

IMPACT OF BAZIAN CEMENT FACTORY ON AIR, WATER, SOIL, AND SOME GREEN PLANTS IN SULAIMANI CITY-IRAQ

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ABSTRACT

This study was carried out to assess impacts of industrial activities on environmental quality in Bazian cement factory, Sulaimani. Environmental impact of factory was carried out from September 2015 to August 2016 at studied area located at north west of city with coordinates of 35°36'242"-045°04'470". Pollutant particles can have as consequence reduction of biodiversity and quality of water, soil and whole ecosystems. Especially, cement dust can be emitted at every stage of cement production which affects on photosynthetic process, leaf stomata, discoloration, enzymatic malfunction, growth reduction and productivity of plants. In this study, water, soil, air and three plants (*Platycladus orientalis*, *Eucalyptus spp.* and *Melia azedarach*) samples were collected. Ten water sources including 6 wells, 3 tanks and control in and around factory were selected in order to evaluate some physicochemical characteristics of water. Concentrations of some heavy metals including cadmium, chromium, lead, copper, nickel, iron and zinc were determined to evaluate pollution status. Soil samples include twelve different sites nine of them are cement dust exposed with three control sites. Same work for them had done. Heavy metal analysis and chlorophyll content for plants also determined. Air gases results had taken online from computer fixed on main stack monthly. Also dust from main stack had collected and analyzed for physicochemical parameters and heavy metals. Results showed that were within normal standards.

Keywords: Cement ; impacts; heavy metals; plants; physicochemical parameters.

الطائي وآخرون

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تأثير مصنع اسمنت بازيان على الهواء والماء والتربة وبعض النباتات الخضراء في مدينة السليمانية-العراق

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المستخلص

أجريت هذه الدراسة لتقييم تأثيرات الأنشطة الصناعية على جودة البيئة في مصنع بازيان للأسمنت، السليمانية. تمت الدراسة لمصنع اسمنت بازيان من أيلول 2015 إلى آب 2016 في المنطقة التي تقع شمال غرب السليمانية بإحداثيات -35°36'242" 045°04'470". يمكن أن تؤدي الملوثات إلى تخفيض التنوع البيولوجي ونوعية المياه والتربة والنظم البيئية بأكملها. وبصفة خاصة، يمكن أن ينبعث غبار الإسمنت في كل مرحلة من مراحل إنتاج الإسمنت مما يؤثر في عملية التمثيل الضوئي، وانتفاخ الأوراق، وتلونها، والعجز الأنزيمي، والحد من النمو وإنتاجية النباتات. في هذه الدراسة تم جمع عينات المياه والتربة والهواء وثلاثة نباتات (بلاتيكلادوس أورينتاليس، ويوكالبتوس، ميليا أزيداراش). تم اختيار عشرة مصادر مياه منها 6 بئر و 3 خزانات وعينة سيطرة في المصنع وحوله لتقييم بعض الخصائص الفيزيائية والكيميائية للمياه. تركيز بعض العناصر الثقيلة الكاديوم والكروم والرصاص والنيكل والزنك تم تقديرها لتقييم حالة التلوث. شملت عينات التربة اثني عشر موقعا مختلفا تسعة منها تحت تأثير غبار الاسمنت مع ثلاثة مواقع مقارنة. وقد تم تحديد ذات الطرق المستخدمة في قياس نسب العناصر لعينات المياه. كما تم تحديد العناصر الثقيلة ومحتوى الكلوروفيل للنباتات. وقد أخذت نتائج الغازات الجوية من الانترنت من الكمبيوتر المثبت على المدخنة الرئيسية شهريا. كما تم جمع وتحليل الغبار من المدخنة لتحديد المعايير الفيزيائية والكيميائية والعناصر الثقيلة. وأظهرت أغلب النتائج أنه في حدود المعايير العالمية.

الكلمات المفتاحية: مصنع الأسمنت. التأثيرات البيئية؛ معادن ثقيلة؛ النباتات. المعلمات الفيزيائية.

INTRODUCTION

Different industrial activities are degrading various environmental components like water, air, soil and plant vegetation. Environmental pollution as a result of cement industry could be defined as adverse impact induced for water, air and soil through various activities, beginning from mining activity of raw material up to its crushing, grinding, and other processes developing in a cement plant. Cement industry is one of 17 most polluting industries listed by Central Pollution Control Board (CPCB) (27).

Water is basic need for survival of any living beings, plants and animals. Establishment and operation of any industry affects water resources of area. Ground water is generally considered cleaner than surface water, on which majority of population depend (11). Both ground and surface water chemistry are controlled by composition of its recharge components, geological and hydrological variations within aquifers (44). Polluted Improved knowledge is required for understanding and evaluating suitability of groundwater for different purposes. Groundwater quality comprises physical, chemical and biological qualities of groundwater (35). Temperature, turbidity, colour, taste and odour make up list of physical water quality parameters. Since most groundwater are colourless, odourless and without specific taste, concern is chemical qualities. Naturally, groundwater contains mineral ions and these ions slowly dissolve from soil particles, sediments and rocks as water travels along mineral surfaces in pores or fractures of unsaturated zone and aquifer (23).

Cement sector is emitting large amount of oxides of sulfur, nitrogen and carbon. These gases can contribute to health problems and environmental impacts, such as acid rain, ground level ozone, global warming, water quality deterioration, and visual impairment (11).

Toxic metals and organic compounds are released when industrial waste is burnt in cement kiln. Other sources of dust emissions include clinker cooler, crushers, grinders, and materials-handling equipment (31). Dust which is emitted during cement processes are

eventually deposited on soil, sediment, water and plants. Dust emissions from cement and other related industries therefore have to be given attention for control. This is necessary in view of pollution load and its impact on the environment (28).

