Assessment of the Environmental Impact of Acid Rains on the Human Health and the Environment in Baghdad City

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Abstract

In this study, the acidity of rainwater and concentration of the carbon dioxide (CO_2) in Baghdad city were measured and calculated. The applicability of the Henry's law of the solubility of gases in water is tested. The measurements of carbon dioxide concentrations in the outdoor air space are carried out in Baghdad city by using indoor air quality meter IAQ-CALC (TSI, USA). The acidity of the collected rainwater samples is measured using portable pH/EC/TDS meter. The concentration of the hydrogen ions from ionization of the carbonic acid are determined by using chemical equilibrium equations. The t-distribution test of the collected data indicates that there is no significant difference between the actual rainwater acidity and the equilibrium values calculated by Henry's law. The findings of this study suggest that there are no harmful effects related to acid precipitation in Baghdad city since the natural rainfalls have pH values between 5.8 and 6.6, which are significantly higher than the pH value of acid rainfall (less than 5.6).

Key Words: Environmental Impact Assessment, Acid Rains and Baghdad City.

تقييم الاثر البيئي للامطار الحامضية على صحة الانسان والبيئة في مدينة بغداد

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** الهيئة العراقية للسيطرة على المصادر المشعة

بغداد – العراق

الخلاصة

جرى في هذه الدراسة قياس وحساب حامضية الامطار عمليا ونظريا، وكذلك قياس نسبة غاز ثاني اوكسيد الكاربون في مدينة بغداد ، اختبر استخدام قانون هنري لذوبان الغازات في المياه في تقدير الامطار الحامضية عن طريق ذوبان غاز ثنائي اوكسيد الكاربون الجوي، جرى قياس تركيز غاز ثنائي اوكسيد الكاربون في الهواء المحيط باستخدام منظومة قياس حقلية نوع (IAQ–CALC) ، قيس الرقم الهيدروجيني لنماذج مياه الامطار التي جرى تجميعها من مناطق مختلفة في مدينة بغداد باستخدام جهاز قياس الرقم الهيدروجيني – الايصالية الكهربائية – المواد الصلبة الذائبة الكلية . استخدمت النماذج الرياضية للتوازن الكيميائي في تقدير تركيز غاز ثنائي اوكسيد الكاربون المذاب في مياه الامطار الذي ادى الى زيادة تركيز ايونات الهيدرجين المتولدة بفعل تاين حامض الكاربونيك. بينت نتائج التحليل الاحصائي باستخدام توزيع t الاحصائي عدم وجود فرق معنوي بين حامضية مياه الامطار الفعلية والتي قيست مختبريا وحامضية مياه الامطار المقدرة باستخدام قانون هنري. اظهرت نتائج هذه الدراسة استبعاد حصول تاثيرات بيئية سلبية بسبب حامضية مياه الامطار في مدينة بغداد حيث تراوحت قيمة الرقم الهيدروجيني لمياه الامطار بين 5.8 و 6.6 خلال فترة الدراسة وهي اعلى من 5.6 والتي تمثل مستوى الرقم الهيدروجيني للامطار الحامضية ذات الاثر البيئي السيء.

الكلمات المفتاحية: تقييم الاثر البيئي، الامطار الحامضية ومدينة بغداد.

Introduction

Air pollution is certainly not a new phenomenon. Indeed, early references to it date to the middle ages. In more recent times, though still decades ago, several serious episodes focused attention on the need to control the quality of the air we breathe. Air pollution may be described as contamination of the atmosphere by gaseous, liquid, solid wastes or by-products that can threat human health and welfare of plants and animals, attack materials, reduce visibility, or produce undesirable odors. Although some pollutants are released by natural sources like volcanoes, coniferous forests, and hot springs. The effect of this pollution is very small compared with that caused by emissions from industrial sources, power and heat generation, waste disposal and the operation of internal combustion engines. Fuel combustion is the largest contributor to air pollution emissions caused by man, with stationary and mobile sources equally responsible (Kumer, 2002).

The main sources of air pollution problem in Baghdad city can be classified into three categories:

- Electrical generators: Portable and stationary electrical generators became quite popular in Iraq soon after the shortage in national electrical energy after 2003.
- Traffic: increase in the number of automobiles and other vehicles in Baghdad city causes increase in air pollutants emissions,
- Some industries.

