/116.35	22/1/2015	0.003	1.5 mg/L
PWA 3	Teqou	171.25/120.25	22/1/2015	0.005	
Beit Fajjar	Teqou	169.60/115.10	22/1/2015	0.002	
Average: 0.003333 mg/L					
Minimum: 0.002 mg/L					
Maximum: 0.005 mg/L					
PWA 11	Teqou	169.30/116.35	20/5/2014	0.003	
PWA 3	Teqou	171.25/120.25	20/5/2014	0.005	
Beit Fajjar	Teqou	169.60/115.10	20/5/2014	0.002	
Average: 0.003333 mg/L					
Minimum: 0.002 mg/L					
Maximum: 0.005 mg/L					

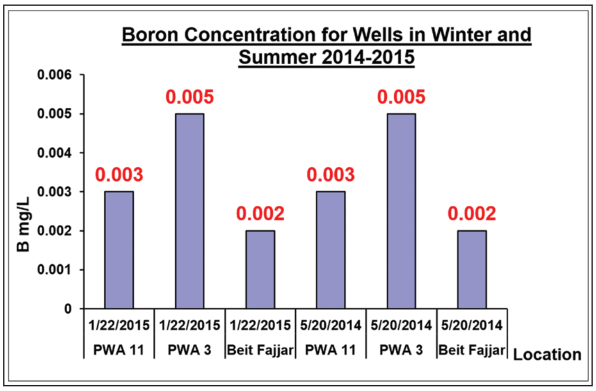

Figure 4. Boron concentration for well samples in the wet and dry season of 2014-2015.

The production wells are in the Herodian – Beit Fajjar field. The yield of the tested wells are within 230 – 250 m^3/hr and the pumpage rate is 1.72 – 1.8 MCM. Based on the World Health Organization recommendations, each person should receive a minimum quantity of 100 liters of fresh water per day. However, Bethlehem receives an average supply of no more than 58 liters per capita per day (PWA, 2015), whereas the daily distribution per capita from consumed water for domestic purposes is 79.1 liters/capita/day (l/c/d) in the West Bank in 2014.As an alternative, the villagers depend on the local springs for their daily domestic use in case of shortage of municipal water supply (Scarpa, 2004).

The average concentration of Boron in springs for the winter season is 0.00422 mg/L with a maximum of 0.01 mg/L and a minimum of 0.002 mg/L. The maximum concentration of 0.01 mg /L is for the sample from Wadi Nar, which is a surface running sewage stream. This is due to high boron contents in detergents, soaps and laundry additives. Sodium perborate ($NaBO_3.H_2O$) is widely used as a bleaching agent in domestic and industrial cleaning products. Boron, like other inorganic ions, is not removed during waste water treatment. It accumulates in domestic water and consequently in natural aquatic systems (Frenkel et al., 2010). The data shows that boron concentration is still within the acceptable limits which are below 1.5 mg/L according to (WHO, 1998; WHO, 2004; WHO, 2011). The average boron concentration in springs for the dry season is 0.00556 mg/L with a maximum of 0.01 mg/L and a minimum of 0.001 mg/L. The results of the analysis of the spring samples are illustrated in Table (2) and in Figure (5).

Table 2. Boron concentration for spring samples in the wet and dry seasons of 2014-2015. Springs Coordinates are from (Abed Rabbo et al., 1999).

Boron in Springs – Bethlehem					
Name	**Location**	**Date**	**B mg/L**	**Code**	**Coordinates**
Beir Ona	Beit Jala	22/01/2015	0.002		167.5/125.7
EinBalad	Ertas	22/01/2015	0.002	CB30	167.5/121.8
Wadi Nar	Wadi Nar	22/01/2015	0.01		
EinJame'-Battir	Battir	22/01/2015	0.004	BB21	162.8/125.6
EinBalad-Battir	Battir	22/01/2015	0.003	BB20	163.3/126.3
EinBalad-Nahalin	Nahalin	22/01/2015	0.005	BB28	161.1/121.6
EinBalad-WadiFukin	WadiFukin	22/01/2015	0.006	BB30	159.3/124.6
Namous-Hussan	Hussan	22/01/2015	0.002	BB27	161.2/123.1
EinBalad-Hussan	Hussan	22/01/2015	0.004		161.9/123.9
Average: 0.00422 mg/L					
Minimum: 0.002 mg/L					
Maximum: 0.01 mg/L					
Beir Ona	Beit Jala	20/05/2014	0.001		167.5/125.7
EinBalad	Ertas	20/05/2014	0.005	CB30	167.5/121.8
Wadi Nar	Wadi Nar	20/05/2014	0.01		
EinJame'-Battir	Battir	20/05/2014	0.003	BB21	162.8/125.6
EinBalad-Battir	Battir	20/05/2014	0.006	BB20	163.3/126.3
EinBalad-Nahalin	Nahalin	20/05/2014	0.006	BB28	161.1/121.6
EinBalad-WadiFukin	WadiFukin	20/05/2014	0.005	BB30	159.3/124.6
Namous-Hussan	Hussan	20/05/2014	0.008	BB27	161.2/123.1
EinBalad-Hussan	Hussan	20/05/2014	0.006		161.9/123.9
Average: 0.005556 mg/L					
Minimum: 0.001 mg/L					
Maximum: 0.01 mg/L					