In a major research on effect of pollutant substances on vegetation performed in areas around cement industry in most parts of world, clearly, destruction of plant life by rising material entry has been proved. Emissions from cement factories toward nature via weather, water and soil that are included as feeder sources of plant and their concentration beside plant disturbs their metabolic activities in providing vital needs (43). Robert G. Blezard defined cement as “adhesive substance capable of uniting fragments or masses of solid matter to a compact whole” (16). Cement industries are generally associated with high dust emissions into atmosphere. Emitted dusts are naturally eliminated as deposits to earth surface through dry or wet deposition in rainfall (34). Damaging consequences of released dust particles for soil, flora and fauna of the cement factory neighborhood could be considerable (8) and damaging effects of dust fall, which is characterized by enriched heavy metals such as Lead (Pb), Nickel (Ni), Chromium (Cr), Copper (Cu), Zinc (Zn), and Cadmium (Cd) (6) and on water (18). A cement factory (Bazian Cement) was situated at Bazian and joined Lafarge Group in 2008 in frame of acquisition of Orascom Cement Group. Aim of present study is: 1. get some information about impacts of bazian cement factory on dust, water, soil, plants and air components in and out of factory to show its effect to environment. 2. study physicochemical parameters in dust, water, soil, plants and air. 3. determine chlorophyll content of study plants. 4. Evaluation of heavy metals concentration in dust, water, soil and plants leaves. 5. evaluate heavy metals bioaccumulation in plants tissue.

MATERIALS AND METHODS

Study area: Sulaimani is one of important Iraqi cities of Kurdistan region. Sulaimani province occupies more than 1200 km² in Kurdistan region of Iraq. Most of region is high plateau, more than 850 m above sea level,

becoming increasingly mountainous towards Zagros mountain in north, from this area the large perennial river, the lesser Zab descends eventually draining to river Tigris. There are also many ephemeral watercourses which become dry during summer; area bounds with springs and sources of underground water, most of which are used for water supply and irrigation purposes (29). Bazian cement factory is one of the greatest and largest cement factory in Kurdistan region, that located at north west of Sulaimani governorate 35°36'245"- 045°04'473" nearly 30 km far from city centre of Sulaimani within the boundaries of bazian. Plant equipments are designed and manufactured by a leading German company "Polysius - AG" and constructed by an Egyptian leading company in Middle East and Mediterranean Basin "Orascom construction". Environmental effects of this factory should be assessed because of its high economic importance. Therefore, impact of emissions should be determined. Geological formation of a certain area have a great impact on water quality due to erosion or leaching land crust or during

percolation toward different aquifers . Kurdistan region of Iraq made of foothills, mountains and alluvial basin (32), so it is playing a vital role in distribution and occurrence of ground water. Area bounded by Latitudes (35°29'50"- 35°42'45") and Longitudes (44°57'30"- 45°16'25") and occupies area estimated to be about 316.5 km². Series of mountains (Kuwaik and Uloblagh) divide whole basin in two-sub basins termed "Recent sub basin" and "Pila Spi basin" (14).

Sampling sites and sample collection

Water samples were collected from ten sampling sites. Selected sites included wells and tanks situated at different locations. Water samples were collected for chemical and physical parameters according to a regular schedule per month interval periods during september 2015 to August 2016. Table 1 show water sources and their coordinates. All water samples were collected following instructions recommended by American Public Health Association APHA (3). 3 plants and their soils collected from four sites in and near factory (1km) (12 sites) as shown in Table 2.

Table 1. show sites of water sources , coordinates

Sites	Coordinates	Description	Symbol used in study
Well 3	35°36'198"- 045°04'684"	Located inside factory near the boiler.	SW1
Well 5	35°36'190"- 045°04'644"	Located inside factory near packing part.	SW2
Well 6	35°36'588"- 045°04'268"	Located inside factory near packing part.	SW3
Well 7	35°36'217"- 045°04'802"	Located outside factory near gate3.	SW4
Well 8	35°36'084"- 045°04'582"	Located inside factory near gate3.	SW5
Well 10	35°36'344"- 045°04'225"	Located inside factory near gate2 and packing part.	SW6
Tank 1000	35°36'362"- 045°04'426"	Located inside factory near water station.	ST1
Tank 2000	35°36'211"- 045°04'457"	Located inside factory near CCR.	ST2
Tank 6000	35°36'364"- 045°04'428"	Located inside factory in water station.	ST3

Table 2. show sites of plants and their soil with coordinates

Sites	Coordinates	Description	Symbol	Plants and their soils
CCR	35°36'242"- 045°04'470"	Occur near main stack with wind direction.	SS1,SS5,SS9 (For soils)	<i>Platyclusus orientalis</i>
			SP1,SP5,SP9 (For plants)	<i>Melia azedarach, Eucalyptus spp.</i>
Gate3	35°36'190"- 045°04'644"	Occur near main stack but against wind direction in the biggining of factory.	SS2,SS6,SS10 (For soils)	<i>Platyclusus orientalis</i>
			SP2,SP6,SP10 (For plants)	<i>Melia azedarach, Eucalyptus spp.</i>
Out	35°36'233"- 045°04'837"	Out of factory (1 km) far from it.	SS3,SS7,SS11 (For soils)	<i>Platyclusus orientalis</i>
			SP3,SP7,SP11 (For plants)	<i>Melia azedarach, Eucalyptus spp.</i>
Control	35°33'726"- 045°21'299"	Occur in city center far from any pollution source.	SS4,SS8,SS12 (For soils)	<i>Platyclusus orientalis</i>
			SP4,SP8,SP12 (For plants)	<i>Melia azedarach, Eucalyptus spp.</i>



Figure 1. Locations of sites and water sources in studied area within Bazian, Sulaimani, Iraq. (Google, 2015)

Field analysis:

Air and water temperature (°C):

Both of air and water temperature were measured by using a clean mercury thermometer with scale marked from (0 to 100 °C), air temperature was measured in shadow while water temperature was measured by immersing thermometer in water for few minutes to obtain a constant reading. Thermometer was rinsed with distilled water after each use (2).

Hydrogen ion concentration (pH): Hydrogen ion concentration of water samples were measured immediately in the field using portable pH meter model. The instrument was calibrated initially by standard buffers of 4, 7 and 9 as describe by (2).

Electrical conductivity (EC) in $\mu\text{S cm}^{-1}$:

Conductivity of water samples were determined using standard procedure of (2), before each sampling, calibration of instrument was done by specific standard solutions (0.1N KCl), final results were corrected at (25°C) and expressed in $\mu\text{S cm}^{-1}$.

Total dissolved solid (TDS) in mg l^{-1} :

TDS were measured with pH-conductivity-TDS meter (COMBO HI model 98130).

Turbidity was determined by using Turbidity meter LP2000 (HANNA Instruments) after instrument calibration by known turbidity standard solutions. Turbidity was expressed with Nephelometric Turbidity Unit (NTU).