The quality of rainwater can be affected by a variety of factors including ambient conditions, season, and roofing material (TWDB, 2011). The chemical substances dissolved in rain water are generally considered to have two atmospheric sources. They may be derived from fairly unreactive dust particles in which case they are deposited as dry fallout، or it may be present as gases or soluble salts which dissolved in rain water itself. The fallout deposited in amount independent of the quantity of precipitation, whereas the substance dissolved in precipitation should have concentration that vary with rainfall amount (Al-Adili and Maatooq, 2008).

The effects of acid deposition on materials, terrestrial ecosystems and aquatic ecosystems are still only partially understood, but some features are emerging quite clearly. Acids degrade building materials, especially limestone, marble (a form of limestone), various commonly used metals such as galvanized steel, and certain paints. In facts, the increased rate of weathering and erosion of building surfaces and monuments was one of the first indications of adverse impacts from acid rain. Terrestrial ecosystems, especially forests, seem to be experiencing considerable stress due to acid deposition, with reductions in growth and increased mortality. Natural rainfall would have a pH value between 5 and 5.6 and anything less is loosely called “acid rain” (Masters, 1991, Kassim *et al.,* 2012).

The major components of acid rains are sulphur dioxide/sulphur trioxide, carbon dioxide and nitrogen dioxide dissolves in rain water. These components are deposited as dry and wet depositions. When these pollutants are dissolved in water during rain it forms various acids. The chemical reactions of these pollutants are discussed as follows.

• $CO_2+H_2O \rightarrow H_2CO_3$ (carbonic acid)

• $SO_2+H_2O \rightarrow H_2SO_3$ (sulphorous acid)

•$NO_2+H_2O \rightarrow HNO_2$(nitrous acid)+$HNO_3$ (nitric acid)(Lanza *et al.*, 2014). The aims of this study are:

(1) Determine whether the acidity of rainwater in Baghdad city pose a threat to the human health and the environment.

(2) Verification of the Henry’s law for solubility of gases in water by omparing the estimated pH values by Henry’s law with the actual (true)

(Germany). The samples of rainwater were collected in a plastic container from Baghdad city (Al- Jadriyah region) and sent to the laboratory for analysis. Rainwater acidity has been monitored in the period from 3/2/2006 to 17/3/2007 depending on the rainfall. The air temperature was measured using thermometer temperature readings in ^{o}F is converted to ^{o}C as below (Masters, 1991):

$$^{o}F = 1.8^{o}C + 32 \quad \ldots\ldots (1)$$

The elevation of Baghdad city above the sea level was measured by using personal navigator (eTrexVista, U.S.A.) Fig. 2(c). The rainwater sampling process and laboratory measurements were carried out in 2006 in the laboratories of Hazardous Materials and Environmental Researches Directorate/ Ministry of Science and Technology.

Field Survey Planning and Design

Statistical analyses were concerned with two aspects related to accuracy and precision. First, the level of accuracy must be specified. The parameter α is the error allowed and (1- α) is the corresponding confidence level. Secondly, a precision requirement (D) is the deviation from the true value (Watts, 1998).

If the observed CO_2 concentrations in the outdoor air spaces are x_1, x_2, … x_n. Then the mean observed concentration of samples of size n will be (Watts, 1998):

$$\overline{X} = \frac{\sum_{1}^{n} X_i}{n} \quad \ldots (2)$$

and the sample variance, a measure of the spread of data about the mean, is (Watts, 1998):

$$S^2 = \frac{\sum (X_i - \overline{X})^2}{n-1} \quad \ldots (3)$$

values inferred from direct measurements.

(3) Investigation of the effect of atmospheric CO_2 growth on the increase of rainwater acidity.

Materials and Methods

Field CO_2 Survey

The CO_2 measurements in the ambient air space were carried out in Baghdad city (Al-Jadriyah region, Fig.1) at monthly rate using indoor air quality meter IAQ-CALC (TSI, USA) Fig. 2(a). The field investigations of ambient CO_2 concentration were carried out at the period from 3/2/2006 to 17/3/2006 depending on the rainfall.

Fig. (1) location of Studied Area

Rainwater Sampling and Laboratory Measurements

Acid rain was measured using a scale called "pH." The lower a substance's pH, the more acidic it was. Normal rain was slightly acidic because carbon dioxide dissolves into it, so it has a pH of about 5.5 (EPA, 2006).

The acidity of the randomly collected rain water samples was measured by using three different measuring instruments:

(1) Portable pH/Ec/TDS meter (HANNA Instruments, Portugal).
(2) pH/^{o}C meter (OAKTON, Singapore) Fig. 2(b).
(3) Laboratory pH meter PB-11 (Sartorius, Germany).

