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Jordan Journal of Earth and Environmental Sciences

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ISSN 1995-6681

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EDITORIAL PREFACE

It is my great pleasure to launch this inaugural issue of the Jordan Journal of Earth and Environmental Sciences (JJEES) with the intent of providing an international forum for the researchers and scientists of the various fields of Earth and environmental sciences to publish their scientific contributions and to disseminate their knowledge. The JJEES is an International Refereed Research Journal hosted by the Hashemite University and sponsored and approved by Jordan's Ministry of Higher Education and Scientific Research. The journal covers diverse areas of research and development in Earth and environmental sciences.

The coverage of the JJEES includes all new findings in all aspects of Earth and environmental sciences and or any closely related fields. The journal also encourages the submission of critical review articles covering advances in recent research of such fields as well as technical notes.

The Editorial Board is very committed to build the Journal as one of the leading international journals in Earth and environmental sciences in the next few years. With the support of the Ministry of Higher Education and Scientific Research and Jordanian Universities, it is expected that a valuable resource to be channeled into the Journal to establish its international reputation.

We have received a good response to the first issue of JJEES from scientists and researchers in Jordanian universities. I am pleased by this response and proud to report that JJEES is achieving its mission of promoting research and applications in Earth and environmental sciences. In the first issue, there are five interesting papers dealing with various aspects of Earth and environmental sciences.

I would like to thank all members of the editorial board and the international advisory board members for their continued support to JJEES with their highly valuable advice. I would like also cordially thank the manuscript's reviewers for providing valuable comments and suggestions to the authors that helped greatly in improving the quality of the papers. My sincere appreciation goes to all authors and readers of JJEES for their excellent support and timely contribution to this journal.

The editorial board of JJEES and me, are looking forward to receiving your valuable scientific contributions. Your support and continued contribution would be highly appreciated.

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JJEES
Jordan Journal of Earth and Environmental Sciences

Volume 1, Number 1, Mar. 2008
ISSN 1995-6681
Pages 1 -9

Enhanced $PM_{2.5}$ Source Apportionment Using Chemical Mass Balance Receptor Modeling and Scanning Electron Microscopy

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Abstract

One of the weaknesses of using receptor models to apportion the sources of ambient particulate matter is their inability to separate collinear sources such as different types of geological material. In order to develop a methodology to separate the different geological source contributions an ambient monitoring and source apportionment study was carried out for the cities of Reno and Sparks, NV during summer 1998. Chemical Mass Balance (CMB) receptor modeling was performed to estimate the contributions of both anthropogenic and natural sources to the observed ambient concentrations. Scanning electron microscopy was used to examine the geological component of the PM2.5 to determine the sources of that component. Chemical mass balance receptor modeling showed the dominant contribution to summertime PM2.5 mass in Reno and Sparks to be motor vehicle sources (~68%). Geological material was the second most abundant component of the PM2.5 (~14.5%). Sulfate was the predominant secondary species during the measurement period (~11%). The remaining components of significance were vegetative burning (~4%), secondary nitrates (~2%), and salt (NaCl) (0.6%). Scanning electron microscopy of selected ambient samples on a particle-by-particle basis showed the mineral component of the PM2.5 was predominantly aluminum-silicate in nature with a wide range of composition percentages for the major aluminum-silicate minerals (Na, Mg, Al, Si, K, and Ca). Virtually all of the particles examined had P and S in the typical aluminum-silicate spectra, which is attributed to contact with mobile source emissions. In approximately 10% of the examined particles were metallic in nature. Barium was also noted as a minor constituent of some particles, suggesting incorporation of diesel vehicle emissions. This evidence suggests that the source of the majority of the PM2.5 of geological origin in Reno and Sparks during the study period was from the resuspension of paved road dust. Thus, the amount of PM2.5 attributed to mobile source activity was in excess of 80%.

Keywords: urban air pollution; PM_{10}; $PM_{2.5}$; sulfate; nitrate; motor vehicles; chemical mass balance; scanning electron microscopy;

1. Introduction

In northern Nevada, particulate and gaseous emissions from anthropogenic and natural sources often combine with meteorology to create high levels of air pollution. The Truckee Meadows, in which the urban centers of Reno and Sparks are located, was designated as moderate non-attainment for CO (carbon monoxide) and PM_{10} (particulate matter with aerodynamic diameter of 10 µm or less) in 1990 (non-compliant for both the 24-hour and annual federal standard) and marginal for O_3 (ozone) in 1992 (U.S. EPA 1997). Washoe County has not violated the National Ambient Air Quality Standard (NAAQS) for ozone since 1990 or for CO since 1991 and was redesigned as attainment for O_3 in 1998. However, the 24-hour PM_{10} standard ($\geq$150 $\mu g\ m^{-3}$) was exceeded on January 6, 1999. This is the first violation for PM_{10} since 1993, and indicates that PM is still an important pollutant that affects air quality in the Truckee Meadows. Despite general improvement in the reduction of PM_{10} violations, there is still a need to understand the various emission sources in the Truckee Meadows, especially their contributions to ambient PM concentrations. This is especially true for $PM_{2.5}$, the pending and potentially more stringent NAAQS standard for PM (U.S. EPA 1997).

There are several different sources of particulate matter in the Reno-Sparks area. These include but are not limited to motor vehicle exhaust, residential wood combustion, resuspended geological material, industrial processes, and secondary species such as ammonium nitrate and

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ammonium sulfate. The apportionment of ambient aerosol mass to different sources of geological particles is a difficult problem because of the similarity of the chemical composition of these sources. The goal of this study was to characterize the current summer $PM_{2.5}$ levels in Reno and Sparks and to identify and apportion the contributing sources, including the fugitive dust. To achieve this goal, twenty-four-hour $PM_{2.5}$ samples on filters were taken at two sites in Reno and Sparks, NV. Sampling for $PM_{2.5}$ took place every third day. The sampling period began on 07-17-98 and ended on 09-11-98. The chemical mass balance (CMB) receptor model (Watson et al. 1990) was used to apportion the $PM_{2.5}$ to its sources. In addition, manual scanning electron microscopy was used to examine the $PM_{2.5}$ particles (Mamane 1988, Mamane et al. 1998) to aid in the identification of the source of the mineral particles.

2. Methodology

2.1. Ambient Measurements

Particulate matter samples were collected using $PM_{2.5}$ medium-volume (MedVol) samplers designed to collect samples for chemical analyses (Gertler et al. 1993). This type of sampler employs a Bendix $PM_{2.5}$ cyclone to determine the size fractions collected. The ambient air is transmitted through the size-selective inlet and into a plenum. The flow rate is controlled by maintaining a constant pressure across a valve with a differential pressure regulator. For the size-selective inlet to work properly, a flow rate of 113 lpm must be maintained through the sampler. Two Savillex filter packs, one with a ringed 47 mm Teflon-membrane filter (Gelman Scientific, Ann Arbor, MI) and one with a 47 mm quartz-fiber filter (Pallflex Corp., Putnam, CT) draw air from the plenum each with flow rates of 20 lpm to collect samples for gravimetric and chemical analyses. The remaining 73 lpm was drawn through a makeup airport. The flow rates were set with a calibrated rotometer and monitored with the same rotometer at each sample change. This type of sampler has been used in many aerosol and visibility studies over the past decade (e.g., Chow et al. 1992, Chow et al. 1997, Watson et al. 1998).

The AirMetrics (AirMetrics, Springfield, OR) Minivol was used to collect $PM_{2.5}$ samples for analysis by scanning electron microscopy (SEM). This type of sampler draws ambient air at a rate of 5 lpm through an impaction plate designed to remove particles greater than $PM_{2.5}$. A 24-hour sample was collected on 47-mm polycarbonate filters (Poretics Products, Livermore, CA).

The Teflon-membrane and polycarbonate filters were weighed on a Cahn 31 Electro-microbalance before and after sampling to determine mass concentrations. Chemical analyses were performed on both the Teflon-membrane and quartz-fiber filters following the methodology described by Watson and Chow (1994). Briefly, the Teflon-membrane filters were analyzed for elements by x-ray fluorescence. One-half of the quartz filter was extracted with distilled-deionizer water and the extract analyzed for chloride, nitrate, and sulfate ions by ion chromatography, for ammonium by automated colorimetry, and for sodium and potassium by atomic absorption spectrometry. Organic and elemental carbon were measured by thermal-optical reflectance on 0.5 cm^2 punches taken from the remaining half of the quartz-fiber filter (Chow et al. 1993).

For scanning electron microscopy analysis of the $PM_{2.5}$, small (~0.4 cm^2) samples were cut from the polycarbonate filters and mounted with conductive adhesive to 10 mm × 14 mm carbon rods. The sample rods were then coated with a fine layer of carbon to allow for analysis of the elemental composition of the particles using the energy dispersive x-ray (EDX) capability of the SEM (JEOL Model JSM-840 A). The samples were loaded into the SEM and for each sample; a randomly selected image field at 3000 magnification was centered on the viewing screen. The image is captured as a bitmap file and formed the basis of the analysis. The particles on the captured image were numbered and then analyzed one by one using the EDX capability and to note characteristic features such as size and shape. The EDX analysis provides a spectrum indicating the elemental composition of the selected particle and a normalized weight fraction for each selected element.

2.2. Chemical Mass Balance

The Chemical Mass Balance (CMB) receptor model was used to apportion PM and its chemical constituents to their sources. CMB steps, model outputs, performance measures, and deviations from model assumptions are discussed elsewhere (Watson et al., 1984; Pace and Watson,1987; Watson et al., 1990; and Lowenthal et al., 1992).

2.3. Scanning Electron Microscopy

Another method for estimating the contribution of different sources to the observed ambient PM concentrations is to apply SEM analytical techniques to characterize the collected particulates. The SEM is useful in distinguishing particles originating from different sources based on their composition and morphological characteristics. This feature makes the SEM technique especially useful in distinguishing between aerosols that have similar chemical compositions, but differ in their morphologies.

3. Results

3.1. Ambient $PM_{2.5}$ Data

38 samples (36 ambient and 2 field blanks) were subjected to full chemical analysis to determine the composition of the collected particulate. Validation of the collected ambient data requires evaluation of the chemical data for internal consistency. In this study data, validations were made for sum of species versus $PM_{2.5}$ mass; physical consistency, including examination of the relationships between sulfate and total sulfur, soluble potassium and total potassium; ammonium balance; and anion and cation

balance. Ratios, correlations, and linear regression statistics were computed and scatter plots prepared to examine the data. Suspect data were flagged and their validity examined.

Because soluble potassium (K^+) concentrations are often used as an indicator of vegetative burning, it is important to assure the validity of this measurement. The average ratio of K^+: K for Reno is 0.47 (±0.11) and 0.43 (±0.11) for Sparks; this indicates a non-crystal source for the K^+. This ratio for a pure vegetative burn source or a crystal source would be around 0.9 and 0.2, respectively (Calloway et al., 1989). Ammonium nitrate (NH_4NO_3), ammonium sulfate ($[NH_4]_2SO_4$), and ammonium bisulfate (NH_4HSO_4), are the most likely nitrate and sulfate compounds to be found in Reno and Sparks. Some sodium nitrate ($NaNO_3$) and/or sodium sulfate (Na_2SO_4) may also be present. Ammonium (NH_4^+) can be calculated based on the stoichiometric ratios of the compounds and compared with that which was measured. Comparing the calculated and measured values revealed that a majority of the sulfate was neutralized and in the form of ammonium sulfate during the study period. However, there were days when ammonium bisulfate predominated. The data for Sparks indicated that for approximately 60% of the days sampled, ammonium bisulfate was the more common ammonium compound, indicating a slightly more acidic environment (Watson et al., 1994).

The calculated mass concentration data are presented in Table 1. Data from both the MedVol and MiniVol samplers are shown. The ambient $PM_{2.5}$ ranges from a low of 4.71 ±0.38 μg m^{-3} measured in Sparks on August 11 to a high of 14.46 ±0.78 μg m^{-3} measured in Sparks on 8/2/98. The average 24-hour concentration observed in Reno was 7.85 ±1.84 μg m^{-3} and 7.80 ±2.22 μg m^{-3} in Sparks. These data are drawn from the higher precision measurements obtained with the MedVol sampler. More data will be needed to test compliance with the pending NAAQS for $PM_{2.5}$.

The variation in $PM_{2.5}$ throughout the sampling period and between Reno and Sparks is shown in Figure 1. Data are shown for both the MedVol and the MiniVol samplers. The relationship between the MedVol and MiniVol samplers for the measurement of $PM_{2.5}$ at both sites is shown in Figure 2. In general, the agreement is good (R^2=0.70), and in a pair-wise t-test the means of the two samplers were not statistically different. It follows that the change in $PM_{2.5}$ levels on a day-to-day basis between the two sites shows about the same degree of correlation (R^2=0.74) (Figure 3). This is indicative of the more spatially independent nature of $PM_{2.5}$, unlike PM_{10}, which can show higher inter-site variability due to the effects of local emission sources and their smaller zone of influence (Chow et al. 1999).

3.2. $PM_{2.5}$ Chemical Composition

The mass and chemical composition measurements for all of the chemically speciated samples are summarized in Table 2. The most abundant species were organic carbon (OC), elemental carbon (EC), sulfate ($SO_4^=$), and ammonium (NH_4^+). These species accounted for 82.4%, on average, of the $PM_{2.5}$ mass. Soil-related species (Al, Si, K, Ca, Ti, Fe, and Zn), without accounting for their oxide forms, accounted for about 9.6% of the mass.

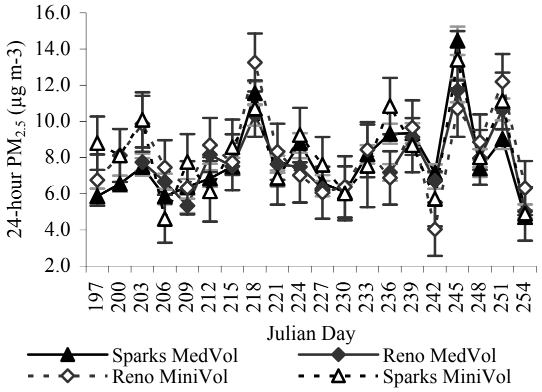

Figure 1. Time series plot of the PM2.5 measured in Reno and Sparks, NV, from July 16 (day 197), 1998 to September 11 (day 254), 1998.

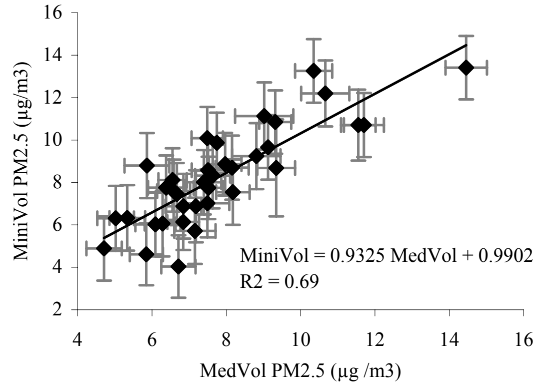

Figure 2. The relationship between PM2.5 measured with the MedVol and the MiniVol samplers for Reno and Sparks.

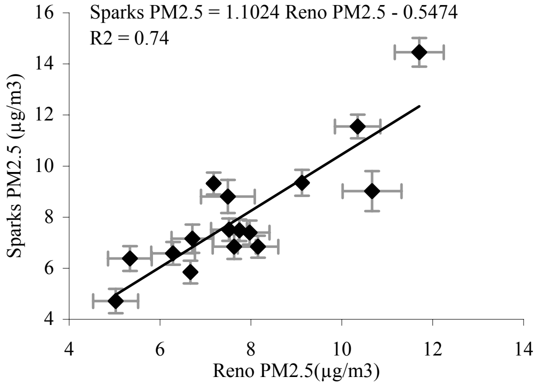

Figure3. The relationship between PM2.5 measured at Reno and Sparks for the MedVol data.