Total hardness: An accurate method was used for determination of total hardness and calcium hardness depending on procedure given by Theroux *et al.* (47). Measurements of total hardness were conducted depending on mathematical model below: $(\text{ppm Ca} \times 2.496) + (\text{ppm Mg} \times 4.115) = \text{ppm Total hardness as CaCO}_3$ Calcium and Magnesium Hardness: hardness of calcium and magnesium in each water sample was measured and calculated according to equations outlined by Theroux *et al.* (47): $(\text{ppm Ca} \times 2.496) = \text{Calcium hardness as CaCO}_3$ $(\text{ppm Mg} \times 4.112) = \text{Magnesium hardness as CaCO}_3$.

Alkalinity: It is measure of ability of water to neutralize acids. Total alkalinity was determined by titration method recommended by (2), after adding (5) drops of methyl orange to 50 ml of water samples, mixture was with H_2SO_4 (0.01N), results were represented as mg l^{-1} using the following equation:

$$\text{Alkalinity as mg CaCO}_3 \cdot \text{l}^{-1} = A \times B \times 50000 / \text{ml of sample}$$

Where: A = ml of H_2SO_4 titrant

B = Normality of H_2SO_4

Sodium and potassium (Na^+ and K^+):

Sodium and potassium are relatively abundant elements, and they are present to some extent in most natural waters (15). Flame photometric method was used as described in APHA

(3) using Corning- 400 Flame-photometer-U.K. Sodium and potassium emission readings were taken at wavelength of 589 and 767 nm, respectively. A series of standard stock solutions (0.1 to 8 mg l⁻¹) of Na⁺ and K⁺ from NaCl and KCl were prepared for calibration of the instrument, and creating calibration curve. Final results were expressed in mg l⁻¹.

Chloride (Cl⁻): Argentometric method (Mohor Method) was used for determination of chloride content in water sample. Silver nitrate solution (AgNO₃) as a titrant and potassium chromate (K₂CrO₄) as indicator were used, as described by Sawyer and MacCarty (42). Chloride (mg Cl l⁻¹) = (V1 - V2) × N × 35.45/Volume of sample × 1000 where V1 is volume of silver nitrate required by the sample (ml), V2 - volume of silver nitrate required by the blank (ml), N - normality of silver nitrate, and 35.45 is molecular weight of Cl⁻.

Reactive phosphorus (PO₄⁻³): All methods for estimating reactive phosphorus are mainly colorimetric dependence, and most are depended on the formation of a blue colour solution above acidic base. For laboratory, procedure is described by Parson *et al.* (36). Water samples were allowed to react with a mixed reagent, consisting of ammonium molybdate, ascorbic acid (kept frozen between analysis), concentration of sulphuric acid, and trivalent antimony 1-tartarate solution. Absorbance of this solution was measured spectro-photometrically using UV-VIS. Spectrophotometer (TU.1800, UK), at wavelength of 885 nm. Results were expressed in mg l⁻¹.

Nitrate nitrogen (NO₃⁻): Nitrate concentration of water samples were estimated by using a special nitrate-sensitive membrane electrode (Ino lab.pH, Ion, Cond.750-Multiparameter laboratory, WTW, Germany). Results were expressed in mg l⁻¹.

Sulfate ion (SO₄⁻²) in mg l⁻¹:

Turbidimetric method as described by (1) was used for sulfate determination, when barium chloride was used, and results were recorded at wave length 420 nm within 30 seconds intervals and the SO₄⁻² concentration is determined by comparison of reading with a standard curve of sulfate concentration in the range 0.0 to 40 mg l⁻¹.

Heavy metals in water samples (mg l⁻¹):

Heavy metals in water samples were determined by atomic absorption as recommended by APHA (3). Procedure of in-situation was conducted depending on direct Air-Acetylene (C₂H₂). (17); 40). Analyst 700-Atomic absorption spectrophotometer and Varian-24fs Flame Atomic Absorption Spectrophotometer was used for determination heavy metals. Chemical digestion was done in laboratories of biology department then sample analysis have done at directorate of environment labs. in Sulaimani city.

Soil laboratory analysis

Soil samples at each location were taken to lab and they were analyzed for chemical and physical properties. Briefly; returning bag to lab soil samples were dried and sieved. Extraction method: 60 g of an air-dried sample were mixed with 300 ml of de-ionised water (if 1:1 or 60 to 300 if 1:5). Mixture was shaken in a rotary shaker for an hour, then left to stand. Extract was passed through a filter paper. Then chemical composition of extracts (K⁺, Na⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻, PO₄ and nutrients) was determined like water samples.

Hydrogen ion concentration (pH):

Approach of this measurement was performed according to (19). Procedure of measuring is as follow: 1. pH value was determined for a 1:5 soil: distilled water suspension, by taking 20 gm of dry ground soil: 100 ml of distilled water. 2. Suspension was shaken using a mechanical stirrer and allow to stand for 30 minutes. 3. Suspension was filtered with filtering papers. 4. Electrode of pH meter (HANA instrument, 024125) was immersed into filtered sample, and pH value was recorded.

Electrical conductivity (EC) in μS cm⁻¹:

Soil EC is a measurement that correlates to soil salinity. Electrical conductivity was determined by method described by (19).

Heavy metals in soil samples (mg l⁻¹):

Acid digestion of soil was used for preparation of samples to be measured by Atomic Absorption Spectrometry (AAS) using Di-Acid (HNO₃-HClO₄) method by (19).

Heavy metals in main stack dust (mg l⁻¹):

Sample of dust had taken from higher point of main stack. Dust had collected in clean bag.

Acid digestion for method was used for preparation of sample to be measured by Atomic Absorption Spectrometry (AAS) using Di-Acid (HNO₃-HClO₄) method by (19).

Plant laboratory Analysis

Chlorophyll determination (mg l⁻¹):

Collection of plant samples: In this study, three commonly green trees (*Eucalyptus spp.*, *Melia azedarach* L. and *Platycladus orientalis*) were collected for experimental purpose. These species are mostly preferred to grow in conditions under effect of main stack. Healthy and uninfected trees were collected at their stage of maturity; and care was also taken during sampling of leaves to avoid mechanical injuries. Fresh leaf samples were wash thoroughly first in tap water followed by distilled water in the laboratory, analyzed for determination of chlorophylls (Chl-a and Chl-b).