The pH measuring instruments were calibrated for pH measurements by using reference solution (pH = 4.01) supplied by the WTW company

where t = students two-sided t-distribution with (n-1) degrees of freedom for a confidence level of (1-α)%.
S^2 = the sample variance for the initial data.
D = a specified limit relative to the sample mean.

The interval from $\overline{X}-(b*S/\sqrt{n-1})$ to $\overline{X}+(b*S/\sqrt{n-1})$ (Watts, 1998) is a random interval having a probability 95% of including the actual CO_2 mean concentration in the outdoor atmosphere. The value of b is selected from the t distribution table.

Application of Henry's Law for Solubility of Atmospheric CO_2 in Rain Water

When air comes in contact with water, some of it dissolves into the water. Different constituents of air dissolve to different degrees and in amounts that vary with temperature and water purity. The behavior of gases in contact with water was reported by W. Henry in 1903, and the resulting relationship is known as Henry's law (Masters, 1991):

$$X = K_H P_g \quad \dots (5)$$

where X = mole fraction of the gas dissolved in liquid, K_H = Henry's law coefficient (atm^{-1}), P_g = the partial pressure of the gas in air (atm), which is simply its volumetric concentration times the air pressure.

Another factor that must sometimes be accounted for when computing P_g is the decrease in air pressure that occurs as altitude increases. One estimate for atmospheric pressure as a function of altitude is the following (Masters, 1991):

$$P = P_o - 1.15*10^{-4} H \quad \dots (6)$$

(a) Indoor Air Quality Meter IAQ-CALC (TSI, 2004)

(b) Portable pH/°C Meter (OAKTON, 1999)

(c) Personal Navigator (GARMIN, 2002)
Fig. (2) Survey instrument

Sample precision is promoted by collecting an adequate number of samples, which is apparent from inspection of equation (3). The variance, which is indirect measure of precision because it describes the spread of data about the mean, decreases as the number of samples (n) increases.

Initial or previous data are usually necessary to determine the number of samples required to achieve a given level of precision. The initial data provide preliminary estimates of $\overline{X}$ and S^2 before the random sampling design is finalized. The number of samples required for a designated level of precision may be calculated by (Watts, 1998):

$$n = \frac{t^2 S^2}{D^2} \quad \dots (4)$$

device and that indicated by Henry's law (Al-Mashhadani, 1989):

$$t = \frac{\sqrt{n}\left(\overline{X} - \mu_o\right)}{S} \quad \dots (10)$$

where $\overline{X}$ and S represent the mean and standard deviation of the predicted pH values by Henry's law of size (n), μ_o is the observed pH value of rainwater inferred from direct measurement.

Results and Discussion

Statistical analysis for field survey data is performed in this study to obtain additional quantitative information to demonstrate that atmospheric CO_2 measurement results have the required precision and are sufficiently free of errors to accurately represent the site being investigated. Eqs.(2), (3) and (4) are used to control uncertainty in the field survey results caused by sampling design and measurement error. Six preliminary readings of CO_2 are carried out with the following results: 341, 311, 310, 299, 298, and 303 ppm. Based on this information, the observed mean and variance of readings are estimated to be 310.33 ppm and 15.97 ppm, respectively. A specified error level of 5% is selected corresponds to 95% confidence that the readings mean value is an accurate estimate of the actual value. For the students t table, $t_{95\%}$ = 2.571 (the α =0.025 column is used because 2×0.025=0.05 or 5% which is the error level for the 95% confidence level). The number of readings required for 95% confidence limits with 7.5 ppm deviation from the actual value is estimated to be 29.97 readings, round up to 30 readings.

The observed concentrations range from 288 to 594 ppm. The mean observed CO_2 concentrations is found to be 349.6 ppm from 30 readings. Accordingly, the interval from $349.6-2.042\times69.59\times/\sqrt{30-1}$ to $349.6+2.042\times69.59\times/\sqrt{30-1}$, or 349.6 ∓ 26.39 ppm is an approximate 95% confidence interval for the true CO_2 concentrations in the ambient air spaces. The mean

where P = atmospheric pressure at altitude H (atm), H = altitude (m), P_o = atmospheric pressure at sea level (atm).