Table 1. Summary statistics for PM2.5 measured in Sparks and Reno

Date	DRI MedVol		AirMetrics Minivol	
	Reno $PM_{2.5}$	Sparks $PM_{2.5}$	Reno $PM_{2.5}$	Sparks $PM_{2.5}$
	(µg m^{-3})	(µg m^3)	(µg m^3)	(µg m^3)
7/16/1998		5.86±0.42	6.76±1.42	8.80±1.47
7/19/1998		6.55±0.45	8.12±1.46	8.12±1.46
7/22/1998	7.75±0.48	7.49±0.49	9.87±1.54	10.09±1.52
7/25/1998	6.67±0.45	5.85±0.43	7.45±1.51	4.62±1.32
7/28/1998	5.34±0.40	6.38±0.44	6.33±1.47	7.75±1.54
7/31/1998	8.16±0.50	6.84±0.46	8.70±1.50	6.14±1.67
8/3/1998	7.52±0.47	7.51±0.48	7.74±1.54	8.58±1.52
8/6/1998	10.35±0.59	11.55±0.65	13.26±1.61	10.70±1.56
8/9/1998	7.63±0.48	6.85±0.44	8.32±1.55	6.88±1.47
8/12/1998	7.49±0.48	8.81±0.54	7.02±1.50	9.24±1.51
8/15/1998	6.29±0.42	6.58±0.45	6.06±1.44	7.60±1.54
8/18/1998		6.09±0.43	6.38±1.70	6.02±1.49
8/21/1998		8.18±0.51	8.44±1.52	7.54±2.29
8/24/1998	7.18±0.46	9.32±0.56	6.88±1.47	10.85±1.56
8/27/1998	9.12±0.54	9.34±0.56	9.66±1.51	8.68±1.50
8/30/1998	6.71±0.44	7.16±0.47	4.04±1.48	5.72±1.52
9/2/1998	11.70±0.65	14.46±0.78	10.70±1.56	13.41±1.58
9/5/1998	7.97±0.49	7.40±0.48	8.86±1.53	8.01±1.52
9/8/1998	10.66±0.60	9.02±0.55	12.19±1.53	11.13±1.56
9/11/1998	5.02±0.38	4.71±0.38	6.31±1.50	4.89±1.48
Mean	7.85	7.80	8.15	8.24
Std. Dev.	1.84	2.22	2.20	2.25

Table 2. Average mass concentrations and standard deviations for the measured species.

Species	Reno $PM_{2.5}$(µg m^3)	Sparks $PM_{2.5}$(µg m^3)
Mass	7.850±1.843	7.797±2.217
Chloride (Cl^-)	0.020±0.032	0.011±0.023
Nitrate (NO_3^-)	0.126±0.050	0.149±0.076
Sulfate ($SO_4^=$)	0.811±0.396	0.794±0.342
Ammonium (NH_4)	0.290±0.149	0.270±0.124
Soluble Sodium (Na^+)	0.026±0.021	0.034±0.023
Soluble Potassium (K^+)	0.051±0.099	0.038±0.068
Organic Carbon	3.379±0.561	3.382±0.534
Elemental Carbon	1.514±0.437	1.499±0.450
Total Carbon	4.881±0.877	4.869±0.870
Sodium (Na)	0.029±0.025	0.032±0.026
Magnesium (Mg)	0.024±0.015	0.026±0.016
Aluminum (Al)	0.087±0.055	0.095±0.067
Silicon (Si)	0.277±0.169	0.312±0.212
Sulfur (S)	0.338±0.157	0.328±0.146
Chlorine (Cl)	0.011±0.036	0.008±0.024
Potassium (K)	0.090±0.124	0.075±0.088

Species	Reno $PM_{2.5}$(µg m^3)	Sparks $PM_{2.5}$(µg m^3)
Calcium (Ca)	0.067±0.036	0.084±0.058
Vanadium (V)	0.001±0.001	0.001±0.001
Manganese (Mn)	0.004±0.004	0.003±0.003
Iron (Fe)	0.133±0.073	0.132±0.080
Cobalt (Co)	0.000±0.000	0.000±0.000
Nickel (ni)	0.000±0.000	0.000±0.001
Copper (Cu)	0.012±0.009	0.024±0.017
Zinc (Zn)	0.009±0.008	0.010±0.008
Gallium (Ga)	0.001±0.000	0.001±0.000
Selenium (Se)	0.000±0.000	0.000±0.000
Bromine (Br)	0.003±0.002	0.003±0.001
Strontium (Sr)	0.003±0.003	0.002±0.002
Zirconium (Zr)	0.000±0.000	0.000±0.000
Molybdenum (mo)	0.002±0.001	0.002±0.001
Palladium (Pd)	0.003±0.002	0.003±0.001
Silver (Ag)	0.000±0.000	0.001±0.001
Cadmium (Cd)	0.003±0.002	0.003±0.002

The average $PM_{2.5}$ $SO_4^=$ for Reno and Sparks was 0.79 ±0.34 µg m^{-3}. On average, $SO_4^=$ accounts for about 11.1% of the $PM_{2.5}$. The average $PM_{2.5}$ NH_4^+ for Reno and Sparks was 0.27 ±0.12 µg m^{-3} that is about 3.9% of the $PM_{2.5}$. The average $PM_{2.5}$ NO_3^- for Reno and Sparks was 0.15 ±0.07 µg m^{-3} or 1.9% of the $PM_{2.5}$.

Total carbon (OC + EC) was the largest component of $PM_{2.5}$ in Reno and Sparks, accounting for 70.0 ±12.2% of the mass, on average. The ratios of OC to TC (sum of OC and EC) averaged 0.70 ±0.05. Elemental carbon originates primarily from direct emissions of particles, whereas organic carbon may originate either from direct primary emissions or from atmospheric transformations of organic gases. The OC/TC ratio has been used to identify the presence of secondary organic aerosol when the OC to EC ratio exceeds ~2 (i.e., OC/TC > 0.67) (Turpin et al. 1990, Hildemann et al. 1991). The proximity of combustion sources to the monitoring sites might have a direct effect on the higher OC/TC ratios. Within the measurement uncertainty, it is not possible to state whether there is a large fraction of secondary organic aerosol in the carbonaceous $PM_{2.5}$ component.

3.3. Scanning Electron Microscopy Results

Manual SEM analysis is a time-intensive analytical methodology. For this reason, a set of samples from the ambient data was selected for analysis. Mamane et al. (1998) recommended filter loadings around 100-300 μg per filter for SEM analysis. Observed mass loadings were between 40 and 93 μg per filter so three samples of the highest mass loadings were selected for analysis: 07-22-98 (69.5 μg), 08-06-98 (93.5 μg), and 09-02-98 (75.5 μg).

The chemical speciation data indicated that carbonaceous material, sulfate, ammonium dominated the ambient samples, and soil-related crustal species (Al, Si, K, Ca, Ti, Fe, and Zn) (Table 2). The SEM analysis also revealed that the majority of particles on the polycarbonate filters were carbonaceous. The size of these particles were, for the most part, ≤1 μm in diameter. Unfortunately, 1 μm is the minimum size of resolution for chemical analysis using the EDX capability of this SEM. Therefore, the SEM analysis had to focus on the particles that were greater than 1 μm diameter. These particles proved to be mostly mineral in nature (i.e., non-organic).

EDX analysis of the individual particles showed that for the most part the particles tended to be aluminum-silicates usually with Fe present. Based upon the observed spectra for the particles sampled, 12 different classes of particle type were arbitrarily established for aluminum-silicate types of particles based on the relative amounts of Na, Mg, Si, K, and Ca. The characteristic relationships for these elements and their average relative proportions observed are shown in Table 3. The greatest variability is observed in the Na: Mg and K: Ca ratios, with the Al: Si and Fe: Si ratios being fairly similar (Table 3).

Table 3. Typical relationships observed between the major aluminum-silicate elements observed in the mineral particles collected in Reno and Sparks, NV.

Spectra Form	Al:Si	Na:Mg	K:Ca	Fe:Si	% Occurrence[1]
Si	0.14	0.84			1 ± 1
Na~Mg, K~Ca, Fe	0.38	0.96	1.32	0.19	15 ± 10
Na~Mg, K>Ca, Fe	0.39	1.01	12.51	0.12	16 ± 5
Na~Mg, Ca>K, Fe	0.17	0.9	0.12	0.07	9 ± 7
Na>Mg, K~Ca, Fe	0.16	2.34	0.57	0.02	3 ± 3
Na>Mg, K>Ca, Fe	0.23	2.24	2.61	0.01	4 ± 2
Na>Mg, Ca>K, Fe	0.37	3.42	0.2	0.04	12 ± 7
Mg>Na, K~Ca, Fe	0.31	0.24	0.51	0.21	4 ± 1
Mg>Na, K>Ca, Fe	0.38	0.39	17.8	0.23	18 ± 12
Mg>Na, Ca>K, Fe	0.22	0.21	0.19	0.31	7 ± 7
Ca>Si	0.31	1.03	0.03	0.00	6 ± 2
Fe (+ other metals)	0.41	0.69	0.54	0.03	10 ± 5

[1] total number particles analyzed = 400

The Fe comprised, on average, 8% of the particle mass considering only the ten spectra types that have Na, Mg, K, Ca, and Fe present. For most aluminum-silicate particles, a distinctive spike of S, P, or Ba was observed in the EDX spectrum. The average percent of mass attributable to S and P for all the particles analyzed was 6.2% and 3.3%, respectively. In addition to the typical aluminum-silicate particles in the samples, particles showing distinctly metallic characteristics were observed. Iron-rich particles accounted for 10 ±5% of all particles examined. The Fe content of these particles ranged between 31 and 87.5% with an average content of 55.9%.

4. Chemical Mass Balance Receptor Modeling

The Chemical Mass Balance (CMB) receptor model (Watson et al. 1990) was used to estimate source contributions to $PM_{2.5}$. In order to ensure reasonable model estimates the CMB applications and validation protocols described by Watson et al. (1991) were applied in this study.

The chemically speciated 24-hour samples collected with the MedVol samplers expressed as mass concentrations with uncertainties formed the database for the CMB receptor modeling exercise. Site-specific source profiles were not determined for this study, so profiles from other studies that represent the major sources in Reno and Sparks were utilized.

Initial tests with different combinations of source profiles were performed to determine which profiles best explain the ambient data and the robustness of the results with respect to choice of source profiles. The tests were done using the average mass concentrations of each species based on the 18 samples collected in Reno and their root mean squared uncertainties. CMB performance measurements were examined to determine how well the ambient concentrations were explained by the CMB source contribution estimates. The results of these initial trials were used as guidance in CMB analysis of the entire sample set. Primary motor vehicle, primary geological material, and secondary sulfate sources were expected to be important contributors at both sites. The results of the test source apportionments are presented as a series of trials representing different combinations of source profiles in Table 4.

For the first trial run, the source profiles used for the CMB modeling were: 1) Mammoth Lakes, CA, road dust (Houck et al. 1989); 2) Northern Front Range Air Quality Study, Denver, CO, dynamometer low emitting gasoline vehicle composite, (Watson et al. 1998); 3) El Centro, CA, agricultural burning (Houck et al. 1989); 4) pure ammonium sulfate; 5) pure ammonium nitrate; and 6) pure sodium chloride. Common sources for sodium chloride include dry lakebeds during summer and road salting during winter. Three performance measures generated by the CMB model, the R SQUARE, the CHI SQUARE, and the PERCENT MASS were examined from each CMB model run to assess the applicability of the chosen source profiles.

The R SQUARE is the fraction of the variance in the measured concentrations accounted for by the variance in the calculated species concentrations. Values of R SQUARE greater than 0.9 indicate a good fit to the measured data. CHI SQUARE represents the weighted sum of the squares of the differences between calculated and measured species concentrations.

Table 4. Sensitivity of source contribution estimates to changes in source profiles for the average Reno sample.

PROFILE	BEST FIT	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6
FGEOL9[1]	1.13 ± 0.14	1.39 ± 0.15	1.16 ± 0.14	1.24 ± 0.13	1.57 ± 0.17	1.84 ± 0.15	
PLAYA[2]							0.42 ± 0.1
NWLCP2[3]	5.75 ± 0.86	5.78 ± 0.86	5.22 ± 0.85	3.83 ± 0.89			7.81 ± 1.04
MTRV3[4]					4.15 ± 0.9		
FMT10[5]						5.71 ± 1.62	
VELAGBC[6]	0.41 ± 0.15				0.31 ± 0.1	0.3 ± 0.14	0.5 ± 0.18
VEGB1[7]			1.1 ± 0.38				
VEGB7[8]				3.34 ± 0.72			
AMSLF[9]	0.93 ± 0.11	0.95 ± 0.12	0.94 ± 0.11	0.96 ± 0.11	0.98 ± 0.12	1.02 ± 0.2	0.91 ± 0.12
AMNIT[10]	0.17 ± 0.04	0.18 ± 0.04	0.17 ± 0.04	0.18 ± 0.04	0.18 ± 0.06	0.17 ± 0.14	0.17 ± 0.04
NACL1[11]	0.05 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.05 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
CHI SQUARE	0.19	0.95	0.82	0.3	0.6	0.88	1.44
R SQUARE	0.98	0.93	0.92	0.98	0.94	0.91	0.86
PERC MASS CLUSTERS	108.6	107.5	97.4	123.5	93.1	116.7	126.7

[1] FGEOL9 Mammoth Lakes road dust (Houck et al., 1989).
[2] PLAYA Playa composite (Gillies et al., 1999).
[3] NWLCP2 NFRAQS low emitting gasoline vehicle composite (Watson et al., 1998).
[4] MTRV3 Las Vegas, NV, motor vehicle composite (Chow et al., 1997).
[5] FMT10 Las Vegas, NV, motor vehicle composite (Chow et al., 1997).
[6] VELAGBC El Centro, CA, agricultural burning (Houck et al., 1889).
[7] VEGB1 Bakersfield, CA, vegetative burning (Houck et al., 1989).
[8] VEGB7 Las Vegas, NV, residential wood combustion composite (Chow et al., 1997).
[9] AMSLF pure ammonium sulfate.
[10] AMNIT pure ammonium nitrate.
[11] NACL1 pure sodium chloride.

Values between one and two indicate acceptable fits; values less than one indicates very good fits to the data. PERCENT MASS is the total mass accounted for by the source contribution estimates.

Values between 80 and 120% are considered acceptable. For the “best fit” profile selection (Table 4), the major contributor to the average Reno aerosol in the summer was motor vehicle emissions (5.75 $\mu g\ m^{-3}$, 68%). The percent of mass accounted for was 108.6%. For Case 1, the vegetative burning profile was removed resulting in a decrease in the R-SQUARE parameter from 0.98 to 0.93 and an increase in the CHI-SQUARE from 0.19 to 0.95 because the soluble and total potassium could not be accounted for without a vegetative burning profile. It is clear that the fraction of soluble to total potassium is too high in both the Reno and Sparks samples to have come solely from geological material. However, it is unlikely that the source of soluble potassium during summer is residential wood combustion, which is commonly used during winter for heating. More likely sources include cooking (barbecuing) and forest fires.

In Case 2, a vegetative burning profile (Bakersfield Majestic fireplace, Houck et al. 1989) was substituted for El Centro, CA, agricultural burning (Houck et al. 1989). The fit was nearly as good as that of the base case. In Case 3, a different residential wood combustion profile (Chow et al. 1997) was introduced. This resulted in an over-prediction of mass by 23.5%, because the soluble potassium content of this profile (1.1%) was lower than that of the El Centro, CA, agricultural burning (Houck et al. 1989) (12.5%) and Bakersfield Majestic fireplace (Houck et al. 1989) (4.1%) profiles. In Case 4, a Las Vegas motor vehicle profile (Chow et al. 1997) was substituted for the NFRAQS profile composite (Watson et al. 1998). This resulted in a lower motor vehicle contribution (4.1 $\mu g\ m^{-3}$, 57%) and a higher CHI-SQUARE (0.60). This profile was not able to fit organic and elemental carbon, the two most prevalent species in motor vehicle emissions. In Case 5, a different Las Vegas motor vehicle profile (Chow et al. 1997) was substituted for the NFRAQS profile composite (Watson et al. 1998). This resulted in a lower R-SQUARE (0.91) and a higher CHI-SQUARE (0.88) than those of the “best fit". Finally, in Case six a profile developed from local playa sediments was substituted for the Mammoth Lakes road dust (Houck et al. 1989). The fit in this case was considerably worse than the “best fit” case, with an R-SQUARE of 0.86 and a CHI-SQUARE of 1.44.