Analytical procedure: Accurately weighted 0.5g of fresh plant leaf sample was taken, and homogenized with 10 ml of extractant solvent (Acetone 80%). Homogenized sample very well by mortar and pestle and must pulverized completely, thus a few grains of sand may help. This is leaf homogenate, then filter leaf homogenate through filter paper. Retentate is removed by filter paper (and discarded) and the extract (or filtrate) is collected in a test-tube. Solution mixture was analyzed for Chlorophyll-a, Chlorophyll-b and content in spectrophotometer. Equation used for quantification of Chlorophyll-a, Chlorophyll-b, and carotenoids are: Arnon's equation to convert absorbance measurements to mg Chl g⁻¹ leaf tissue (13): Chl a (mg g⁻¹) = [(12.7 × A663) - (2.6 × A645)] × ml acetone / mg leaf tissue

Chl b (mg g⁻¹) = [(22.9 × A645) - (4.68 × A663)] × ml acetone / mg leaf tissue

Total Chlorophyll = Chlorophyll a+Chlorophyll b.

Heavy metals in plant samples (mg l⁻¹):

Acid digestion of plant leaves samples was used for samples preparation to be analyzed by Atomic Absorption Spectrometry (AAS) using Di-Acid (HNO₃-HClO₄) method by (19).

Statistical Analysis

Basic statistics of measured parameters were estimated. Patterns of variation due to different plants and different sites were tested by using one-way ANOVA. Range test was used as a post hoc test to compare between means at p>0.05. Software SPSS, version10 (SPSS, 1998) was used.

RESULTS AND DISCUSSION

Physicochemical parameters and heavy metals of water:

Summary of physical and chemical parameters from ten stations of water are given in Table 3, including mean of values and WHO standards. Concentration of heavy metals of water samples (Cd, Cr, Pb, Cu, Ni, Zn and Fe) are shown in Table 4.

Physicochemical parameters and heavy metals of Soil:

Both of table 5 and 6 give the same results but for soil samples. Different from water samples, control samples for every type of plants here we take fourth site far from any pollution source in city centre (garden). That mean here become three controls.

Parameters of plants leaves:

Chlorophyll determination for three types of plants during study period by determination of both chlorophyll a and b had done.

After digestion of leaves of collected plants, determination of heavy metals by atomic absorption spectrophotometer for same seven metals those were determined for water and soil. Table 7 and 8 show total chlorophyll concentrations and heavy metals concentrations in collecting plants leaves respectively.

Physicochemical parameters and heavy metals of dust:

A summary of physical and chemical parameters of dust sample are given within Table 5. Concentration of heavy metals (Cd, Cr, Pb, Cu, Ni, Zn and Fe) are shown in Table 6

Table 3. Physico-chemical parameters of water samples of the studied sites during the studied periods from September 2015 to August 2016

S/N	Parameter	WHO	Well3	Well5	Well6	Well7	Well8	Well10	Control	Tank6000	Tank1000	Tank2000
1.	Air Temp.	-	25.45±6.61a	25.69±6.57a	26±7.35a	26.18±7.21a	26.09±6.52a	26±6.36a	25.55±6.30a	26.82±6.38a	26.55±6.49a	26.64±6.39a
2.	Water Temp.	-	19.63±2.76a	20.36±2.46a	20.36±2.54a	20.18±2.04a	20.09±2.16a	20.18±2.31a	20.45±2.01a	20.45±2.54a	20.54±2.38a	21.45±2.06a
3.	pH	6.5-8.5	7.40±0.26a	7.50±0.32a	7.43±0.32a	7.41±0.28a	7.40±0.28a	7.48±0.28a	7.47±0.56a	7.45±0.28a	7.39±0.23a	7.18±0.30a
4.	EC	400-1400	323.7±39.1b	332.2±21.8b	346.5±14.2b	385.7±19.3b	383.6±27.5b	342.4±27.3b	560.3±202.2a	361.6±35.5b	339.5±42.9b	360.6±68.7b
5.	T.D.S	500-1500	252.3±50.3b	254.2±42b	256±44.1b	271.5±48.2b	260.5±62.6b	256.9±53.6b	357.9±123.2a	271.9±54.5b	269.3±49b	313.4±122.1a
6.	Alkalinity	200	172.4±26.6a	181.6±22.9a	187.2±20.3a	189±27.7a	197.2±33.5a	180.1±25.2a	191.1±57.4a	176.46±25.8a	179.8±21.9a	183.3±22.6a
7.	Turbidity	5	6.24±4.81a	4.20±1.28ab	5.04±2.66ab	6.22±3.32a	3.55±1.15b	3.30±1.36b	3.82±1.81b	3.25±1.55b	3.61±1.12b	3.020.96b
8.	Total Hardness	100-500	220.6±56.8a	247.8±44.4a	260±53a	281.5±84a	279.5±71.5a	290.5±78.7a	285.2±137a	244.2±68.5a	266.5±79.7a	259±63.6a
9.	Chloride Cl ⁻	250	19.23±7.77a	26.89±11.14a	29.13±19.85a	30.12±17.8a	33.07±18.45a	26.09±13.84a	38.91±24.69a	37.95±32.67a	29.12±18.49a	27.75±14.43a
10.	Sodium Na	20	6.45±0.723bc	5.32±5.327c	5.35±5.355c	7.10±0.700ab	8.10±1.171a	5.61±0.987c	8.19±6.00a	6.43±0.693bc	6.28±1.262bc	6.71±2.199bc
11.	Potassium K		0.73±0.648a	0.77±0.808a	0.77±1.036a	0.86±1.202a	0.66±0.550a	1±1.504a	1.18±1.187a	1.05±1.187a	0.80±0.746a	0.94±0.897a
12.	Magnisium Mg	30	30.45±12.38a	35.38±13.19a	31.99±13.92a	35.51±18.05a	34.15±17.86a	32.15±10.99a	25.64±19.57a	23.09±7.97a	26.04±10.77a	30.15±11.08a
13.	Calcium Ca	100	49.39±13.60b	43.12±8.11b	47.17±10.54b	52.06±6.87b	54.06±7.98b	60.15±32.77ab	73.6±51.8a	53.52±26.75b	53.79±22.61b	55.49±13.96b
14.	Sulphate	250	17.56±10.14a	20.69±9.52a	20.51±9.51a	18.59±7.60a	15.26±7.96a	23.78±19.16a	39.6±33.5a	17.88±11.37a	18.39±11.79a	37.171.5a
15.	Nitrate	10-45	1.46±1.213a	1.75±1.592a	1.96±1.925a	1.77±1.782a	1.47±1.554a	0.98±0.700a	1.74±2.020a	1.32±1.288a	1.016±0.833a	1.47±1.299a
16.	Phosphate	1	0.31±0.0937a	0.35±0.1005a	0.35±0.1084a	0.37±0.0992a	0.35±0.1179a	0.34±0.0907a	0.34±0.1371a	0.32±0.1048a	0.30±0.1051a	0.31±0.1152a

Note: means followed by same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Table 4. Heavy metal concentration (mg/l) in water samples of the studied sites during the studied periods from Sept. 2015 to August 2016.