Almost all the samples taken from the springs and wells showed similarity in concentrations which were below the acceptable limit of 1.5 ppm recommended by WHO in 2011

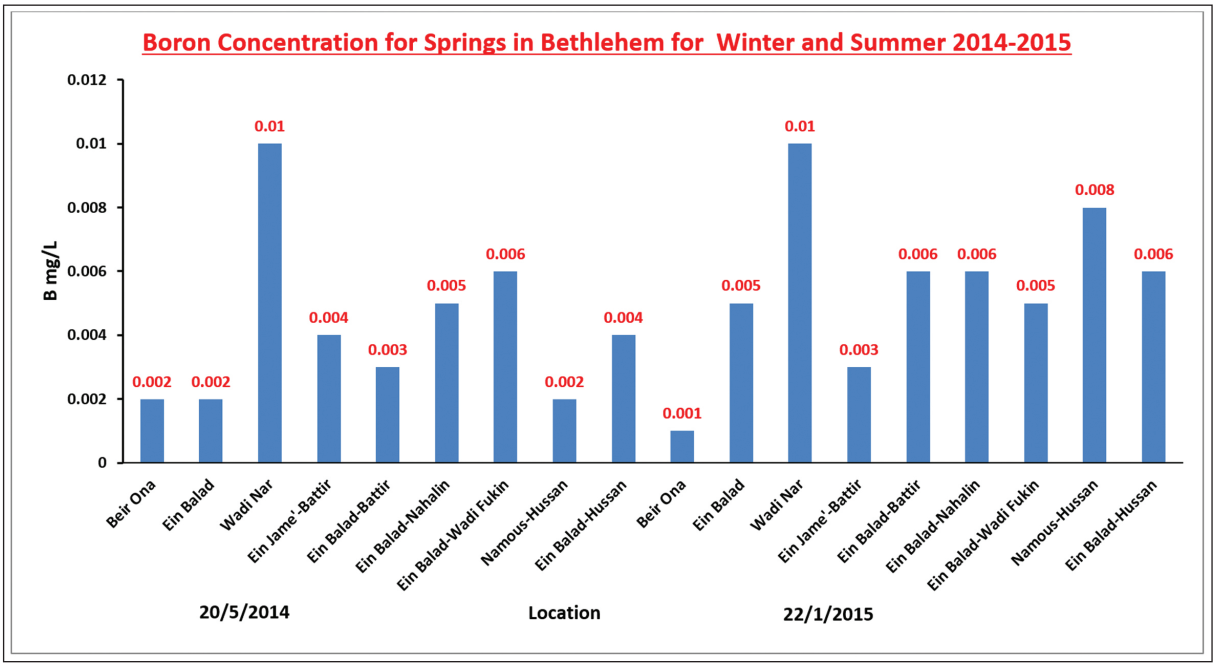

Figure 5. Boron concentration for spring samples in the wet and dry seasons of 2014-2015

The sludge samples taken from Wadi Nar showed acceptable values. The sludge samples were taken per season from three different locations for a depth of 30 cm with 100 m apart. The standard chemical analysis for water was followed. The results of the analysis of the sludge samples are illustrated in Table (3) and in Figure (6).

Table 3. Boron concentration for sludge samples in the wet and dry seasons of 2014-2015.

Boron in Sludge– Bethlehem				
Name	**Location**	**Soil**	**Date**	**B mg/L**
sludge 1	Wadi Nar	Soil	22/1/2015	1.145
sludge 2	Wadi Nar	Soil	22/1/2015	1.11
sludge 3	Wadi Nar	Soil	22/1/2015	1.15
Average: 1.135 mg/L				
Minimum: 1.11 mg/L				
Maximum: 1.15 mg/L				
sludge 1	Wadi Nar	Soil	20/5/2014	1.537
sludge 2	Wadi Nar	Soil	20/5/2014	1.51
sludge 3	Wadi Nar	Soil	20/5/2014	1.522
Average: 1.523 mg/L				
Minimum: 1.51 mg/L				
Maximum: 1.537 mg/L				