The sensitivity analysis demonstrates that in the summer, motor vehicles, geological material, and secondary sulfate were the major contributors to the average Reno $PM_{2.5}$ aerosol. It also shows that a vegetative burning profile is required to account for soluble and total potassium. The choice of motor vehicle profile had a significant effect on the ability of the CMB to account for elemental and organic carbon and on the magnitude of the motor vehicle source contribution.

One of the most important assumptions of the CMB model (Watson et al. 1984) is that the source profiles are linearly independent (i.e., they are statistically different). The degree to which this assumption can be met in practice depends to a large extent on the types and quality of chemical measurements made at the sources and receptor. The CMB model has been subjected to a number of tests to determine its ability to tolerate deviations from the model assumptions (e.g., Watson 1979, Gordon et al. 1981, Henry 1982 1992, Currie et al. 1984, Dzubay et al. 1984, DeCesar et al. 1985, Javitz et al. 1988, Lowenthal et al. 1992). The impacts of collinearities among the source profiles vary from case to case. These collinearities tend to inflate the variances of the source contribution estimates. The sensitivity analysis did not indicate any significant collinearity problems.

CMB source apportionments were performed for each valid MedVol $PM_{2.5}$ sample. The same geological, motor vehicle, and vegetative burning profiles were used for all samples. The sodium chloride profile was used in all cases to account for soluble sodium, but the contribution to mass was very small. The choice of secondary sulfate profile, ammonium sulfate, or ammonium bisulfate was based on which profile produced the best fits for ammonium and sulfate. A secondary ammonium nitrate profile was also used in all cases. The average R-SQUARE, CHI-SQUARE, and PERCENT MASS were 0.97, 0.41, and 106%, respectively. Most of the source apportionments experienced no collinearity clusters, with a few exceptions involving the geological and vegetative burning profiles. This resulted from very low source contribution estimates (SCEs) with relatively large uncertainties.

On average, the source contributions were similar at the two sites, with motor vehicles, geological material, secondary sulfates, vegetative burning, secondary nitrate, and salt accounting for 68 and 67%, 13 and 16%, 12 and 10%, 5 and 3%, 2 and 2%, and 0.5 and 1% of predicted mass at Reno and Sparks, respectively. T-tests demonstrated that differences between the major source contributions (motor vehicle, geological, secondary sulfate, and vegetative burning) at Reno and Sparks were not statistically significant. This demonstrates the spatially homogeneous nature of $PM_{2.5}$

The Sparks summer 1998 results can be compared with CMB results previously reported for Sparks $PM_{2.5}$ for the summer of 1997 (Gofa et al. 1998). In that case, the average motor vehicle contributions were somewhat lower (4.1 versus 5.7 $\mu g\ m^{-3}$) while the average geological contribution was over two times higher (3.0 versus 1.3 $\mu g\ m^{-3}$). These differences are due to the use of different motor vehicle profiles in the CMB for the summer, 1997 data. As demonstrated by the results of CMB sensitivity tests presented in Table 4, the Denver NFRAQS motor vehicle profile produced a better fit to the 1998 data, especially elemental and organic carbon, than did the Las Vegas profiles used by Gofa et al. (1998) in their study. Further, a vegetative contribution was not presented for the 1997 case, even though the same soluble potassium enrichment was observed.

To check for consistency of the source apportionment between 1997 and 1998, CMB model runs were carried out on the summer, 1997 data of Gofa et al. (1998) using the current "best fit" profiles. The results for the summers of 1997 and 1998 are remarkably similar, differing by no more than 3% for any source. In 1997 the dominant source was motor vehicle emissions (61%), followed by geological (17%), secondary sulfate (11%), and vegetative burning (6%).

5. Discussion

The CMB source apportionment of the Reno and Sparks ambient data defined the major source categories for the $PM_{2.5}$ affecting the air quality in northern Nevada. Based on the SEM analysis some qualification of the source of the geological component can be advanced. The SEM analysis indicated that the non-carbonaceous $PM_{2.5}$ was composed of aluminum-silicate mineral particles, many of which show a distinct signature in their spectra of S and P. In addition, metallic particles rich in Fe, Ti, and Cu, were observed. These characteristics are consistent with resuspended road dust as opposed to fugitive emissions from construction and playas.

Recent studies by Mamane et al. (1998) and Gillies et al. (1999) have examined the chemical and physical characteristics of fugitive dust types that could affect air quality in Reno and Sparks, NV. These studies examined PM_{10} and $PM_{2.5}$ samples from playas, construction sites, and paved roads that they assumed were the most likely sources of PM of geological origin. These samples were collected on filter media using a resuspension technique (Gillies et al. 1999) and examined using SEM, computer-controlled SEM, as well as other analytical methods (XRF, instrumental neutron activation analysis) in order to develop chemical and morphological marker for separating the geological sources. Mamane et al. (1998) reported that in the fine particle component of road dust collected from streets in Reno and Sparks the mineral particles were predominantly aluminum-silicates (>80%) with a wide range in the relative proportions of the typical aluminum-silicate elements (Na, Mg, Al, Si, K, and Ca). This was also observed in the ambient samples in this study. The variability in the samples could be a reflection of the wide range of aggregate source material used in the construction of paved roads. Several other physical and chemical characteristics of paved road dust in Reno and Sparks observed by Mamane et al. (1998) are mirrored in the ambient samples taken in this study. For example, Mamane et al. (1998) observed that only a small portion of the particles in road dust samples showed enrichment in Ca as compared to Si. This was also observed for the particles collected for the ambient samples. Playa dusts were observed by Mamane et al. (1998) to have more Ca-rich particles (17%). The low percentage of Ca-rich particles in the ambient samples (6%) suggests that this source type did not contribute significantly to the ambient samples during the sampling period.

The presence of P and S in the spectra of the particles from the road dust collected from paved roads in Reno and Sparks was considered by Mamane et al. (1998) to be indicative of an anthropogenic influence. They suggested that these elements, whose source may be fuel-derived, become incorporated or coated onto the mineral particles, thus creating a "marker" species for road dust when it is found in association with mineral particles. Mamane et al. (1998) reported that S and P were seen as small peaks in many of the spectra for road dust source material and reached significant proportions in about 5% to 2% for S and P, respectively. For the ambient samples taken in this study the average percent of mass attributable to S and P, considering all the particles analyzed were 6.2% and 3.3%, respectively. In addition to S and P in paved road dust particles, Mamane et al. (1998) also noted there was a noticeable presence of Ba. Ba was also found in some of the ambient particles examined in this study and its presence can be linked to its emission from diesel-fueled vehicles (Truex et al. 1980).

The metallic particles in the ambient samples also suggest a roadway source. Mamane et al. (1998) reported that about 3% of the road dust particles they examined with SEM were predominantly composed of Fe. Gillies et al. (1998) reported Fe contributed ~5% to the total $PM_{2.5}$ in ambient samples taken in the Sepulveda Tunnel in Los Angeles, CA, where mobile source emissions and resuspended road dust can be expected to dominate the particulate matter composition due to the confined space. In the ambient samples taken in this study, the metallic particles made up around 10% (±5%) of the non-carbonaceous particles with Fe being the dominant metal, but Ti and Cu were commonly observed. The sources of these metallic particles are likely wear processes acting on vehicles. As the primary mechanism of resuspension of road dust is by entrainment in the turbulent wakes of vehicles and by injection due to the tires (Nicholson et al. 1989), the contribution of road dust to ambient $PM_{2.5}$ in Reno and Sparks can be attributed to the mobile sources. The inclusion of resuspended road dust in the mobile source category raises the contribution from mobile sources to ~84% of the total ambient $PM_{2.5}$.

6. Conclusions

Summertime monitoring of $PM_{2.5}$ during a period from 07-17-98 through 09-11-98 on an every third day sampling schedule showed average levels in Reno and Sparks, NV, to be 7.85 ±1.84 $\mu g\ m^{-3}$ and 7.80 ±2.22 $\mu g\ m^{-3}$, respectively. Within measurement uncertainties, these values are the same and indicate that the $PM_{2.5}$ levels in this area appear to be relatively homogeneous.

The CMB modeling efforts carried out for this study suggest that the most important contributors to the ambient $PM_{2.5}$ in Reno and Sparks, NV, in summer 1998, are in order of importance: motor vehicle emissions (67-68%), geological (13-16%), secondary sulfate (10-12%), and vegetative burning (3-5%).

One of the deficiencies of standard CMB analysis is the inability to separate the different sources of geological material. This study demonstrated that adding SEM analysis methods to the standard suite of analyses allowed for the attribution of the source of geological material. The similarity of the elemental composition for $PM_{2.5}$ mineral particles in this area, as determined by SEM analysis, in both the paved road dust (Mamane et al. 1998) and the ambient samples collected for this study indicates that this type of $PM_{2.5}$ is road dust resuspended by vehicle activity. That potentially 13 to 16% of the $PM_{2.5}$ that the CMB attributed to geological material could have a road dust source indicates that the $PM_{2.5}$ levels could be reduced with a strategy to limit this emission source.

Acknowledgements

We would like to thank the Air Quality Management Division, Washoe County District Health Department for supporting this research with U.S. EPA 105 grant funds. Colleagues at the DRI we would like to acknowledge for their assistance in sample analyses include Barbara Hinsvark, Steve Kohl, Mark Morrison, Dale Crow, and Cliff Frazier. Dr. John McCormack, Department of Geological Sciences, University of Nevada, Reno, was a great help during the SEM analysis.

References

[1] Calloway, C.P., Li, S., Buchanan, J.W., Stevens, R.K., 1989. A refinement of the potassium tracer method for residential wood smoke. Atmospheric environment 23 (1): 67–69.

[2] Chow, J.C., Watson, J.G., Green, M.C., Egami, R.T., Lowenthal, D.H., Gillies, J.A., Rogers, C.F., DuBois, D., Frazier, C.L., Derby, J., Freeman, D.L., Kohl, S., and Minor, T., 1997. Fugitive Dust and Other Source Contributions to PM10 in Nevada's Las Vegas Valley. Final Report, DRI Document No. 4039.2D1. Prepared for Clark County Department of Comprehensive Planning, Las Vegas, NV.

[3] Chow, J.C., Watson, J.G., Green, M.C., and Lowenthal, D.H., 1999. Cross-border transport and spatial variability of suspended particles in Mexicali and California's Imperial Valley. Atmospheric environment, 34: 1833-1843.

[4] Chow, J.C., Watson, J.G., and Pritchett, L.C., 1993. The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation, and Applications in U.S. air quality Studies. Atmospheric environment, 27 (8): 1185-1201.

[5] Chow, J.C., Watson, J.G., Richards, L.W., Haase, D.L., McDade, C., Dietrich, D.L., Moon, D., and Sloane, C., 1991. The 1989-1990 Phoenix PM10 Study. Volume II: Source Apportionment. DRI Document No. 8931.6F1, prepared for Arizona Department of Environmental Quality, Phoenix, AZ.

[6] Currie, L.A., Gerlach, R.W., Lewis, C.W., Balfour, W.D., Cooper, J.A., Dattner, S.L., DeCesar, R.T., Gordon, G.E., Heisler, S.L, Hopke, P.K., Shah, J.J., Thurston, G.D., and Williamson, H.J., 1984. Interlaboratory comparison of source apportionment procedures: results for simulated data sets. Atmospheric environment, 18: 1517-1537

[7] DeCesar, R.T., Edgerton, S.A., Khalil, M.A.K., and Rasmussen, R.A., 1985. Sensitivity analysis of mass balance receptor modeling: methyl chloride as an indicator of wood smoke. Chemosphere, 14 (10): 1495-1501.

[8] Dockery D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., and Speizer, F.E., 1993. An association between air pollution in six U.S. cities. New England Journal of Medicine, 329: 1753-1759.

[9] Dockery D.W., Schwartz, J., and Spengler, J.D., 1992. Air pollution and daily mortality: associations with particulates and acid aerosols. Environ. Res. 59: 362-373.

[10] Dzubay, T.G., Morosoff, N., Whitaker, G.L., and Yasuda, H., 1981. Evaluation of polymer films as standards for x-ray fluorescence spectrometers, In: Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

[11] Dzubay, T.G., Stevens, R.K., Balfour, W.D., Williamson, H.J., Cooper, J.A., Core, J.E., DeCesar, R.T., Crutcher, E.R., Dattner, S.L., Davis, B.L., Heisler, S.L., Shah, J.J., Hopke, P.K., and Johnson, D.L., 1984. Interlaboratory Comparison of receptor model results for Houston aerosol. Atmospheric environment, 18: 1555-1566.

[12] Gertler, A.G., Coulombe, W.G., Watson, J.G., Bowen, J.L., and Marsh, S., 1993. Comparison of PM_{10} concentrations in high and medium volume samplers in a desert city', Environ. Mon. Assess. 24: 13-25.

[13] Gillies, J.A., Gertler, A.W., Sagebiel, J.C., and Dippel, W.A., 1998. On-road emissions in the Sepulveda Tunnel, Los Angeles, California, in $PM_{2.5}$: A Fine Particle Standard, Chow J.C. and Koutrakis P., eds., Air & Waste Management Association, Pittsburgh, PA, 677-698.

[14] Gillies, J.A., O'Connor, C.M., Mamane, Y., and Gertler, A.W., 1999. Chemical profiles for characterizing dust sources in an urban area, western Nevada, USA. Zeitschrift fur Geomporpholgie Supplementband, 116: 19-44.

[15] Gofa, F., Gertler, A.W., and Gillies, J.A., 1998. PM and VOC Source Apportionment in the Truckee Meadows, Nevada, 1998. Prepared for Washoe County District Health Department, Reno, NV.

[16] Houck, J.E., Pritchett, L.C., Roholt, R.B., Watson, J.G., Chow, J.C., Goulet, J.M., and Frazier, C.A., 1989. Determination of Particle Size Distribution and Chemical Composition of Particulate Matter from Selected Sources in the San Joaquin Valley. Final Report prepared for San Joaquin Valley Air Pollution Study Agency and California Air Resources Board, CA.

[17] Lowenthal, D.H., Chow, J.C., Watson, J.G., Neuroth, G.R., Robbins, R.B., Shafritz, B.P. and Countess, R.J., 1992. The effects of collinearity on the ability to determine aerosol contributions from diesel- and gasoline-powered vehicles using the chemical mass balance model. Atmospheric Environment, 26A (13): 2341-2351.

[18] Mamane, Y., 1988. Estimate of municipal refuse incinerator contribution to Philadelphia aerosol – I. Source analysis. Atmospheric Environment, 22 (11): 2411-2418.

[19] Mamane, Y., Gillies, J.A., O'Connor, C.M., and Gertler, A.W., 1998. Distinguishing Among Fugitive Dust Emission Sources Using Scanning Electron Microscopy, X-Ray Fluorescence, and Instrumental Neutron Activation Analysis. Final Report Prepared for Washoe County District Health Department, Reno, NV.

[20] Nicholson, K.W., Branson, J.R., Geiss, P., and Cannell, R.J., 1989. The effects of vehicle activity on particle resuspension. J. Aerosol. Sci. 20: 1425-1428.

[21] Pace, T. G., & Watson, J. G., 1987. Protocol for applying and validating the CMB model. EPA 450/4-87-010. US Environmental Protection Agency. Research Triangle Park, NC.

[22] Turpin, B.J., Huntzicker, J.J., and Adams, K.M., 1990. Intercomparison of photo acoustic and thermal-optical methods for the measurement of atmospheric elemental carbon. Atmospheric Environment, 24A: 1831-1835.

[23] U.S. Environmental Protection Agency, 1997. National Ambient Air Quality Standards for Particulate Matter, Federal Register 62, 38651. Research Triangle Park, NC.

[24] Watson, J.G., Cooper, J.A., and Huntzicker, J.J., 1984. The effective variance weighting for least squares calculations applied to the mass balance receptor model. Atmospheric Environment, 18: 1347-1360.