Heavy metal	WHO	Well3	Well5	Well6	Well7	Well8	Well10	Control	Tank6000	Tank1000	Tank2000
1. Cadmium (Cd)	0.003	0.0008*	0.0001*	N.D	0.0024*	0.0081*	N.D	N.D	N.D	N.D	0.0001*
2. Chrome (Cr)	0.05	0.0045*	0.0003*	0.0101*	0.0110*	0.0111*	0.0001*	0.0022*	N.D	0.0001*	0.0001*
3. Copper Cu	2	0.0189±0.00723 c	0.0061±0.00413 d	0.0226±0.01427 b	0.0109±0.0120 1cd	0.0187±0.01809 c	0.0345±0.019 15a	0.006±0.0041 7d	0.0394±0.010 13a	0.0262±0.0060 9b	0.0255±0.0143 5b
4. Lead (Pb)	0.01	0.00025±0.0000 75b	0.0001±0.00000 0b	0.00025±0.0002 12b	0.0003±0.0002 83b	0.00035±0.0003 54b	0.0001±*	0.0001±*	N.D	N.D	0.0026±0.0019 8a
5. Nickel (Ni)	0.07	0.01198±0.0121 9a	0.0386±0.0376a	0.00385±0.0043 9a	0.00462±0.003 84a	0.00305±0.0043 1a	0.0204±0.032 6a	0.0083±*	0.01805±0.02 22a	0.017625±0.01 841a	0.0269±0.0049 5a
6. Zinc (Zn)	3	0.01233±0.0039 5a	0.01652±0.0041 2a	0.00628±0.0068 1a	0.00997±0.007 09a	0.01068±0.0085 4a	0.02613±0.01 705a	0.00630±0.00 985a	0.01598±0.00 900a	0.01660±0.006 97a	0.0487±0.0549 a
7. Iron (Fe)	0.3	0.0924±0.0545a	0.1449±0.0634a	0.2120±0.1003a	0.1586±0.0582 a	0.1484±0.0807a	0.1133±0.021 3a	0.2886±0.307 a	0.1674±0.061 8a	0.11580.0662a	0.1696±0.0980 a

Note: Means followed by the same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Table 5. Physico-chemical parameters of soil samples of the studied sites during the studied periods from September 2015 to August 2016.

Parameter	1	2	3	4	5	6	7	8	9	10	11	12	Main stack
1. pH	7.46±0.34 3a	7.57±0.38 9a	7.45±0. 1787a	7.42±0. 2118a	7.45±0. 364a	7.60±0.272 6a	7.58±0.27 08a	7.51±0.22 80a	7.41±0.333 a	7.54±0.2806 a	7.52±0.3103 a	7.46±0.2827 a	7.20±0.2280 a
2. EC	342.1±276 .4b	350.4±281 .6b	340.6± 274.9b	370.8± 281b	320.3± 230.2b	314.2±212. 3b	353.7±279 .4b	380.7±281 .4b	372.5±318. 7b	334.5±235b	324.6±242b	369.9±248.3 b	1182±641a
3. Alkalanity	522.7±178 .9b	584.3±319 .3b	588.7± 325.9b	541.6± 296.4b	546.5± 303.6b	555±334b	578.8±324 .9b	516.4±290 b	682±461b	554±376b	646±424b	521.8±305b	1107±596a
4. Total Hardness	838±439b	805±465b	615±41 6b	757±38 4b	812±52 8b	741±459b	684±451b	757±439b	782±737b	833±587b	836±625b	857±680b	2603±4452a
5. Chloride Cl	317±577c	233±382c	192±29 9.3c	480±10 91c	314±54 6c	898±2552b	242±332c	325±573c	247±424c	415±747c	303±483c	371±551c	1380±2358a
6. Sodium Na	23±2.169b c	22.3±17.2 32c	20.4±1 8.32c	26.43.2 1ab	24.3±1 1.1a	29.4±2.88a	23.3±2.11 bc	27.4±2.87 a	20.7±12.2c	20.1±17.3c	19.6±1.22a	33.3±5.38b	60.4±18.28 bc
7. Potasium K	15.04±11. 55b	19.2±39.9 b	7.67±9. 40b	8.82±1 0.42b	3.807± 2.541b	5.69±4.51b	5.388±2.7 23b	7.83±5.94 b	6.30±4.00 b	9.89±9.72b	4.435±2.914 b	10.70±10.44 b	95.4±131.4a
8. Magnisium Mg	103.6±79. 1b	98.6±88.9 b	77.3±7 4.7b	90.4±8 5.6b	98.8±8 8.4b	95.7±86.0b	89.3±75.9 b	98±94.2b	59.6±53.3 b	87.3±56.0b	88.7±66.5b	114.1±132.9 b	273±400a
9. Calcium Ca	132.7±8.3 4b	136.9±20. 29b	118.8± 50.4b	126.7± 30.22b	132.4± 45.4b	120.1±10.3 b	123.4±65. 4b	122.3±64. 8b	203±66.6b	185.2±69.9b	153.6±70.1b	167.6±58.6b	230.5±240a
10. Sulphate	67.8±34.5 b	70.8±34.9 b	78.5±5 0.1b	74.9±4 0.8b	90.9±6 8.1b	82.8±69.5b	85.1±79.3 b	86.4±79.7 b	89.7±92.9 b	95.5±96.5b	90.5±81.4b	86.5±70.6b	734±1222a
11. Nitrate	23.9±35.4 a	32.9±46.2 a	33.2±5 0.1a	28±36. 6a	29.3±4 9.5a	30.4±46.2a	31.4±48.0 a	26.9±38.0 a	27.8±49.8a	29.1±46.3a	28.3±46.9a	25.3±38.6a	30±58.7a
12. Phosphate	1.923±0.9 97a	2.341±1.4 68a	2.491± 1.484a	1.732± 1.040a	1.977± 1.066a	2.170±1.46 9a	2.032±1.4 56a	1.836±1.2 46a	1.977±1.10 4a	2.050±1.009 a	1.964±1.106 a	2.027±1.161 a	2.223±1.104 a

Note: Means followed by the same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Table 6. Heavy metal concentration (mg/l) in soil samples of the studied sites during the studied periods from September 2015 to August 2016.