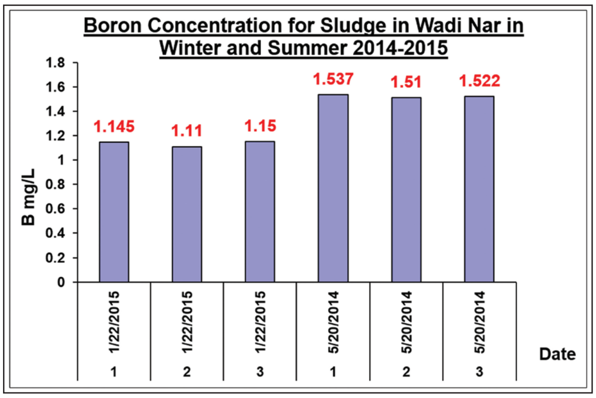

Figure 6. Boron concentration for sludge samples in the wet and dry seasons in 2014-2015.

Although a survey over one year provides interesting data, further study over two or three successive years would provide more precise indicators.

The average concentration of boron in the sludge samples for the dry season was 1.523 mg/L, whereas for the wet season the average was 1.135mg/L. These concentrations are high when compared with concentrations in fresh water. The high level of boron in Wadi Nar in the dry season is higher than that in the wet season due to direct evaporation. The high level of boron in the Wadi Nar is due to the excessive presence of detergents and cleaning products rich in boron contents such as borax. Moreover, many sewage tanks discharge sewage directly into the stream and some sewage tanks are filled with calcium sludge from neighboring stone cutting plants which may have boron traces (WSI, 2005). However, the increased concentration of boron in the sludge samples can be attributed to the accumulative sedimentation of boron over time. Although it shows higher concentrations than in the samples from wells and spring, it is still within the permissible limits for surface running water. However, the concentration of boron in sludge samples may increase over time due to the excessive use of borax in detergents and bleaching. Boron concentration may also rise over time in wells and springs due to the locations of springs near intensive neighborhood activities which depend mostly on cesspits for their sewage water. The common use of cesspits in some neighborhoods may be the cause for the higher concentrations of boron in local spring discharge.

Bethlehem has six major soil types which are mainly rich in calcium, sodium, potassium, clay, marl, limestone, chalk and conglomerates. These soil types enhance the presence of boron as a natural constituent particularly in clay-rich marine sediments (Vengosh et al., 2005). According to laboratory analysis conducted by the Water and Soil Environmental Research Unit (WSERU) at Bethlehem University for the period 2013-2014, the average concentration of calcium as Ca mg/L in the Bethlehem wells is 72.6 mg/L and 77.4 mg/L in the Bethlehem springs (WSERU, 2014).

Finally, the results of Boron concentration in wells and springs in Bethlehem Governorate show that boron concentrations are below 1.5 mg/L and are within the acceptable limits of the WHO guidelines of 2011. The sludge samples also indicate acceptable concentrations in comparison to the quality of the sewage samples.

5. Conclusions

Boron is a naturally occurring element that is found mainly in sedimentary rocks rich in clay marine sediments. Some industrial commercial products release boron into the environment. This includes the use of borate compounds such as borax, boric acid, and other refined products in the manufacture of glass, fiberglass, washing products, alloys and metals, fertilizers, wood treatments and insecticides. Boron is an essential micronutrient for plant growth at low levels depending on the plant species.

The survey examined samples from available wells and springs in the Bethlehem area and from waste water and sludge from the Wadi Nar in the wet and dry seasons of 2014-2015.

The total number of samples for both seasons was around thirty samples for the study. The sludge samples were taken from a depth of 30cm. The chemical analysis was performed by the standard method of water analysis. The Curcumin method was used for the detection of boron in drinking water. The samples were acidified and evaporated in the presence of red curcumin forming rosocyanine. The rosocyanine is compared with the standard curve by the spectrophotometric method at a wavelength of 540 nm. Boron in soil is found in the crystalline structures of soil minerals. The detection of boron in soil is by the spectrophotometric method of Azomethine – H as a complex agent with the boric acid H_3BO_3 in aqueous media at a wavelength for 420 nm. Finally, the results of the analysis show that the concentration of boron in the water and sludge samples are within the permissible limits of WHO guidelines.

Recommendations

Implementing the survey of boron presence in other parts of the West Bank is highly recommended in order to have additional scientific information on the presence of boron in the West Bank for future generations. Further studies on other parameters such as nitrates, phosphates, salinity and with major cations and anions in water resources will be very useful to check for its correlations with the presence of boron. In addition, an elaborate study on the presence of boron in agricultural field crops irrigated or sprayed with water or fertilizers that might be rich in boron is also highly recommended.

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