[25] Watson, J.G., Lioy, P.J., Mueller, P.K., 1989. The measurement process: Precision, accuracy, and validity, in Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Hering, S.V., ed., American Conference of Governmental Industrial Hygienists, Cincinnati, OH: 51-57.

[26] Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B.M., Pace, T.G., Meyer, E.L., and Nguyen, Q., 1990. The U.S. EPA/DRI chemical mass balance receptor model. CMB 7.0. Env. Soft. 5 (1): 38-49.

[27] Watson, J.G. and Chow, J.C., and Pace, T.G., 1991. Chemical Mass Balance, in Data Handling in Science and Technology - Volume 7: Receptor Modeling for Air Quality Management, Hopke, P.K., ed., Elsevier Press, New York, NY, 83-116.

[28] Watson, J.G. and Chow, J.C., 1993. Ambient air sampling, in Aerosol Measurement: Principles, Techniques and Applications, Willeke, K. and Baron, P.A., eds., Van Nostrand, Reinhold, New York, NY, 622-639.

[29] Watson, J.G. and Chow, J.C., 1994. Particle and gas measurements on filters, in Sampling of Environmental Materials for Trace Analysis, Markert, B., ed., VCH-Publisher, Weinheim, New York, Tokyo, 83-175.

[30] Watson, J.G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H., Lawson, D.R., Ashbaugh, L.L., 1994. Chemical mass balance source apportionment of PM10 during the Southern California Air Quality Study. Aerosol Science and Technology, 21: 1–36.

[31] Watson, J.G., Lioy, P.J., Mueller, P.K., 1995. The measurement process: Precision, accuracy, and validity, in Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Cohen, B. and Hering, S.V., eds., American Conference of Governmental Industrial Hygienists, Cincinnati, OH: 187-194.

[32] Watson, J.G., Fujita, E., Chow, J.C., Zielinska, B., Richards, L., Neff, W., and Dietrich, D., 1998. Northern Front Range Air Quality Study Final Report. Prepared for Colorado State University, Fort Collins, CO, and EPRI, Palo Alto, CA, by Desert Research Institute, Reno, NV.

JJEES

Jordan Journal of Earth and Environmental Sciences

Volume 1, Number 1, Mar. 2008
ISSN 1995-6681
Pages 11 -21

Marble Production and Environmental Constrains: Case Study from Zarqa Governorate, Jordan

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Abstract

Along the rapid growth of human needs in many sectors, a significant decrease in the availability and viability of the natural resources is always faced. The high volume production is always associated by considerable amount of waste materials that may adversely impacts the surrounding environment. One of the major waste generating industries is the marble production industry, by which ornamental stone manufacture acquires special mitigation process and environmental assessment to minimize the negative environmental impacts that may generate. Efforts on bypassing such dilemma were intensified looking for new regulations and legislations to minimize and reuse the generated waste. This paper addressed the possible environmental impacts that might generate from ornamental stone production as a rapid growth industrial sector in Jordan and to review the adequacy of Jordanian environmental legislations in controlling the environmental protections norms associated with such industry. Preliminary environmental impact assessment was conducted at eight marble manufacturing enterprises distributed in Zarqa Governorate at north-west of the capital city Amman. The assessment included testing of major chemical and physical environmental resources, products and byproducts generated from each establishment according to the production stages and in accordance to the Jordanian environmental regulations and legislations in force. Results indicated that noise levels were above the International Standards, which require a special attention. In terms of water and land resources, ornamental waste products; estimated to be around 10% of the prime material consumed; may form a source of contamination through the unsuitable solid and liquid waste disposal strategies adopted by the inspected manufacturers. The paper addressed the implementation of chemical-stabilization wastewater treatment units to treat wastewater before disposing it into the domestic sewage system, whereas solid waste should be disposed only in specialized industrial plants.

Keywords: Marble industry; Environmental legislation; Waste Disposal; Environmental Impact Assessment; Environmental management; Zarqa- Jordan;

1. Introduction

Along the rapid growth of human needs in many sectors, a significant decrease in the availability and viability of the natural resources was always faced. Neither the less, the high volume production is always associated by considerable amount of waste materials, which may adversely impacts the surrounding environment. Efforts on bypassing such dilemma were recently intensified in many countries and international establishments looking for new regulations and legislations to minimize and reuse the generated waste (UMTC, 1995; OECD, 1997).

One of the major waste generating industries is the marble quarry and production industry by which around 70% of this precious mineral resource is wasted in the mining, processing, and polishing procedures. Around 40% of marble waste is generated world widely during quarrying operations in the form of rock fragments and being dumped either in nearby empty pits, roads, riverbeds, pasturelands, agricultural fields, or landfills leading to wide spreading environmental pollution (Çelik, 1996; Akbulut and Gürer, 2003).

Jordan is one of the leading marbles producing countries in the Middle East, where marble production sector in Jordan contributes about 18.7% of Gross National Product (GNP) (DOS, 2000). Recently, marble production in Jordan is considered a key supporter for hard currencies along 66% industrial exports contribution of gross national exports (DOS, 1998). Internationally, marble production and consumption in Europe has been continuously increasing over the last two decades with an annual increase rate of 7% (Harold and Taylor, 1993) by which projected demand for dimensional marble was estimated to be 600,000 tons for the year 2000 (Official Gazette, 2000).

Zarqa Governorate in Jordan, the third biggest city after the capital city Amman and Irbid in size and population

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are considered the largest industrial zone by which half of Jordanian industrial establishments' lies within the Zarqa Governorate (DOS, 2004). The number of Jordanian industrial establishments had reached around 23,000 in 1997 (Jordanian Sanitary Drainage System Instructions, 1998). In addition, and according to the Zarqa industrial chamber (2002), there are about 23 marble manufacturing plants of small and medium sized enterprises, which are centralized within the southwest of Zarqa city.

Growing concerns for environmental protection against industrial impacts on human health has motivated many studies to activate and legislate environmental protection laws. According to Zarqa Governor (the environmental status of Zarqa Governorate Workshop, 2006), the industrial plants within Zarqa Governorate claims the responsibility for about 75% of the total pollution of the Kingdom, where various pollution sources are contaminating most of the Zarqa natural resources. The main pollution sources are derived from industrial enterprises that pollute air considerably by gas emission from existed power plant and fuel refinery while overspill and bad management of existed wastewater treatment plants are polluting groundwater considerably. Thus, many regulations and legislations were enforced in all industrial sectors to protect the existing natural resources. However, some specific industries were not included within these legislations. Manufacturing of Ornamental stone is one of these industries that need to be evaluated to determine the certain norms required to regulate their action and to control the possible generated environmental impacts.

The main objectives of this study were to evaluate the possible environmental impacts that might generate from ornamental stone production as a rapid growth industrial sector in Jordan and to review the adequacy of Jordanian environmental legislations in controlling the environmental protections norms associated with such industry. More specifically the study assesses through simple preliminary EIA for the major effective impacts of wastewater and solid waste disposal strategies adopted in marble manufactures along other environmental norms.

2. Review of Some Jordanian Related Regulations and Legislations

The concerned environmental Jordanian legislations dealing with environmental aspects are regulated by five ministries: the Ministry of Environment (ME), Ministry of Agriculture (MA), Ministry of Water and Irrigation (MWI), Ministry of Planning (MP), and Ministry of Health (MH).

Although marble industry is not included directly in TEP 2003 and EPL 1995 legislations, the following legislations and regulations can be related through one or more of environmental norms:

1. According to ME in concern of water quality, Article (17) of the (EPL) - 12 of 1995, provides that the corporation shall, in coordination with the competent authorities, undertake the assurance of general standards for water in all its usages and examination of water sources with respect to pollution with respect to the water sector.
2. According to ME in concern of waste disposal, Article (26) of the (EPL) number 12 of 1995, prohibits the dumping, disposal of and piling up of any substances that are harmful to the environment whether solid, liquid, gaseous, radial, or heat in water sources, or the storage of any of these substances in close proximity to the water sources and within a distance to be specified by the Minister (the Minister of Municipal, Rural and Environmental Affairs) in accordance with the recommendations of the General Manager of the Corporation.
3. According to land use classification accomplished by the MA and enforced by the MP the *Agriculture Law Number 20 For The Year 1973* (Official Gazette, 1973) and supported by the *Law Of Managing The Country Properties Number 17 For The Year 1974* (Official Gazette, 1974), prohibits land use for other non-classified purposes (i.e. lands that are classified according to their potential capability as agricultural lands can not be used for industrial activities).
4. According to MP, the *Law of Regulating Cities, Villages and Buildings Number 79 for The Year 1966* (Official Gazette, 1966) and its modifications, and *Municipalities Law Number 29 for The Year 1955* (Official Gazette, 1955) prohibits the establishment of any industrial activity within pedestrian city limits, thus, industrial establishments are forced to be held at the industrial cities in accordance to the *Industrial Cities Institution Law number 59 for the year 1985* (Official Gazette, 1985).
5. According to ME in concern of air emission protocols, *Traffic Law number 14 for the year 1984* (Official Gazette, 1984) provided a standards for the permitted emission level of each gas.
6. According to MH in concern to health, *General Health Law number 21 for the year 1971* (Official Gazette, 1971) states that "the Ministry of Health shall be responsible for all matters pertaining to heath in the Kingdom including (i) The provision of preventive and curative health care, (ii) Prevention of contagious diseases, (iii) Promotion of health awareness and medical culture through available means, and (iv) Establishment and management of all types and levels of educational institutions for medical professions and setting their curriculum, appointing their teaching staff, and issuing certificates for their graduates provided that educational institutions for medical professions that exist at the time of the enactment of this Law shall be deemed established in accordance with its provisions".

In addition, according to the subsection TEP law article 13-B, existing factories have to introduce mitigation actions that gradually minimize the negative environmental impacts with the support of the ME. Since all existed factories within the Zarqa Governorate were operating before the TEP law came to force, it is environmentally relevant to evaluate the performance of the existing marble industry through conducting EIA analysis and to provide proper management plan as proposed to such cases. Lately, the article 13.A of the TEP law (annex 2 number 11.B for extracting industries and surface mining and their derived industries) states that "Any establishment, company, or entity, or any enterprise the provisions of this law come into force, and which conducts an activity that might adversely affect the environment, shall be bound to prepare an evaluation study on the environmental effect of its projects and submit it to the ministry, in order to take the appropriate resolution in its respect". Finally, article 13-B states "the minister shall be entitled to request any establishment, company, enterprise, or party, which conducts any activity that affects the environment, to prepare an evaluation study on the environmental effect of its projects."

3. Materials and Methods

The manufacturing of marble involves cutting and finishing marble obtained from quarries, where specific dimensional marble is prepared for various uses in specialized mills equipped with saws, polishing machines, and others. Marble sawing equipment includes large circular saws, where various types of diamond and other equipment are used for smoothing, polishing, and edging the raw marble. The marble production process includes several steps. In the first phase, blocks (usually have a weight between 15 and 20 Metric Ton) and slabs are stored and deposited in the park of prime materials by means of two bridge cranes for great tonnage (See Figure 1). Saws (gang saw or slab cutting machines) are used for cutting blocks into more governable units (slabs) for the following processes of production (See Figure 2).

Figure 1: Blocks and Slabs in the storage of prime materials

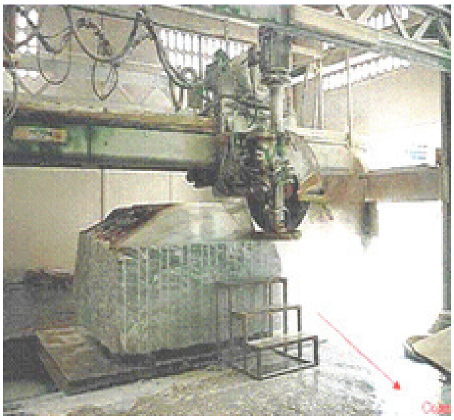


Figure 2: Cutting of Blocks

According to direct inspection of the manufactures, the cutting process is carried either in dry or in wet medium. Slabs obtained are rough unpolished and appear in different formats and sizes (usually between two and 4 m width). A cutter is used next to obtain different sizes of flagstones of (60-cm × 30-cm × 2-cm dimensions). In some cases, flagstones are sold directly without polishing. However, a polish unit of chemical treatment is adopted followed by a refining process.

The study was conducted at the Zarqa Governorate at the Northwest of the capital city Amman. The biggest eight manufactures out of the 23 existed marble establishments have been environmentally assessed in detail to identify the environmental constrains and influences. Field survey as well as questionnaire fillings that is especially prepared for data collection to be considered as a response, with 34.8% response rate, the refusals to participate were 8 plants with a rate of 34.8%, the incomplete fillings were for 3 plants with a rate of 13.0%, and the withdrawals after contacts was 4 plants with a rate of 17.4%. The products and byproducts generated from each establishment have been assessed individually from environmental prospect according to the production stages and in accordance to the Jordanian environmental regulations and legislations in force.

The impacts of the marble manufacture can be estimated and evaluated according to production stage or process. Each process includes some action that adversely affects the environment through one or more environmental norm. For example the sawing or cutting phase involve noise effect and dust emission, while cutter and polishing phases involve chemical uses and contamination of water. However, the following list of aspects was assessed in detail; land take for the development and change of land use, impact on site characteristics during and after marble production operations, economic impacts during operation, social impacts, solid waste disposal, sewage system and volume of liquid wastes, private and public traffic on the way to the site, and air and water pollution during marble manufacture operations.

The final evaluation was based on raw material consumption and marble production (production index), energy consumption, water consumption and reuse, types and quantities of waste products, effluent water quality, particulate and gaseous emissions, and noise levels. Solid waste disposal was evaluated according to waste type while wastewater was assessed chemically through providing a monitoring program. Effluent water samples were collected and chemically analyzed for contaminants loads through a year monitoring program. In addition, noise levels were measured at each stage of production using sound level meters and noise dosimeters.

Finally, the paper addressed the significance of the impacts as evaluated and compared to the existed environment baseline, including alternatives and mitigation strategies distinguishing between impacts in form of positive or negative, reversible or irreversible, temporary or permanent, short term or long term, and direct or indirect.

4. Results and Discussion

4.1. Landtake and Change of Land Use

First, as inspected through the foundation records for the eight different marble manufactures, the existed establishments violate the *Agriculture Law Number 20 for The Year 1973* and the *Law of Managing the Country Properties Number 17 for The Year 1974* by being established on agricultural lands and not industrial ones. Neither the less, existed marble establishments also violated the *Law of Regulating Cities, Villages and Buildings Number 79 for The Year 1966* and *Municipalities Law Number 29 for The Year 1955* by being within pedestrian limits. Therefore, existed established marble companies had a permanent negative impact on land use leading to the loss of ecological habitats with negative effects on flora and fauna populations by reducing the green-agricultural spots and might increase the risk of agricultural contamination. The industrial chamber along the authorized ministries should adopt a mitigation process to translocate those existed establishments outside the pedestrian or agricultural limits.

4.2. Site Characteristics During and After Work Operations

According to field inspection of the surrounding areas for the marble establishments, marble production negatively and directly damaged the existing landform by intrusion of urban development and by loss of attractive features such as vegetation and hills. The general landscape features will be changed partially or totally depending on the size of the establishment as well as associated activity and location. From landscape point view, formation of edges, corridors, boundaries will be formed which in turn will block the connectivity between ecosystem components as a genetic resources for the adjacent habitat.

4.3. Social and Economic Impacts

Jordan is primarily an agrarian society. The agricultural sector accounted for 7% of GNP in 1991(DOS, 1991), a proportion which has gradually decreased as farm workers are drawn in from the land to serve the expanding construction and industrial sectors. To date, Jordan has lacked the detailed database on soil and land characteristics that is necessary to allow rational planning of land and water resources utilization, especially in setting priorities for the efficient use of the very limited surface water and groundwater reserves. Jordan is classified among few countries of the world with limited water resources and it is one of the lowest on a per capita basis. The available water resources per capita are falling because of population growth and are projected to fall from less than 160 m^3/capita/year at present to about 90 m^3/cap/year by 2025, putting Jordan in the category of an absolute water shortage. The scarcity of water in Jordan is the single most important constrains to the country growth and development because water is not only considered a factor for food production but a very crucial factor of health, survival and social and economical development.