Heavy metal	1	2	3	4	5	6	7	8	9	10	11	12	Main stack
1. Cadmium (Cd)	1.355±0.87 9c	3.54±2.62a b	4.43±4.14a	0.878±0.528c	0.863±0.646c	0.1975±0.0763a b	0.845±1.171c	0.225±0.1841 c	1.56±2.5 0bc	1.527±0.895bc	5.20±6.6 6a	0.185±0.3 44c	0.1000±0.000c
2. Chrome (Cr)	2.800*f	5.350*e	13.38*b	10.70*c	8.030*d	12.04*b	13.19*b	9.820* cd	9.360*cd	9.330*c d	6.230*e	5.350*e	26.76*a
3. Copper (Cu)	5.52±3.65c d	3.720±0.67 9d	4.88±2.72 d	3.710±0.156d	1.43±1.94d	15.3±18.3c	12.3±1.48c	1.545±0.926d	60.6±63.4a	48.9±49.7b	59.1±61.5a	44.2±48.7 b	4.131.88b
4. Lead (Pb)	37.5±50.3a	43.6±67.3a	33.7±54.6a	31.4±53.6a	6.45±6.74b	9.07±10.57b	5.93±8.77b	5.80±6.88b	0.443±0.569b	1.97±2.07b	1.623±1.809b	2.47±4.10 b	12.71±12.8 5b
5. Nickel (Ni)	7.880±0.31 1a	7.195±1.13 8a	3.845±0.92 6a	5.02±2.8 5a	4.28±5.69a	3.42±4.6 5a	4.80±6.42a	3.84±5.20a	5.92±2.9 5a	2.32±1.81a	4.52±2.4 3a	11.67±12.26a	9.910±1.13 1a
6. Zinc (Zn)	12.52±8.86 a	12±8.28a	10.25±5.85 a	8.810±1.985a	7.44±4.55a	7.98±3.8 7a	10.618±1.280 a	6.92±3.85a	15.21±14.67a	21.73±1 0.09a	15.41±12.67a	14.62±10.64a	21.73±18.6 2a
7. Iron (Fe)	116.3±23.2 ab	135.1±47.4 a	106.44±4.3 2bc	77.6±45.9d	52±76.1ef	56.5±33.2ef	68.4±5 3.8de	47.8±3 9.7f	52.88±9.90ef	97.8±13 2.8c	78.765.3 d	60.5±42.1 de	3.17±2.23g

Note: Means followed by the same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Table 7. Total chlorophyll conc. (mg/l) in the leaves of plant samples of the studied sites during the studied periods Sept. 2015 to Aug. 2016.

Heavy metal	1	2	3	4	5	6	7	8	9	10	11	12
Total chlorophyll	1.373±0.728b c	1.800±0.907 b	2.811±1.6 44a	2.487±1.40 2a	1.163±0.4 72c	0.933±0.568c	1.021±0.437c	1.273±0.455 bc	0.891±0.424 c	0.740±0.395 c	1.300±0.837 bc	1.306±0.506b c

Note: Means followed by the same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Table 8. Heavy metal concentration (mg/l) in the leaves of plant samples of the studied sites during the studied periods Sept. 2015 to Aug. 2016.

Heavy metal	1	2	3	4	5	6	7	8	9	10	11	12
1. Cadmium (Cd)	5.78±9.97a	6.19±9.76a	6.80±10.03a	7.60±12.6 9a	7.42±11.80a	7.36±1.50a	7.42±11.88a	10.01±16.54a	1.570±1.3 72a	0.783±0.2 92a	0.407±0.1 79a	0.513±0.2 51a
2. Chromium (Cr)	3.88±2.89a	5.78±3.89a	5.05±1.8 20a	2.04±1.22 3a	4.74±3.9 0a	4.77±3.88a	6.54±3.41a	2.95±1.84 a	8.06±2.09 a	6.21±4.73 a	3.48±1.70 3a	2.57±1.68 3a
3. Copper (Cu)	18.40±11.54b	14.72±9.82 bc	18.25±3.79b	16.80±6.3 1bc	27.56±3.04a	20.70±2.94b	14.14±3.35bc	14.54±4.4 7bc	11.88±7.5 5c	12.76±5.6 4c	16.72±5.0 6bc	12.26±1.3 96c
4. Lead (Pb)	8.93±10.86e	13.6±18de	18.6±28.7d	25.5±41.7 c	25.77*c	18.4±2.89d	13.9±21.5de	6.42±9.30 de	19.1±24.5 d	8.33±5.78 e	60.43±*a	34.40*b
5. Nickel (Ni)	17.26±12.89a	20.73±16.2 0a	17.77±8.71a	10.75±8.4 6a	22.03±1.597a	21.70±10.74a	17.92±1.593a	10.84±8.7 7a	10.76±11.50a	9.10±8.67 a	8.85±11.4 8a	6.01±0.69 a
6. Zinc (Zn)	50.6±28a	52.6±23.5a	79.8±67.8a	97±139.9 a	130.1±1.069a	101.3±73.9a	98.2±75 a	63.1±21.4 a	73±112.5a	63.7±80.5 a	78.7±51.5 a	72.2±69.3 a
7. Iron (Fe)	1318±1434a	1861±2380 a	1975±28 41a	1487±226 4a	1722±21 81a	1588±2 038a	802±11 68a	1319±181 8a	837±867a	1922±306 3a	1090±119 0a	1903±320 7a

Note: Means followed by the same letter are not significantly different at (P<0.05) according to one-way ANOVA. Range test.