Aqueous CO_2 is formed when atmospheric CO_2 dissolves in water, its concentration in fresh water can be found using Henry's law (Masters, 1991):

$$\left[CO_{2(aq)}\right] = 55.56 K_H P_{CO_2} \quad \dots (7)$$

where the concentration is in mol/l and P_{CO_2} is the partial pressure of gaseous CO_2 in the atmosphere. K_H is Henrys law coefficient (atm^{-1}).

Aqueous CO_2 then forms the carbonic acid (H_2CO_3) which, in turn, ionizes to form hydrogen ions (H^+) and bicarbonate (HCO_3^-) (Masters, 1991):

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

The bicarbonate (HCO_3^-) ionizes to form more hydrogen ion (H^+) and carbonate (CO_3^{-2}):

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{-2}$$

If sufficient time is allowed for the system to reach equilibrium, then the equilibrium constant can be used to analyze the system (Masters, 1991):

$$\left[H^+\right]^2 = K_1 * \left[CO_{2(aq)}\right] + 10^{-14} \quad \dots (8)$$

The pH value of rainwater is estimated from Equation below (Masters, 1991):

$$pH = -\log\left[H^+\right] \quad \dots (9)$$

A wide variety of particles and gases that exist in the ambient environment have either been directly or indirectly linked to the phenomenon of acid rain formation (Spenglert, 1985). Acid deposition has a variety of effects, including damage to forests and soils, fish and other living things, materials, and human health. Acid rain also reduces how far and how clearly we can see through the air, an effect called visibility reduction (EPA, 2006).

Test for Goodness of Fit

The t- distribution is used to see if there is any orderly relationship between data observed by measuring

hypothesis that there is no significant difference between mean value of expected rainwater acidity indicated by Henry's law and the actual (true) values indicated by measuring device. The appropriate values of $\overline{X}$ = 5.56, μ_o = 5.8, n = 30 and S = 0.0196 are substituted into Eq.(10). The estimated t value (-66.75) is found to be less than the tabulated t-value at 5% significance level of 2.042 (Volk, 1969). This result indicates that the predicted data are consistent with the actual (true) rainwater acidity measured by using laboratory pH meter.

Table (1) pH of Rainwater Inferred from Direct Measurements

Rainfall date	pH
3/2/2006	5.80
5/11/2006	6.66
6/11/2006	6.15
23/12/2006	6.03
5/1/2007	6.13
12/1/2007	6.28
16/2/2007	6.19
17/3/2007	6.66
Mean ∓ SD	6.23 ∓ 0.29

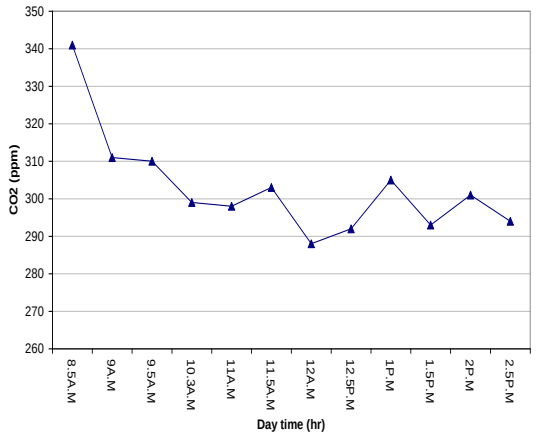

Fig. (3) Variation of Observed CO_2 Concentrations Along Day Time

observed atmospheric CO_2 concentration in Baghdad city (349.6 ppm) is found to be less than the clean, dry earth's atmosphere concentration (355 ppm) exists now (Masters, 1991).

The variation of the observed CO_2 concentrations along the day time and along the measurements period are shown in Fig. 3 and 4, respectively. The frequency distribution of the collected data is shown in Fig. 5. 65% of the observed concentrations fall in the range from 300 to 400 ppm. Fig. 6 shows variation of measured acidity of rainwater for the period from 3/2/2006 to 17/3/2007. The pH of rainwater range from 5.8 to 6.6 during this period.