Raw material consumption and production can be used as an indication for the intensiveness of manufacture day activity loads, thus the potential of daily pollution if contamination exists. Raw material consumption varies significantly along the eight manufactures ranging from 33 to 990 m^3/day (working day) with an average of 405.6 m^3/day and a standard deviation of 352.9 m^3/day (Table 1). According to the statistical analysis using JMP program (JMP IN, 2004); the huge variation of the standard deviation indicates the large variability between the marble manufactures in Zarqa Governorate given by a coefficient of variation of 87%.

Marble production also varied significantly from 28 to 890 m^3/day with a mean of 368.8 m^3/day, a standard deviation of 321.7 m^3 / day and a coefficient of variation between manufactures of 87.3% (Table 1). According to linear regression by forcing the origin pass using the JMP statistical program, the average marble production was proportional by around 90% to raw material consumption (i.e. for each one-m^3/day increase in the average raw material consumption, the production increases by 0.90 m^3/day), with a root mean square error of only 12.74 m^3/day. Subsequently, waste products calculated by the difference between raw material consumption and production, where ranging from five to 100 m^3/day, with an average of 36.9 m^3/day and a standard deviation of 33.9 m^3/day (Table 1). According to statistical analysis (Tables 2 and 3), the generated waste residues forms about 10% of the prime material entered in processing. However, the difference between raw material consumption and production is not necessary assigned as waste products but rather could be byproducts. According to site investigations, some of the generated residues derived from all marble manufacturing steps may reuse for other ornamental or construction appliances as garden landscaping, house floor flagstones and roads.

According to the surveyed income of the establishments, the gross annual return varied from 10,000 to 100,000 JD depending on the establishment size and trade. From economic standpoint, the marble production offers a positive impact by providing cash currencies and long-term benefits during operation. The local community of the village is of low standard living as surveyed. The average income of each family is less than 200 JD per month. Most the families hold at least four persons and increase up to 12 person per house (Un–published data from Zarqa Industrial Chamber and questionnaire answers). Due to fact that the existed lands are far from large cities and being classified as agricultural lands, the area is considered a rural village that is not urbanized yet. The presence of marble establishments within their limit in the theory of industrial development gave the rise for the local community for better living standard for increasing the cost of the land itself and provides working opportunities within the establishments with a wage level exceeding 200 JD a month. However, women contribution was not a matter of improve since the working environment and the cultural values required heavy-male actions. At the same time, educational levels were not a matter of concern. Therefore, one of the positive social impacts of such establishments away from environmental consideration is the creation of job and opportunities as well as the activation of the business sector, which have positive effects on the economic welfare of the local population.

4.4. Energy Consumption

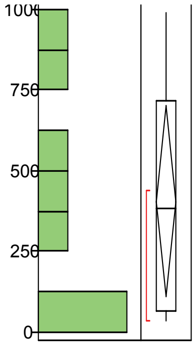
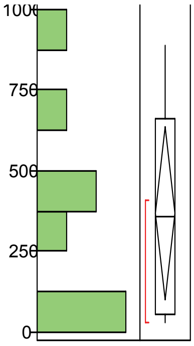
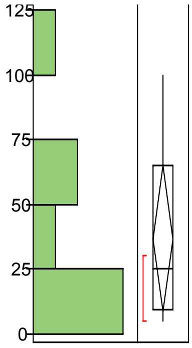
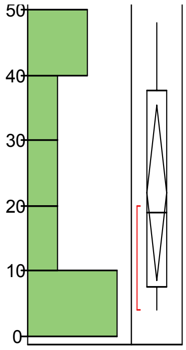
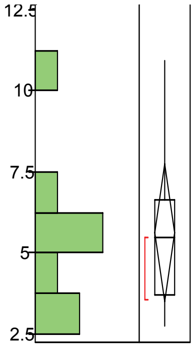
The utilized energy at the marble factories was only generated directly from electric source. No old fuel burning devices were detected at the sites, which in turn, minimize the environmental impact from energy consumption sources. Therefore, energy consumption is not a considerable focus of local environmental impact within this study. However, energy consumption was also variable between inspected manufactures by which the energy consumption varied from 2.7 to 11 KW/day with an average of 5.6 KW/day and standard deviation of 2.54 KW/day (Table 1).

4.5. Solid Waste Disposal

Wastes produced from marble manufacture can be categorized as either by-product or waste, in all cases; the wastes disposal should follow specific regulations according to type and quantity. Unfortunately, there are few regulations that control the disposal strategy of waste products. The TEP law within articles (6, 7, 13, and 17), and Article (26) of the (EPL) number 12 of 1995 state that environmentally detrimental waste disposal is prohibited to be dumped or disposed whether if it is solid, liquid, gaseous, radial, or heat in water sources in accordance with the recommendations of the General Manager of the Corporation and their disposal in landfills should be regulated by the Governorate authority.

The sources of the generated residues in marble manufacture can be categorized into (i) gravels and broken slabs, (ii) slurry and sludge, (iii) used oils and lubricants, and (iv) others (Table 4). According to European Community Regulations (CER), gravels, broken slabs and small-unwanted flagstone are classified as inert of code number (CER 010202 and CER 010406) by which they are formed from the process of refined cuttings, and rough dressing accumulating for 10% of the prime material entered into processing.

Table 1: Raw Material Consumption and Production for the studied marble manufactures

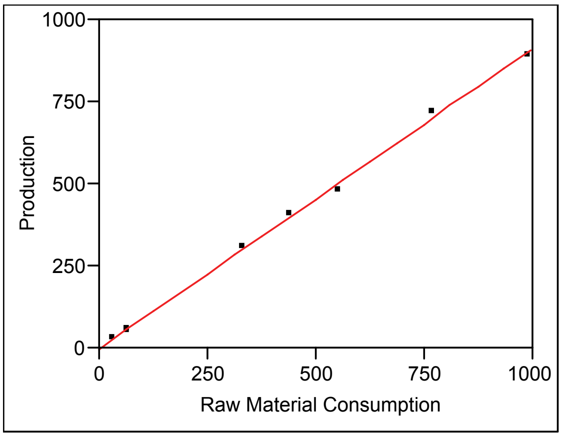
	Raw Materials Consumption (m^3/day)	Production (m^3/day)	Waste (m^3/day)	Water Consumption (m^3/day)	Utilized Energy (KW/day)
Manufacture # -1	66	57	9	7	5.5
Manufacture # -2	330	310	20	18	4. 2
Manufacture # -3	550	480	70	30	5. 5
Manufacture # -4	33	28	5	4	2.7
Manufacture # -5	770	720	50	40	7.1
Manufacture # -6	990	890	100	48	11.0
Manufacture # -7	66	55	11	9	3.6
Manufacture # -8	440	410	30	20	5. 5
Quintiles					
Mean	405.625	368.75	36.875	22	5.6181507
Std Dev	352.85527	321.67985	33.90928	16.044581	2.540933
Std Err Mean	124.75318	113.731	11.988741	5.6726159	0.8983555
upper 95% Mean	700.61939	637.68109	65.223868	35.413605	7.7424239
lower 95% Mean	110.63061	99.818912	8.5261323	8.5863948	3.4938775
Sum	3245	2950	295	176	44.945205
Variance	124506.84	103477.93	1149.8393	257.42857	6.4563406
Skew ness	0.5223071	0.4890057	1.0437163	0.5738727	1.3915138
Kurtosis	-0.905606	-0.99907	0.0996302	-1.017245	2.5727495
CV	86.990513	87.235215	91.95737	72.929912	45.227214

Their disposal strategy adopted by the manufactures varied according to the quantity of waste. Some manufactures were investigated to dispose their small-quantity wastes illegally on roadsides while others were disposing their large-waste loads into specialized landfills. However, obligation of disposal in specific landfills is predetermined by the local municipality as indicated by the Jordanian Law of Regulating Cities, Villages and Buildings number 79 of 1966 (Official Gazette, 1966) and its amendments.

Slurry, on the other hand, is prohibited to be disposed into the sanitary drainage system according the Sanitary Drainage System Law number 1 of 1998 (Official Gazette, 1998), where it is forced to implement a pretreatment plant to eliminate solids from liquid. According to this study, on average of only 2 m^3 /day of slurry or sludge were produced from marble manufacture, where mud produced before polishing were dried and packed for liming agent, animal feedings, and construction purposes, while mud produced just after polishing process were disposed into the sanitary drainage system. This type of mud requires more detailed investigation for defining the best disposal strategy.

The second type of waste is the used oil produced from cutting units, lawn mower, polisher, and wheelbarrows. According to Jordanian legislation as well as the European Community Regulations, used oil is considered as dangerous waste which require a special management if the quantity exceeds the standard limits of one m^3/year. According to inspected marble sites, the quantity of used oil has reached a maximum of 500 l/year (year is 200 working days), thus, their disposal strategy in Jordan compiles the European regulation by which used oil quantity must be declared by the local authority and should be stored in special containers and collected by oil refiner companies. In all cases, it is prohibited to dispose used oil in the municipal drainage system as indicated in article 3-G of the Jordanian Sanitary Drainage System Instructions of 1998 and the directive number 66 for the year 1994 (Official Gazette, 1994)

Table 2: Bivariate Fit of Production By Raw Material Consumption



Linear Fit

Production = 0 + 0.909825 Raw Material Consumption

Summary of Fit

RSquare	.
RSquare Adj	.
Root Mean Square Error	12.74374
Mean of Response	368.75
Observations (or Sum Wgts)	8

Analysis of Variance

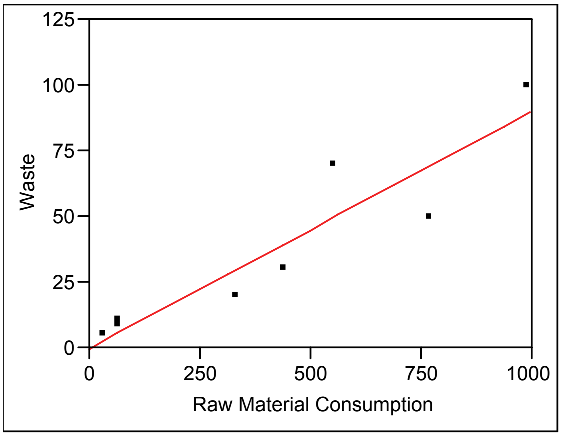
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1811021.2	1811021	11151.4
Error	7	1136.8	162	Prob > F
C. Total	8	1812158.0		<.0001

Tested against reduced model: Y=0

Parameter Estimates

Term		Estimate	Std Error	t Ratio	Prob>|t|
Intercept	Zeroed	0	0	.	.
Raw Material Consumption		0.909825	0.008616	105.60	<.0001

Table 3: Bivariate Fit of Waste by Raw Material Consumption



Linear Fit

Waste = 0 + 0.090175 Raw Material Consumption

Summary of Fit

RSquare	.
RSquare Adj	.
Root Mean Square Error	12.74374
Mean of Response	36.875
Observations (or Sum Wgts)	8

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	17790.179	17790.2	109.5434
Error	7	1136.821	162.4	Prob > F
C. Total	8	18927.000		<.0001

Tested against reduced model: Y=0

Parameter Estimates

Term		Estimate	Std Error	t Ratio	Prob>|t|
Intercept	Zeroed	0	0	.	.
Raw Material Consumption		0.090175	0.008616	10.47	<.0001

Table 4: Types of Wastes produced from Marble Manufactures

Denomination	Classification	Metric	Storage
Flagstones	Byproducts	10% of raw material	In-Plant Disposed area
Mud's or Slurry	Inserts	0.7 m^3 /year	In-Plant Disposed area
Flocculent agents (PRAESRO, 2540)	Dangerous	6.57 m^3/year	Special Containers
Plastic	Not dangerous	0.2 ton/year	Containers
Wood	Not dangerous	0.2 ton/year	Containers
Oil lubricant	Dangerous	< 1 m^3 /year	Special Container
Powder	Dangerous	varies	

Plastic and wood are minor waste type produced from marble manufactures by which they are used as complementary materials as holders or packing materials. Both of two waste types did reach a maximum of 0.2 ton per working year where they are stored and sold by the end of the year to some private companies under the authority of the Zarqa Governorate.

Disposal of solid waste as inspected, when inefficient, might lead to its accumulation affecting therefore the comfort and general health conditions of the local community. Thus, regulation actions should take more control in forcing the marble establishments to dispose their solid wastes in specialized industrial landfills outside the pedestrian areas.

4.6. Sewage System and Volume of Liquid Wastes

Massive amount of water were used for cooling, cutting, calibrating and polishing machines (See Figure 3). Water consumption varied from four to 48 m^3/day with a mean of 22 m^3/day and standard deviation of 16 m^3/day (Table 1). Some manufactures collects wastewater produced in cutting process through special drains to be used for further applications after solid removal by mechanical treatment were collected in a settling tank for recycling (See Figure 4), by which the recycled water are collected in a reservoir tank, while the sludge is disposed in landfills outside the processing plant.

Table (5): Chemical analysis mean values for one-year monitoring program for marble wastewater effluents

Manufacture	#1	#2	#3	#4	#5	#6	#7	#8	JS[1]
pH	8.30	8.02	8.31	8.15	8.24	8.25	8.04	8.15	6.5-9.0
EC (dS/m)	3.21	2.32	2.73	2.69	3.98	2.33	3.98	3.33	-
TDS (mg/ L)	2693.38	2623.71	2821.95	2655.43	3253.81	3385.27	3352.21	3281.17	3000
Hardness (mg/ L)	1268.62	1515.31	1553.05	1104.57	1026.19	934.73	2026.19	1934.73	1500
HCO_3	367.2	402.1	356.1	385.5	406.5	365.8	401.5	386.5	-
Ca^{2+} (mg/ L)	321.44	434.25	245.2	280.25	275.2	465.8	324.1	354.1	-
Mg^{2+} (mg/ L)	240.2	250.8	262.5	312.3	272.1	330.2	341.1	332.5	-
K^+ (mg/ L)	23.5	24.1	35.2	30.4	28.6	36.2	31.4	28.4	-
Cl^-(mg/ L)	175.6	211.1	222.6	144.4	244.9	166.2	344.9	366.2	500
NO_3^- (mg/ L)	3.58	4.86	0.77	0.22	1.55	0.88	1.55	1.88	12
SO_4^{2-} (mg/ L)	287.1	239.1	245.1	304.3	291.3	239.1	391.3	442.1	500
Na^+ (mg/ L)	273.12	285.5	441.3	343.2	415.2	356.4	455.5	421.2	-
Al^{3+} (mg/ L)	2.11	2.51	2.34	3.21	2.01	2.34	3.21	3.54	5
Fe (mg/ L)	0.04	0.05	0.04	0.07	0.08	0.04	0.06	0.05	1
Mn (mg/ L)	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.2
Zn (mg/ L)	0.04	0.06	0.07	0.05	0.06	0.04	0.05	0.04	15
Cu (mg/ L)	0.1	0.05	0.12	0.13	0.04	0.04	0.05	0.1	2
Cr (mg/ L)	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.1
Pb (mg/ L)	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.1
Cd (mg/ L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Ni (mg/ L)	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.2
Se (mg/ L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
BOD_5 (mg/L)	45	43	35	26	35	42	24	47	50
COD (mg/L)	20	25	22	23	24	32	22	24	150
Total Coliform (MPN/100ml)	285	154	125	218	142	165	224	217	1000
Fecal Coliform (MPN/100ml)	101	104	132	145	152	120	147	125	1000

1 Jordanian Standards 202/1991 for Industrial Wastewater disposal.

(_) Undetermined: it depends in its determination on standard and general stipulations.

Figure 3: Polisher

Figure 4: Settling Tank

Generally, the massive water produced at the end of the production is either recycled in order to be reused again for the same purpose or disposed into the domestic sewage system (municipal network) that flows into the nearby Assamra Waste Water Treatment Plant (WWTP). In both conditions, the MWI should undertake the assurance of general standards for water in all its usages and examination of water sources with respect to pollution according to Article (17) of the (EPL) number 12 of 1995 by which the effluent quality of the marble manufacture must fit the Industrial Wastewater Standard Specification (Jordanian Standard No.202 of 1991), in order to be recharged to wadis, or to reuse in agriculture and industry, or to be used for artificial groundwater recharge.