Water: Air temperatures in this study were between (14-38°C). Different variation in Sulaimani was found by Al-Shaheen (9), who recorded air temperature ranged from 3 to 43 °C, and by Farkha and Abdulrahman (21) who recorded air temperature between 21 and 40 °C as minimum and maximum temperature, our results agreed with those observed by Muhammad (32) through his work at cement factory in Sulaimani and recorded air temperature ranged from 16.56 to 23.45 °C. **Water temperature** is most important factor of water which has a great deal of influence on various chemical and biological reactions taking place in water. Temperature of groundwater was ranged between 15 to 24°C, and this reflected seasonal variations throughout monitoring period. **pH** indicate slightly acidic to basic character at a given temperature. pH is a significant factor that decides the suitability of water for various purposes (7). Range of pH values in water samples (6.67 to 8.23), which are within 6.5 to 8.5 recommended by WHO (50) in drinking water as shown in Table 3 indicated that all groundwater collected from study areas are excellent. Closeness of value may be due to similarity in parent material of study area. **Electrical Conductivity** is a useful tool to evaluate purity of water (4). **EC** ranges from 226 to 935 μScm^{-1} . Value found in the present study indicated that all wells and tanks water were under 2,250 μScm^{-1} as suitable. Large variation in EC is mainly attributed to lithologic composition and anthropogenic activities prevailing in area. Normally, irrigation water with an EC of < 700 μScm^{-1} causes little or no threat to most crops, while EC > 3000 μScm^{-1} may limit their growth (48). **Total dissolved solids** usually related to conductivity. Water containing more than 500 mg/l of TDS is not considered desirable for drinking water supplies, though more highly mineralized water may be used where better quality water is not available (26). Maximum value of TDS during study period was found as 630 mg l^{-1} at sampling location (ST2) in December and minimum was 189 mg l^{-1} in (SW1) in September. TDS values of all water samples of selected sites are within limits. **Hardness** is property of water which prevents lather formation with soap and increases

boiling points of water (37). Total Hardness was found in water samples ranges from 143 mg l^{-1} (ST3) to 475 mg l^{-1} (SW6), which shows values higher than permissible limit prescribed by WHO (50). **Turbidity**: In most waters, turbidity is due to colloidal and extremely fine dispersions. Turbidity values varied between 0.38 NTU (SW6) to 18.7 NTU (SW1). Many of water samples shows greater value than limit prescribed by (50).

Sodium is a common element present to some extent in most natural waters. Its concentration varied from negligible in fresh water to considerable in seawater and brackish water. When combined with certain anions, sodium imparts a salty taste to drinkable (15). Average abundance of sodium cation in ground water is generally less than 5 mg l^{-1} ; moreover sodium cation consists about 0.02-0.62% of soil and about 2.5% of the earth's crust (3). Most water supplies contain less than 20 mg l^{-1} , but in some countries its level may exceed 250 mg l^{-1} . Saline intrusion, mineral deposits, and sewage effluents can all contribute significant quantities of sodium to water. An overall mean sodium ion concentration recorded for the present work was 2.12 mg l^{-1} . Minimum sodium ion concentration was 0.8 mg l^{-1} determined at (ST2) during mid-March, while maximum sodium ion concentration was 10.2 mg l^{-1} measured at (SW5) during same month. No firm conclusion can be drawn concerning the possible association between sodium in drinking water and occurrence of hypertension; therefore, no health based guideline value is proposed. However, maximum permissible concentration of sodium was 250 mg l^{-1} (50). Accordingly, all studied groundwater samples during this investigation were within desirable concentrations and were in safe side for drinking purpose. **Potassium**: Potassium is slightly less common than sodium and more abundant in sedimentary rocks. Sources of potassium are principal potassium minerals of silicate rocks, such as mica and microcline (24). It is well known that potassium concentration is less than that of sodium in natural waters (22). Potassium occurs in ground water as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff (3). Potassium ion concentration showed an overall mean 1.13

mg l⁻¹. Minimum potassium ion concentration was 0.12 mg l⁻¹ noted at (ST2) during December, while Maximum potassium ion concentration was 5.4 mg l⁻¹ observed at (SW6) during August. Samples revealed lower concentrations of potassium than sodium in accordance to results obtained in Sulaimani city by Mustafa (33). According to previously mentioned standards, and correspondingly present results, at all studied sites water were within desirable levels and were in safe side for drinking water purpose. **Calcium and magnesium:** source of calcium and magnesium in natural water are various types of rocks, industrial waste and sewage (49). Values of calcium varied from 33.3 mg l⁻¹ (SW2) to 156 mg l⁻¹ (SW6) and values of magnesium ranged from 13 mg l⁻¹ (ST3) to 63 mg l⁻¹ (SW5). Sequence of mean concentration **values of cations** in groundwater of study area is K > Na > Mg > Ca as shown in Table 3. Ca²⁺, Mg²⁺ and pH are primarily controlled by water-rock interaction in area (5). **Chloride** content ranges from 1.72 to 88 mg l⁻¹ with values within 250 mg l⁻¹ recommended by WHO (50) recorded in all water sources. **Alkalinity** is an important characteristic of natural and polluted water, in which measurement of potential hydrogen differentiates between their alkalinity or acidity (24). Minimum level of alkalinity in studied area was 133 mg l⁻¹ recorded from (ST3) in May while maximum value observed was 285 mg l⁻¹ recorded for (SW5) during March. Result can be concluded that variation in alkalinity may be connected with more than one factor, among them dissolved carbon dioxide concentration, microorganism activities, and hydrolysis of bicarbonate ions. Anon (12) explained that most Iraqi waters are generally dominated by HCO₃ ions which hydrolyses to give an alkaline solution. Bicarbonates in feed water act as a major source for carbonate, bicarbonate and hydroxide alkalinity. Carbon dioxide is insoluble in warmer water and so is removed with hot water. This cause an increase in pH again and a shift in alkalinity forms from bicarbonate to carbonate and from carbonate to hydroxide (42). **Sulphate concentration** ranges from 5.01 to 251.8 mg l⁻¹ which are within normal range recommended for