In Baghdad, at the observed elevation above sea level by personal navigator (84 ft or 25.6 m), atmospheric pressure is estimated by Eq.(6) to be 0.997 atm or approximately 1 atm, so the partial pressure of CO_2 in air is simply its volumetric concentration times the 1 atm air pressure. The saturation values of dissolved CO_2 are estimated from Eq.(7), where K_H was taken to be (0.000823 atm^{-1}) at the observed average air temperature (15.08 ^oC). The hydrogen ion concentration $[H^+]$ in the rainwater is estimated from Eq.(8) where k_1 = 4.47×10^{-7} mol/L (Masters, 1991). The pH value of rainwater is estimated from Eq.(9). The variation of expected rainwater acidity estimated by Henry's law is shown in Fig. 7, with a mean value of 5.56. The pH analysis of the rainwater samples gives an approximate characterization of the range of the rainwater acidity. The true pH of rainwater inferred from direct measurement for some rains occur at Baghdad is given in Table (1). Individual rain water acidity measurements are averaged in Table (1) to provide a representative level. The acidity of rainwater has been monitored in Baghdad city in the period from 3/2/2006 to 17/3/2007.

Eq. (10) is used to ensure accuracy and reliability of the collected data. The t-distribution is applied to test the

weak solution of carbonic acid (H_2CO_3) with a mean pH value of about 6.23 ± 0.29 in Baghdad city.

(2) The adverse impacts from acid rain are excluded in Baghdad city since the natural rainfalls have pH values between 5.8 and 6.66, which are significantly higher than the pH value of acid rainfall (< 5.6).

(3) The statistical analysis of the collected data by the t-distribution test shows that the mean pH value of rainwater indicated by Henry's law (pH = 5.56) is entirely consistent with the actual (true) values indicated by measuring instrument (pH = 5.8).

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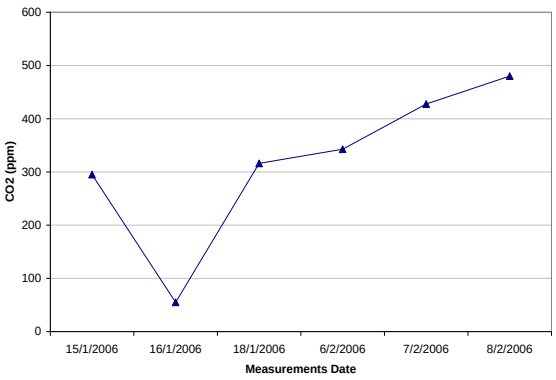

Fig. (4) Variation of CO_2 Concentrations During the Studied Period

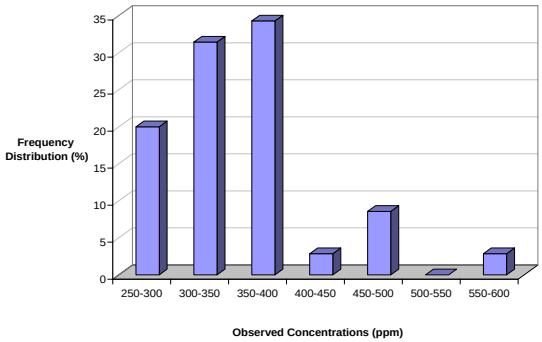

Fig. (5) Frequency Distribution of the Ambient Atmospheric CO_2 Concentrations.

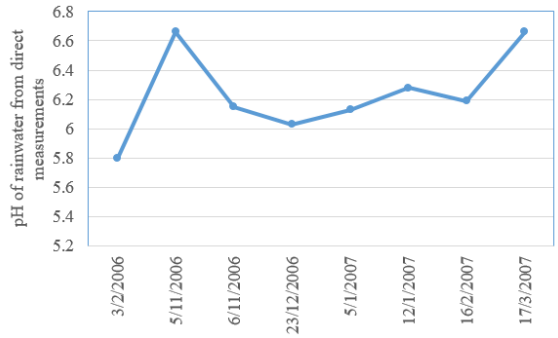

Fig. (6) Variation of Measured Acidity of Rainwater

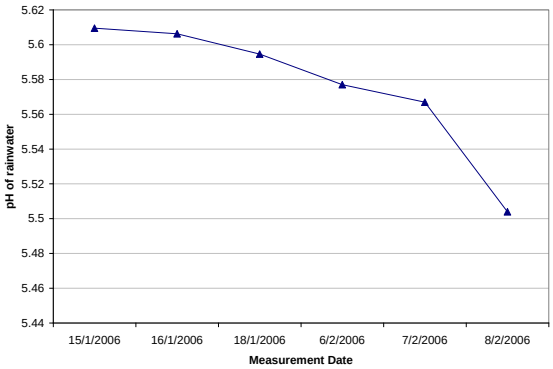

Fig. (7) Variation of Expected Acidity of Rainwater as Calculated by Henry's Law

Conclusions

(1) Rainfall water in equilibrium with atmospheric carbon dioxide forms a

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