From environmental point view, wastewater should be disposed into industrial treatment plants located within the same Governorate and not into the domestic WWTP. Three out of eight manufactures where inspected to violate the wastewater disposal strategy directing their effluents into the domestic sewage system. The eight manufactures should implement a preliminary chemical-treatment plant system at the plant area before disposing into the industrial sewage system. The chemical-treatment plant system should include a settling reservoir with a chemical stabilization unit to allow the reuse of water for cooling the machines only. The sludge obtained after the chemical stabilization unit is pressed by high-pressure machine to retrieve absorbed water, while cubed solid sludge as a solid waste is then transported outside the processing plant.

4.7. Private and Public Traffic

Traffic is usually an issue for urban development. The baseline at the inspected sites includes either one large highway crossed by unsealed roads or only sealed cross by non-sealed roads. Neither railways nor ports were inspected at the village or nearby forcing most of the transportation to be achieved by large vehicle. The existing traffic flow before the establishment is much lower since the village is only of local agricultural lands. The existence of marble infrastructure had anticipated in more traffic flow especially during operation with large diesel type vehicle, which moves according to establishment production to either 10 or more frequent moves a day. The presence of such vehicles requires safety issues for roads and driving controls. Commonly, diesel vehicles emit SOX, NOX, CO_2, CO and Hydrocarbons that are considered hazardous pollutants. The gaseous emissions to air from vehicles may result in negative effects on the health of the local population. The negative impact can be only resolved by the mitigation action of the marble manufactures translocation to industrial zones, otherwise, reduction in traffic may cause the reduction in production, and therefore cash return.

4.8. Air Pollution

Particulate emissions or fugitive dusts were the main environmental concern of marble manufacture. Dust was associated with raw handling material, plant maintenance, and water suspended materials by which emission sources were investigated to be derived from (i) court units, (ii) lawn mower, and (iii) polishers. Dust emission to the atmosphere from marble cutting process allocated at only one manufacture by which dust emissions had deteriorated the adjacent soils, plants, and surface water. Out of the eight manufacture plants, seven were implementing a wet medium cutting process.

Dusts have been found migrating and running in roads and side walks, accumulation of more than 5 cm above the soil surface knowing that Jordanian soils is already calcareous of pH around 8.2 restricting the availability of some nutrients for plant uptake. Dust may be arises from vehicle movements on unsealed roads and can also occur as a result of winds or storms or neighboring industries such as marble. The existing dust levels in the inspected sites are strongly affected by weather and particularly the strength of winds. Generated dust during operation may affect human, plant and animal growth at the surrounding community. Therefore, a management strategy should be implemented to avoid the negative impacts of dust contamination and to reduce the translocation of dust outside the plant, which can be achieved by plantation of wind-brake plants, sprinkling devices, collection of produced slurry from the cutting process directly to special tanks and entered into the slurry treatment process again.

4.9. Water Pollution

Effluent water quality of marble manufacture must fit the Industrial Wastewater Standard Specification (Jordanian Standard No.202 of 1991), in order to be reused for different purposes under the authority of Ministry of

Water and Irrigation. At the same time, reclaimed water are allowed to discharge or reuse when only its quality complies with the properties and defined quality standards in accordance to Reclaimed Domestic Wastewater Standard Specification, Jordanian Standard, No.893 of 2002 (Article (17) of the (EPL) number 12 of 1995). Disposing of treated wastewater can be achieved if and only if the treatment allows rendering or clearance from any environmentally detrimental substance according to Article (26) of the (EPL) number 12 of 1995. Effluent water samples were collected through a year of study and tested for chemical loads. Results indicated minor concentrations of Ca, Mg, K and SO_4 derived from marble itself, however, some samples showed high loads of Na (Table 5). The high sodium loads where derived from those manufactures adopting the wastewater treating units. Waste water treating process adopted by some manufactures were inspected to use a flocculating agent known as *PRAESTOL 2540 TR* (Stockhausen, 2003) to flocculate the colloidal Calcium Carbonate particles in the settling tanks. The coagulative chemical was inspected to be highly molecular of medium anionic polyelectrolyte copolymer of acryl amide and sodium acrylate. The compound was used in a diluted form of 0.05-0.1% by which it is environmentally friendly if used in such precise dilution range.

According to CER, the wastewater containing such chemical compound is classified as non-dangerous waste with code number (CER 01045), as their chemical type and concentration does not exceeds the permitted levels (2000 mg/kg), however, the direct contact to the chemical should be avoided especially the respiratory system and the direct eye contact if dust is produced. Toxicological information derived from the producing company (Stockhausen GmbH & Co. KG, Krefeld) based on knowledge of the properties of the components; adverse effects on human health are not to be expected in normal use. From the ecological standpoint, because of its specific substantively, the product can be eliminated well in biological waste effluent treatment plants (binding on digestive sludge).

The predictions of changes in water quality is evaluated based on the anticipated effluent discharges including the huge volume of discharge, the high concentration of suspended solids, and some concentration of harmful substances. Improving effluent quality and reducing effluent volumes to levels were taken into consideration, however, impact on the water resources will still a concern. Since waterborne effluent may reduce water quality with impacts on human health particularly where water is reused in some marble manufactories regardless of the inappropriate disposal strategies adopted, it is suggested to an alternative methodology by implementing an in-situ wastewater treatment plant to allow the disposal of their water into the sanitary drainage system or reuse it in irrigation non-edible trees or for cooling process if the chemical loads still within the allowed range.

4.10. Noise

Jordanian norms that control noise are not different from the European ones. The instructions for control and preventing noise of 1997 (Official Gazette, 1997) explains article 27 of the environmental protection Law number 12 of 1995 (Official Gazette, 1995) by which adopting the International Standards ISO- 2204-1979 (E), as well as the European regulations that determine the permitted noise level in the industrial areas to be less than 75/65 dB (A-scale).

Noise was monitored along the marble manufactures at Zarqa Governorate using (sound level meters and noise dosimeters) and over a number of 15-minute periods during a typical working day. Ideally, 4 or 5 periods was monitored at each sensitive receptor location. Results indicated background noise levels of 35 dB (A) and extent to 100 dB (A) during operation time. The measured noise level was on average of 100 dB (A) for eight continuous working hours per day which had exceed the allowed safe level. Therefore, it is highly recommended that new factories should be established at least 100 m away from the pedestrian area knowing that almost 6 dB sound level reduces for each 10 m.

As inspected at all marble production sites and surveyed by local community, noise resulting from traffic movement was much less than noise produced by cutting phase stage in marble production. Regardless that in both cases the noise level detected at the nearest residential area near marble manufactures did not reach 60 dB (A), however, noise in all case still disturbing people in residential areas of homes and schools.

According to the short negative sound impact, the existed establishments should implement noise safety plan. The safety plan should include noise abatement, machinery noise reduction via redesigning or replacement source receiver isolator. At the same time, internal employees should not be exposed to noise more than two hours especially within the first meter exposure to the noise source. Therefore, regular schedule work plan should be implemented for regular time change every two hours. The employer must develop a monitoring program for noise exposure through audiometric testing devices, while the employee, on the other hand, should use safety audiometric hearing protection device and should run a periodic otologic exam.

5. Conclusions

Marble production, as an industrial sector, has a great contribution to Jordanian gross national income due to both large Jordanian industrial capacity and marble reserve. However, there are some potential risk of such industry lying on the environmental, which requires attention, mitigations, and management to protect the existing human health and natural resources. From environmental point of view, results indicated that marble industry has few human impacts with minor environmental risks, however, each factory needs an intensive evaluation to determine the certain norms to regulate their action and to control the possible impact produced. However, new factories must be established within industrial zones to prevent environmental-community inflects and to allow better safe competition. On the other hand, existing factories have to introduce mitigation actions to minimize gradually the environmental impacts through providing proper managements relevant to environmental performance test.

According to this study, the existed marble establishments violated the land use classification and municipality limits by being established on agricultural lands within pedestrian city limits away from industrial zones. According to site characteristics during and after work operations, marble production negatively and directly damaged the existing landform by intrusion of urban development and by loss of attractive features such as vegetation and hills. The major impact produced by marble manufacture is the direct negative social impact. Particulate dust is main environmental impact of marble production as inspected to be produced from marble cutting phase that requires implementation of wet medium cutting process to be legislated in marble manufactures. Dust impacts were obvious in deteriorating adjacent soils by accumulating more than 5 cm at the surface. However, dust emission requires a special management plan by plantation of wind-brake plants, sprinkling devices, collection of produced slurry from the cutting process directly to special tanks and entered into the slurry treatment process again. As inspected at all marble production sites and surveyed by local community, noise resulting from traffic movement was much less than noise produced by cutting phase stage in marble production. Regardless that in both cases the noise level detected at the nearest residential area near marble manufactures did not reach 60 dB (A), however, noise in all case still disturbing people in residential areas of homes and schools. Also, safety plan should be implemented including noise abatement, machinery noise reduction via redesigning or replacement source receiver isolator, regular employee schedule work plan, a monitoring program for noise exposure through audiometric testing devices, use of safety audiometric hearing protection device, and periodic employee otologic exam.

According to private and public traffic, the existence of marble infrastructure had anticipated in more traffic flow especially during operation with large diesel type vehicle, which moves according to establishment production to either 10 or more frequent moves a day. The presence of such vehicles requires safety issues for roads and driving controls. From economic standpoint, the marble production offers a positive impact and economic welfare of the local population by providing cash currencies and long-term benefits during operation and provides working opportunities. Waste products produced from marble manufacture were estimated to be around 10% of the prime material entered in processing. However, the difference between raw material consumption and production is not necessary assigned as waste products but rather could be byproducts since factories can sell flagstones as ornamental or construction units for garden landscaping, house floor flagstones and roads. The sources of the generated residues in marble manufacture can be categorized into (i) gravels and broken slabs, (ii) slurry and sludge, (iii) used oils and lubricants, and (iv) others. Disposal of solid waste as inspected, when inefficient, might lead to its accumulation affecting therefore the comfort and general health conditions of the local community. Thus, regulation actions should take more control in forcing the marble establishments to dispose their solid wastes in specialized industrial landfills outside the pedestrian areas.

The massive amount of water ranging from four to 48 m^3/day can be reused if treated properly in-situ by implementing chemical-stabilization wastewater treatment unit. If chemical treatment is implemented, then coagulated liquid sludge should be disposed into industrial treatment plants while cubed solid sludge can be disposed into landfills. According to site inspections, some manufactures violated the wastewater disposal strategy directing their effluents into the domestic sewage system. According to wastewater chemistry at the inspected factories, no chemicals other than the flocculating agent *PRAESTOL 2540 TR* were found with few minor impurities from the marble rock itself. The flocculating agent was used in marble process to flocculate the colloidal calcium carbonate particles in slurry. According to manufacture regulations, the coagulative chemical is highly molecular that is environmentally friendly which can be eliminated well in biological waste treatment plants where it is classified as non-dangerous waste with code number (CER 01045).

References

[1] Akbulut H, Gürer C. The environmental effects of waste marble and possibilities of utilization and waste minimization by using in the road layers. Proceeding of the fourth national marble symposium, Afyonkarahisar, December 2003. p. 371–8 [in Turkish].

[2] Çelik MY. Recycling of waste marble. MSc thesis, Afyon Kocatepe University, Natural Science Institute, Department of Mining Engineering, Afyonkarahisar; 1996 [in Turkish].

[3] Department of statistics – Jordan. 1991.

[4] Department of statistics – Jordan. 1998.

[5] Department of statistics – Jordan. 2000.

[6] Department of statistics - Jordan. 2004.

[7] Harold A. Taylor, Jr. 1993. U.S. Dimension Stone in 1991. Report of U.S.B.M. ROC MAQUINA No. 11, December 1993.

[8] JMP IN. 5.1.2. 2004. Statistics and graphics guide, SAS Institute Inc. Cary, NC.

[9] Jordanian Sanitary Drainage System Instructions for the year 1998. The disposal instructions of the industrial wastewater to the Sanitary Drainage System.

[10] OECD. Road transport research: recycling strategies for road works. Organization for Economic Co-operation and Development (OECD), Paris, France; 1997.

[11] Official Gazette of Jordan. 1955. Modifications of Municipalities law number 29 for the year 1955. Volume.

[12] Official Gazette of Jordan. 1966. Law of Regulating Cities, Villages and Buildings number 79 for the year 1966, and its modifications. Volume 1952. 25.9.

[13] Official Gazette of Jordan. 1971. Control and prevent noise impacts. Volume 2294. P747. 16.5.1971.

[14] Official Gazette of Jordan. 1973. Agriculture law number 20 for the year 1973 Volume 2449. P882. 16.5.

[15] Official Gazette of Jordan. 1974. Law of managing the country properties number 17 for the year 1974. Volumes 2486. P545. 16.4.1974.

[16] Official Gazette of Jordan. 1984. The traffic law number 14 for the year 1984. Volume 3229. P597. 2.5.1984.

[17] Official Gazette of Jordan. 1985. Industrial cities institution law number 59 for the year 1985. Volumes 3343. P1426. 1.10.1985. Law of Water Authority number 18 for the year 1988.

[18] Official Gazette of Jordan. 1994. Sanitary Drainage System Law number 66 for the year 1994. Volume 4011. P3117. 17.12.1994.

[19] Official Gazette of Jordan. 1995. The Environment protection law number 12 for the year 1995. Volumes 1225. P403. 1.5.1995.

[20] Official Gazette of Jordan. 1997. Volumes 4238. P4710. 1. 11. 1997.

[21] Official Gazette of Jordan. 1998.

[22] Official Gazette of Jordan. 2003. Temporary Environmental Protection Law. Volumes 4580. P1. 13. 1. 2003.

[23] Rawabdeh, I. 2002. Assessment of products' standards in Jordanian manufacturing companies. Emerald Journal, Vol. 9 No. 1 (pp. 28 - 42).

[24] Stockhauste GMBH and Co. KG, 2003. Product description sheet.

[25] The environmental status of Zarqa Governorate Workshop, Department of Environment- Zarqa – Jordan. 2006.

[26] UMTC. Use of recycled materials and recycled products in highway construction. University of Massachusetts Transportation Center Report UMTC-95-1.US; 1995.

[27] Zarqa industrial chamber, 2002. Zarqa – Jordan.

JJEES

Jordan Journal of Earth and Environmental Sciences

Volume 1, Number 1, Mar. 2008
ISSN 1995-6681
Pages 23 -31

Determination of the Vuggy Porosity of Some Oolitic Building Limestones and the Practical Implications

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Abstract

This study shows that a better correlation between different variables such as on sonic velocity, total porosity and water saturation, and other secondary porosity values, can be obtained when dealing with a database, consisting of one petrographic class or Lithological group. This study is based mainly on oolitic limestones of Jurassic age commonly used as building stones in France, Britain and other countries. Few samples have also been taken from Jordan's Holocene. The total porosity is divided into matrix and secondary porosity. Using the cementation exponent (m), only secondary porosity of the moldic or vuggy type was emphasized in the present study. The relationships between the different porosity types and the other measured or derived properties were delineated, by extrapolation, using correlation. Mathematical formulae were presented to derive additional, complex properties from those more easily measured. Although the findings of this study are based on a limited available database about Jordanian building limestone, they have been verified. Practical implications of the present study and its limitations are also discussed.

Keywords: secondary porosity estimation; vug porosity; limestone; oolitic; petrophysics; Jurassic; France; UK; building stone;

1. Introduction

Carbonate rocks (limestone and dolomite) are significant oil and groundwater reservoirs, as well as, building stone resources. Their complicated porosity systems impart heterogeneity to reservoirs (Mazzullo and Chillingarian, 1992) and strongly affect many technical and industrial aspects related to their exploitation. Hence, the specific types and relative percentages of pores present, and their distribution within the rock, exert a strong control on the production and stimulation characteristics of carbonate reservoirs (Jordy, 1992; Chillingarian et al., 1992; Hendrickson et al., 1992; Honarpour et al., 1992; Wardlaw, 1996); salt crystallization (Leary, 1983) and on the restoration and repair of building stones (Ashurst and Dimes, 1990; Spry, 1982).