drinking water by WHO (50). Obtained results was lower than result obtained by Mustafa (33) and Rashid (39) for well water, but they agree with that obtained by Hussien and Gharbie (25) who concluded that presence of the sulphate ion in groundwater is due to dissolution of leached sulphate, and gypsum, which exists in soils. **Nitrate concentration** ranged between 0.001 to 6.96 mg l⁻¹ which were all within WHO (50) acceptable limit of 50 mg l⁻¹ in drinking water. This implies that all industrial and anthropogenic activities in area do not affect groundwater sources. High nitrate concentration causes methemoglobinemia with symptoms of paleness, bluish mucous membranes, digestive and respiratory problems (30). **Reactive Phosphorus:** Phosphorus is a chemical commonly material found in soil, rock and plants. It is an essential nutrient for plants' growth. Ground water rarely contains more than 0.1 mg l⁻¹ phosphorus unless they have passed through soil containing phosphate or have been polluted by organic matter (15). Phosphorus concentration during period of this investigation ranged between (0.2-0.68) mg P-PO₄ l⁻¹. High levels of phosphorus may be a result of excessive use of fertilizers such as super-phosphate in area which lead to increase of phosphate concentrations in ground water. Both phosphate and clay particles have negative charges resulting in passage of the ion through soil during rainfalls and recharging aquifers as described and observed by Shekha (45). Majority of heavy metals were not detected in groundwater of study area, while other heavy metals (Pb, Mn and Ni) are within range recommended by WHO (50) in drinking water. Statistical results for physicochemical parameters revealed only significant differences at (P<0.05) among studied sites for most parameters. TDS, turbidity and calcium values revealed significant differences among sites and months. Sodium vice versa had revealed significant differences among months only. And for heavy metals were revealed significant differences among seasons for Cadmium and chromium only. But for zinc and iron were non significant for both. Copper revealed both in seasons and sites. Lead only in seasons. Nickel in sites.

Soil: Physicochemical properties for soil samples summarized in both tables 5 , 6. Physicochemical parameters were used to determine quality of soil for growth of plants and if there are any effect of cement components on them. pH values of soil samples revealed no significant differences at all sites, although it ranged from 7.07 to 8.44 and showed no appreciable differences within localities. Differences among pH values may attributed to differences of water physicochemical which affects gases and organisms activities, due to the reduction in CO₂ while Photosynthesis and Respiration (10). Soil with pH greater than 8.5 is generally called as sodic soil. But pH of all soils samples are less than 8.5 indicating that soil samples are free from sodicity hazards. This redaction could be due to the decreased amount of carbonate and bicarbonate. Differences within sites may attribute to site of main stack and wind. Also pH of water that used for irrigation ranged from 6.67 to 8.23. Statistically there were significant differences in soil total soluble salts content between sites but within normal ranges and not far from results in control sites. Concentrations of detected metals (Cd, Cr, Cu, Pb, Ni, Fe, and Zn), showed variable values depending upon the sampling site. Increment of soil metals in the same area may be a result of precipitation of heavy metals over years and that was clear from the results of main stack soil. These results are lower than results mentioned by Baban and Aziz (14). Also here for heavy metals results showed it like control. Using this factory for 12 years did not increase concentration of heavy metals to toxic levels in the soil. Statistical results for physicochemical parameters revealed significant differences at (P<0.05) among both studied sites and months for most parameters. pH, nitrate and phosphate values revealed significant differences only among sites. And for heavy metals were significant for both seasons and sites just for nickel and zinc were only in sites.

Plants: Total chlorophyll concentration is a unifying parameter for indicating the effect of specific interventions. However, it is important to record changes in two components of chlorophyll, chlorophyll A (chl_a) and chlorophyll B (chl_b) and especially their ratio. This is due to the fact that heavy metals could affect each component at a different level creating changes in some part of plants physiology and not in others. Concentrations of chl_a and chl_b and total chlorophyll (total chl/chl_a/chl_b), were calculated using the

methodology developed by Arnon (13). Here in this study there were normal values of heavy metals against normal values of chlorophyll. Statistical results for total chlorophyll revealed significant differences at (P<0.05) among both studied sites and months. This study indicates that total chlorophyll in control plants was always higher but not much. Exposure to particulate deposition may alter plant growth without physical damage to plant. Moreover, accumulation of dust particulates on studied plant leaves could be a major problem in their production. It was proposed that the pigments content of light harvesting complex is an important aspect related to tolerance of plants to dust pollution. Chlorophyll content is essential for the photosynthetic activity and reduction in chlorophyll content has been used as indicator of air pollution it is fairly sensitive to air pollutants. Continuous cement factory pollution closes stomata so interfering with gaseous exchange. In all three plants species growing near factory were having lesser quantity of chlorophyll (41). In present study it was not clearly indicates that cement industry pollution affect photo synthetic activity and chlorophyll content adversely. Mean concentrations of some heavy elements in plants are presented in table 8, for (*Platyclus orientalis* , *Eucalyptus spp.* and *Melia azedarach*) respectively. All selected elements Pb, Cd, Cr, Ni, Fe, Cu and Zn are low and values are generally below 100mgKg⁻¹ and not far from control samples results. Statistical results for heavy metals in plants leaves revealed significant differences only among sites for most metals, only for copper and lead were for both. In this study *Melia azedarach* was more sensitive to dust pollution followed by *Eucalyptus spp.* and *Platyclus oreintalis*. It was not clearly indicates that cement factory pollution affect photo synthetic activity and chlorophyll content. In comparison to gaseous air pollutants, only limited studies have been carried out on effect of particulates air pollutants on plants especially in Sulaimani city.

Dust of main stack: Cement dust changes elemental concentration of soil and its physicochemical properties . It is also major source of such particulate matter as SO_x,

NO_x, and CO₂ emissions. In this study, it clearly show increase in physicochemical parameters and heavy metals in dust. Cause of these results because of it is first point of dust eject before spreading in air. Plants results for heavy metals showed that they can use for biomonitoring of environment quality, either as bioindicators of quality or as bioaccumulators of atmospheric deposition. All results show that most of parameters were within permissible limits set by WHO (50). Reasons for this normality in values is might be due to main stack filters and continuously measurements for all parameters in and out of factory, so other factories must follow same tools, as a result not all industrial factories are pollution source, if they follow environmental information.

RECOMMENDATIONS

Other studies should complete other parameters. Study of bioremediation by micro-organisms in future. This study must conducted by other study by genetic tools to give another evidence for these plants for accumulation and biomonitoring pollution.

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