Limestone porosity can be subdivided according to Choquette and Pray (1970) into the following two types: (1) depositional or primary porosity; such pores could be present between particles or crystals (*inter-particle or inter-crystalline porosity*), or within them (*intra-particle or intra-crystalline porosity*), or formed by gas bubbles and sediment shrinkage (*fenestral porosity*), and as *shelter* or *growth-framework pores* (common in reef buildups); and (2) secondary porosity: which is formed as a result of later, generally post-depositional dissolution or fracturing. Such pore types include those mentioned earlier (when subsequently cemented and later have had all or some of that cement dissolved), as well as vugs (large pores that transect the rock fabric) and dissolution-enlarged fractures.

Primary porosity is substantially reduced by cementation and compaction during post depositional burial diagenesis. Thus, most of the porosity in limestone reservoirs is of secondary origin. However, primary porosity may be preserved because of the early influx of hydrocarbons into pores (e.g. Feazel and Schatzinger, 1985). Also, secondary porosity in carbonate rocks can be formed at, or near the Earth's surface by freshwater dissolution, as well as deep in the subsurface by chemically aggressive (corrosive) fluids. Assigning the pores to one of these two environments (Mazzullo, 2004), requires careful observation, thin-section petrographic study and stable carbon-oxygen isotope analysis.

Oolites are spherical to ellipsoidal bodies, about 0.25 to 2.0 mm in diameter, which may or may not have a nucleus and have concentric or radial structure or both (Glossary of Geology and Related Sciences, 1962). Recent and ancient calcareous ooids and pisoids have been known in the following depositional environments (Flugel, 1982):

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1. Terrestrial (caliche-ooids, cave pearls, pisoids in shallow pools on a playa surface)
2. Fluviatile
3. Lacustrine
4. Marine.

Cavernous and associated vuggy porosity present in oolitic and bioclastic limestones are dominant in some building stones (Honeyborne, 1982; Leary, 1983) and constitute major attributes of hydrocarbon production (Newell et al. 1987; Mazzulo and Chillingarian, 1996; Yousef and Norman, 1997; Fox and Albrandt, 2002).

In developing countries, such as Jordan, where sophisticated laboratory tests are rarely performed due to lack of facilities, there is the need to develop simple estimation techniques by which different porosity types and volumes can be measured. This will be of importance in exploration projects for hydrocarbons, water and minerals currently carried out in Jordan mainly by the National Oil Company, Water Authority and Natural Resources Authority. In this context, (Moh'd, 2002) derived some pore-related properties from bulk density and water saturation, and further work on the secondary porosity of some Jordanian building limestones has been carried out (Moh'd, 2007).

The present work characterizes the vuggy porosity and its volume in French, British and Jordanian building limestones using only Vp (longitudinal sonic waves), total porosity and water saturation. To calculate the cementation exponent (m), there is a need to determine water resistivity (R_w). This value was assumed to be 0.005 ohm-m. It has been reported (Focke and Munn, 1987) that formation's resistivity factors (and consequently cementation exponents) are not affected by the brines resistivity.

2. Materials and Methods

The studied limestones along with their salient petrographic features are summarized in Table 1. Fifty-four samples have been studied in the present work (16 from France, 16*2 from Britain, and 6 from Jordan). As far as the studied UK stones are concerned, each reported reading represents the average of two samples. Studied building stones from France and UK are of Jurassic age and one is of Cretaceous age; all are dominantly ooidal limestones. Jordanian ooidal limestones are of Recent age.

Table 2 characteristics of the studied oolitic building limestones (after Leary, 1983).

The results of porosity, degree of saturation, and sonic velocity (Vp) tests (Brown, 1981), carried out following the BRE testing procedures (Ross and Butlin, 1989), have been taken from Honeyborne (1982) and Leary (1983) for the reported French, and British stones, respectively and measured by the author for the Jordanian oolitic limestones (J1-J6). A set of vuggy non-oolitic Jordanian limestones (J7-J11) (Moh'd, 2007) has been included for comparative purposes. The derived properties include:

Modified saturation: this was obtained by multiplying total porosity with degree of saturation.

Cementation exponent (m): this was calculated using Archie formula and assuming that water resistivity as 0.005 where m= log (0.005/water saturation squared)/log total porosity. This parameter can also be estimated from total and sonic porosity for fractured (Rasmus, 1983) and vuggy carbonates (Nugent, 1983).

Permeability: was obtained using Jorgensen equation (1988) by multiplying 84105 by porosity index = $\Phi^{m+2}/(1-\Phi)^2$. The obtained values were found to correlate well with measured air permeability using API standards.

Table 1 Characteristics of the studied building limestones (after Honeyborne, 1982; Leary, 1983; Moh'd, 2001 and Moh'd, 2007).

Stone Originee	Stone	Description
French Stones	Savonnieres Stone	shelly oolitic limestone, numerous small pockets (6: demi-fine, 7: demi-fine choix, 8: eveillee). Upper Jurassic (Portlandian).
	Brauvilliers Stone	oolitic limestone with occasional shell fragments and some vacuoles (9: liais, 10: liais marbrier, 11: doux demi-fin). Upper Jurassic (Portlandian).
	Anstrude Stone	crinoidal oolitic limestone (14: roche Claire, 15: roche jaune claire, 16: roche jaune). Jurassic (Bathonian).
	Massangis Stone (20)	oolitic limestone with shell fragments (occasional siliceous or pyritized nodules). Jurassic (Bajocian to Bathonian).
	Vilhonneur Stone	oolitic limestone (37: dur, 38: marbrier, 39: roche).
	Sireuil Stone (40)	fine-medium, ooliths, quartz, microfossils, matrix: microgranular, numerous small pockets. Cretaceous (Cenomanian).
	Terce Stone (50)	chalky oolitic limestone. Jurassic (Callovian).
	Chauvigny Stone (53)	oolitic limestone, micritic matrix with macropores. Jurassic (Bathonian).
UK Stones	Ketton Stone	oolitic limestone. Middle Jurassic.
	Portland Stone	oolitic limestone. Late Jurassic.
	Taynton Stone	oolitic limestone from the Great Oolite of Jurassic age.
	Weldon Stone	oolitic limestone. Middle Jurassic.
Jordanian Stones	Oolitic limestones (J1-J6)	from Irkheim Formation, Holocene, hot-water Lake.
	Vuggy non-oolitic limestones	J7-J11
	Hayyan Stone (J7)	fossiliferous limestone, Turonian (Middle Cretaceous).
	Siwaqa Stone (J8 and J9)	Travertine, Holocene.
	Tafih Stone (J10)	Crystalline limestone, slightly phosphatic, Santonian (Upper Cretaceous).
	Izrit Stone (J11)	red chalky limestone, Eocene.

Sonic porosity: is equivalent to velocity of sound – 141/(28.59); where 28.59 is the inverse of 100/(3000-141); 141 and 3000 are transit time (in µ s/m) in calcite crystal and air, respectively.

Vuggy porosity and *Fracture porosity*: are estimated from the dual porosity chart of Aguilera and Aguilera (2003).

Matrix porosity is the total porosity minus the sum of vug and fracture porosities.

3. RESULTS

The results of the present work are listed in Table 2 and shown as bivariate cross-plots in Figures 1 to 20. A simple statistical summary showing the mean, minimum and maximum values of the studied properties are shown in Table 3. A matrix showing the correlation coefficients between the different variables is shown in Table 4. These are usually the minimum values of correlation coefficients because in these softwares (such as Excel which was used to obtain the correlation matrix here) linear relationships are assumed between the variables. As shown in the Figures, higher values of correlation coefficients can be obtained when fitting the data using nonlinear models.

Table 2 Measured ([1, 2, 3] after Honeyborne, 1982) and derived properties of the studied stones.

Stone	Subtype	Bed	Sound Velocity1 m/s	Total Porosity2 %	Water Saturation3	modified saturation	Cementation Exponent	Permeability millidarcies	Sonic porosity %	Secondary Porosity %	Vuggy Porosity %	Matrix Porosity %
Ketton		Old	3450	23.8	0.65	15.44	3.09	96	5.2	18.5	13.5	10.3
		New	2750	23.7	0.65	15.41	3.08	96	7.8	15.9	13.5	10.2
		White	2900	24.8	0.65	16.12	3.18	109	7.1	17.7	14.0	10.8
Portland	Independ.	Whit	3850	13.6	0.92	12.47	2.57	12	4.2	9.4	6.3	7.3
		Base	3950	13.0	0.96	12.43	2.55	10	3.9	9.0	5.3	7.7
	Kingston	Roach	3925	19.6	0.59	11.58	2.61	72	4.0	15.7	9.5	10.1
		Whit	3775	22.2	0.62	13.75	2.88	89	4.3	17.9	13.5	8.7
		Base	3875	19.1	0.70	13.36	2.77	58	4.1	15.0	11.0	8.1
	Sheat Q.	Top Tier	3900	20.2	0.60	12.09	2.67	74	4.0	16.1	9.9	10.3
		Mid Tier	3550	20.6	0.59	12.12	2.68	81	4.9	15.6	10.0	10.6
		SeedyTier	3700	17.6	0.68	11.97	2.61	41	4.5	13.1	8.0	9.6
		Base	4100	16.5	0.67	11.06	2.50	36	3.6	12.9	7.5	9.0
		Roach	3300	21.0	0.64	13.44	2.82	73	5.7	15.3	12.4	8.6
Taynton			3550	23.5	0.69	16.22	3.15	83	4.9	18.6	14.0	9.5
Weldon		Fine G.	2600	27.1	0.68	18.43	3.47	125	8.5	18.6	15.5	11.7
		Coarse G.	1900	27.2	0.66	17.92	3.43	133	13.5	13.7	15.5	11.7
		6	2881	36.1	0.52	18.77	3.92	495	7.2	28.9	22.5	13.6
		7	2684	34.7	0.50	17.35	3.70	473	8.1	26.6	22.0	12.7
		8	2702	30.6	0.68	20.81	3.82	177	8.0	22.6	18.0	12.6
		9	3106	27.0	0.57	15.39	3.19	177	6.3	20.7	17.0	10.0
		10	2966	32.6	0.54	17.60	3.63	336	6.9	25.7	19.0	13.6
		11	3045	33.7	0.47	15.84	3.48	493	6.6	27.2	20.0	13.7
		14	3376	21.9	0.81	17.74	3.21	31	5.4	16.5	13.0	8.9
		15	3374	20.6	0.66	13.60	2.83	65	5.4	15.2	10.0	10.6
		16	4282	18.1	0.65	11.77	2.60	48	3.2	14.9	8.5	9.6
		20	4276	15.1	0.88	13.29	2.67	17	3.3	11.9	10.0	5.1
		37	4684	13.1	0.89	11.66	2.49	12	2.5	10.6	5.0	8.1
		38	4259	11.7	0.94	11.00	2.41	8	3.3	8.4	4.1	7.6
		39	4606	11.9	0.64	7.62	2.07	19	2.7	9.3	1.3	10.7
		40	2069	36.0	0.76	27.36	4.65	230	12.0	24.0	22.5	13.5
		50	3332	23.7	0.88	20.86	3.50	53	5.6	18.1	14.0	9.7
		53	4014	18.7	0.71	13.28	2.75	44	3.8	14.9	5.3	13.4
		J1	4005	15.1	0.65	9.82	2.35	31	3.8	11.3	5.0	10.1
		J2	3991	16.7	0.69	11.52	2.55	35	3.8	12.9	6.0	10.7
		J3	4090	15.2	0.68	10.34	2.40	29	3.6	11.6	5.4	9.8
		J4	3899	17.1	0.66	11.29	2.53	41	4.0	13.1	7.0	10.1
		J5	3945	14.3	0.69	9.87	2.34	25	3.9	10.4	4.8	9.5
		J6	4020	15.4	0.73	11.24	2.50	26	3.8	11.6	7.2	8.2
		J7	4704	14.8	0.77	11.37	2.50	21	2.5	12.3	5.5	9.3
		J8	3792	17.9	0.76	13.59	2.76	35	4.3	13.6	9.9	8.0
		J9	4085	17.8	0.79	14.05	2.79	32	3.6	14.2	10.0	7.8
		J10	4012	22.9	0.56	12.81	2.81	118	3.8	19.1	12.5	10.4
		J11	3849	19.9	0.85	16.94	3.08	36	4.2	15.8	11.2	8.7

Table 3 Mean, minimum and maximum of the studied properties.

	Mean	Minimum	Maximum
Sonic Velocity	3544.24	1900.00	4684.00
Total Porosity	21.38	11.70	36.10
Water Saturation	0.69	0.47	0.96
Modified Saturation	14.26	7.62	27.36
Cementation Exponent	2.94	2.07	4.65
Permeability	106.71	8.39	494.61
Sonic Porosity	5.35	2.54	13.48
Secondary Porosity	16.03	8.42	28.89
Vuggy Porosity	11.23	1.25	22.50
Matrix Porosity	10.15	5.10	13.70

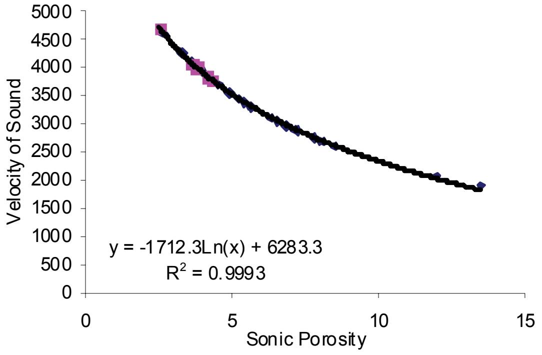

Figure 1 Deriving sonic porosity from velocity of sound.

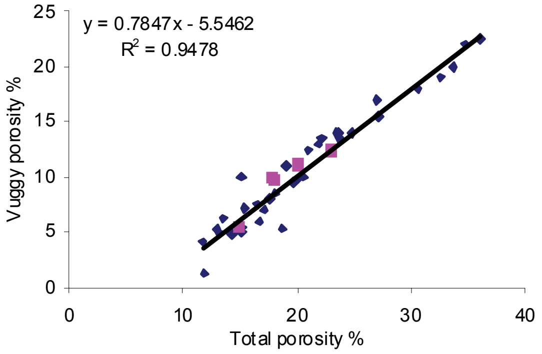

Figure 2 Deriving vuggy porosity from total porosity.

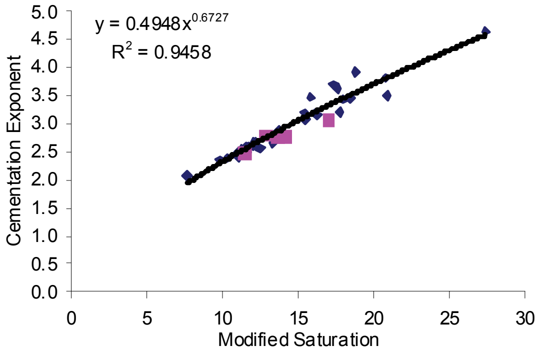

Figure 3 Deriving cementation exponent from modified saturation.

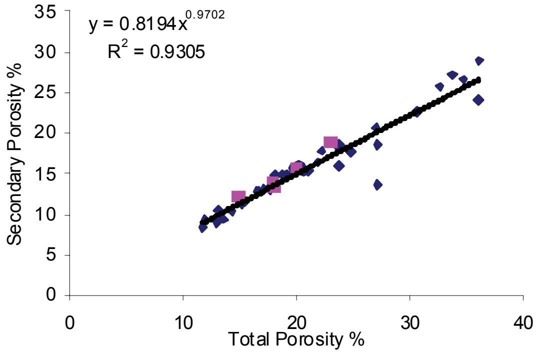

Figure 4 Deriving secondary porosity from total porosity.

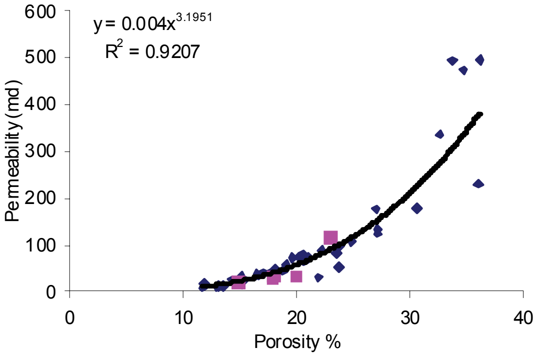

Figure 5 Deriving permeability from porosity.

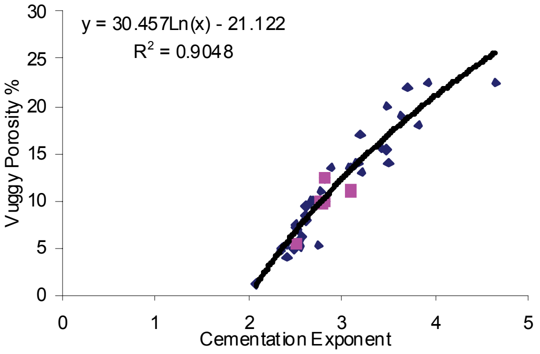

Figure 6 Deriving vuggy porosity from cementation exponent.

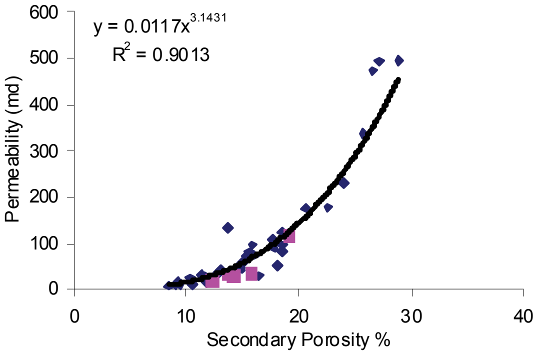

Figure 7 Deriving permeability from secondary porosity.

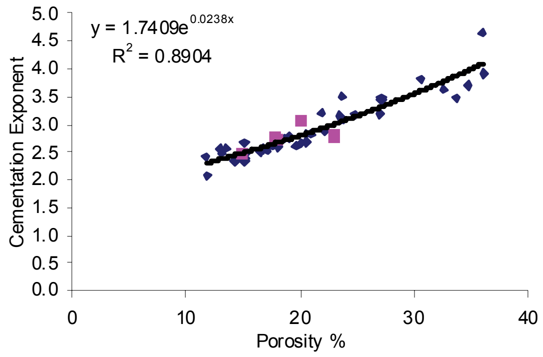

Figure 8 Deriving cementation exponent from total porosity.

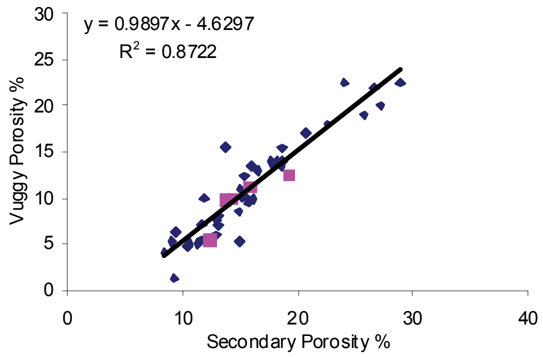

Figure 9 Deriving vuggy porosity from secondary porosity.

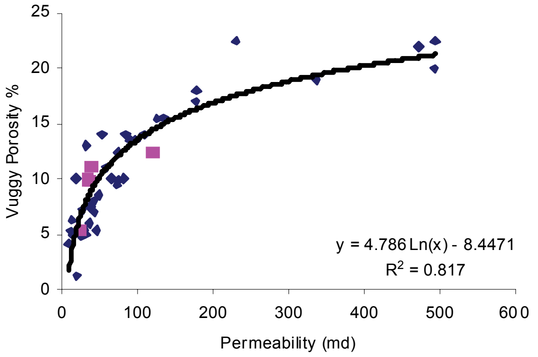

Figure 10 Deriving vuggy porosity from permeability.

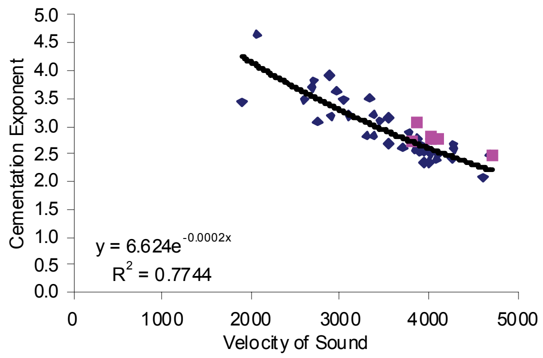

Figure 11 Deriving cementation exponents from velocity of sound.

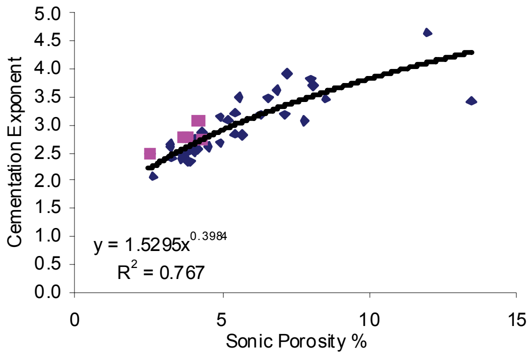

Figure 12 Deriving cementation exponents from sonic porosity.

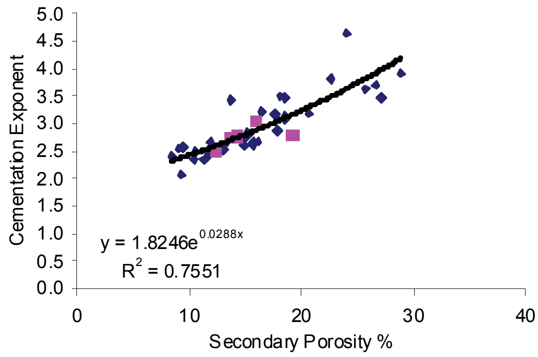

Figure 13 Deriving cementation exponents from secondary porosity.

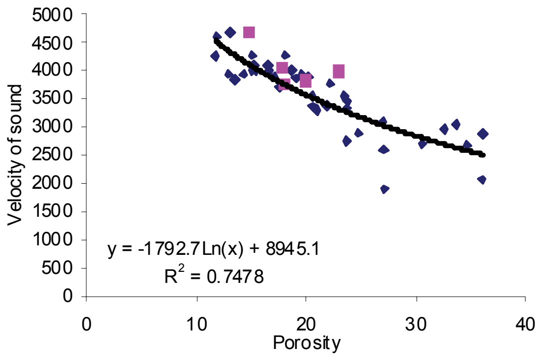

Figure 14 Deriving velocity of sound from total porosity.

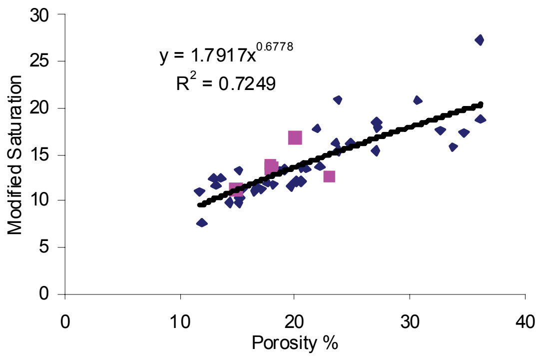

Figure 15 Deriving modified saturation from total porosity.

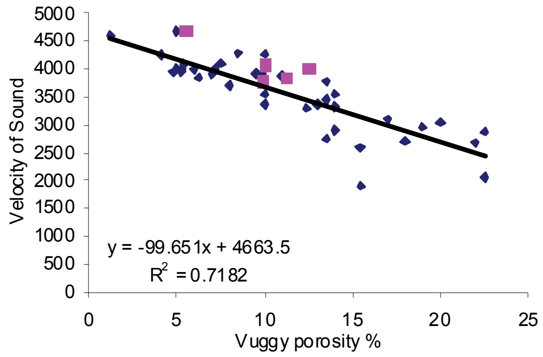

Figure 16 Deriving vuggy porosity from velocity of sound.

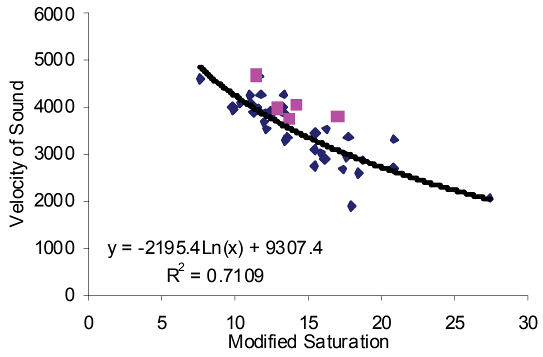

Figure 17 Deriving velocity of sound from modified saturation.

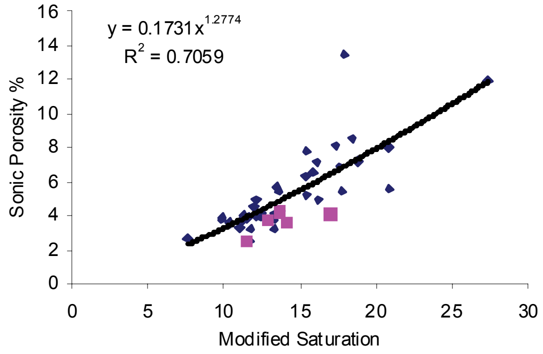

Figure 18 Deriving sonic velocity from modified saturation.

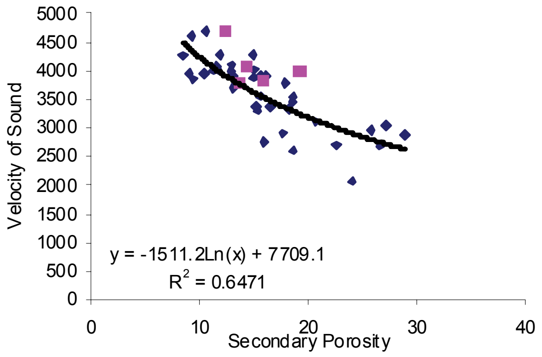

Figure 19 Deriving velocity of sound from secondary porosity.

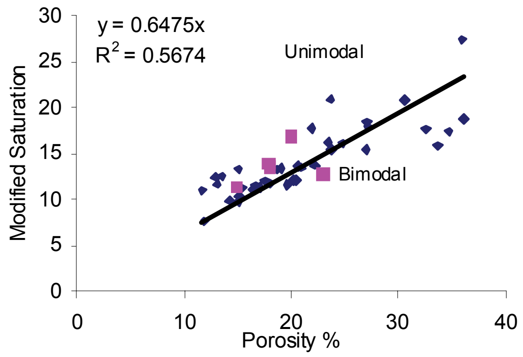

Figure 20 Inferring uni-modality and bi-modality of pores from porosity and modified saturation.

4. Practical Implications

In the case of clean vuggy oolitic limestone, and when it is difficult to have access to sophisticated equipment, the easiest parameter to measure is bulk density, which can be inverted to total porosity (Moh'd, 2002). This method is used to derive secondary porosity (Figure 4), vuggy porosity (Figure 2), permeability (Figure 5), cementation exponent m (Figure 8), and velocity of sound (Figure 14).

Table 4 Correlation matrix between the different measured and derived properties.

	Sound Velocity	Total Porosity	Water Saturation	Modified Saturation	Cement. Exponent	Permeability	Sonic Porosity	Secondary Porosity	Vuggy Porosity	Matrix Porosity
Sound Velocity	1.00									
Total Porosity	-0.86	1.00								
Water Saturation	0.36	-0.57	1.00							
Modified saturation	-0.83	0.83	-0.07	1.00						
Cementation Exponent	-0.87	0.94	-0.27	0.97	1.00					
Permeability	-0.61	0.87	-0.63	0.54	0.72	1.00				
Sonic Porosity	-0.97	0.79	-0.28	0.81	0.83	0.54	1.00			
Secondary Porosity	-0.69	0.96	-0.62	0.73	0.86	0.90	0.58	1.00		
Vuggy Porosity	-0.85	0.97	-0.47	0.85	0.94	0.82	0.77	0.93	1.00	
Matrix Porosity	-0.62	0.76	-0.65	0.51	0.64	0.72	0.59	0.73	0.59	1.00

Modified saturation is estimated from either porosity (Figure 15) or velocity of sound (Figure 17). From the sonic velocity, the sonic porosity is estimated (Figure 1). Subtracting sonic porosity from total porosity gives secondary porosity. Cementation exponent and other porosity types are estimated from sound velocity. The important relations between other parameters were shown in the Figures, which are arranged in descending order according to the value of correlation coefficient (r).

5. Discussions

In Table 3, there are wide ranges in the different properties of the examined oolitic limestones. Vuggy porosity ranges from almost 1% to 25% compared with a total porosity ranging from 11.7% to 36.1%. Sonic velocity is also widely variable ranging from 1900 m/s to 4684 m/s. The almost perfect negative correlation between velocity of sound and sonic porosity (Figure 1) is the outcome of the derivation of the latter from the former. Most of the relationships between the different variables except those involving permeability are linear or semilinear. Cross-plots involving permeability show high curve-linearity (Figures 5, 7, 10). These figures reveal that permeability is a function of porosity (total porosity, secondary porosity and the vuggy porosity). Permeability is defined as the easiness with which fluids move through materials and it is mainly controlled by pore and throat size distribution, and tortuousity of the pore space. Permeability should be correlated with effective porosity (connected pores and fractures) than total porosity as the latter may have isolated or blocked pores.

Vuggy porosity is strongly correlated with total porosity (r = 0.97, Figure 2), cementation exponent (r= -0.95, Figure 6), and secondary porosity (r = 0.93, Figure 9). The higher the cementation exponent is, the higher the vuggy porosity becomes. Similarly, as vuggy porosity is the only secondary porosity type present, it increases as the secondary porosity increases. As far as the relationship with total porosity is concerned, it may be easier for solutions to enlarge the already existing pore space than to create a new one. These variables are derived using the following equations:

$$\text{Vuggy Porosity} = 0.7847 * \text{Total Porosity} + 5.5462$$

$$\text{Vuggy Porosity} = 30.457 \ln \text{Cementation Exponent} - 21.122$$

$$\text{Vuggy Porosity} = 0.9897 * \text{Secondary Porosity} - 4.6297$$

Cementation exponent is controlled by the total porosity (r = 0.94, Figure 8) and the modified saturation, which shows the volume of water that can fill the connected pore space (r = 0.97, Figure 3). The following equations reveal these relationships as follows:

$$\text{Cementation Exponent} = 1.7409\, e^{0.0238 * \text{Total Porosity}}$$

$$\text{Cementation Exponent} = 0.4948 * \text{Modified Saturation}^{0.6727}$$

The permeability of some vuggy and fractured Jordanian limestones was measured (Moh'd, 1996) and found to correlate well with those derived using Jorgensen's equation (Moh'd, 2007). This indicates that this equation, used in this study to estimate permeability, yields reasonable results. By utilizing the relationships between total porosity and cementation exponent, some researchers (e.g. Focke and Munn, 1987) classified vuggy carbonates into different permeability groups (<0.1, 0.1-1, 1-100, >100 millidarcies) based on studying hundreds of vuggy carbonate samples from the oil reservoirs of the Persian Gulf. The permeability of the examined oolitic limestones lies in groups three and four (1-100, >100 millidarcies) of Focke and Munn Classification. The advantage of Jorgensen method over that of Focke and Munn's method is that the former gives exact permeability figures, whereas the latter gives the permeability group.

Taken into account that oolitic limestones are encountered in the surface and subsurface of Jordan in the Cambrian, Jurassic, Cretaceous and Pleistocene (Moh'd and Muneizel, 1998; Powell, 1988; Moh'd, 1993; Moh'd, 2001), the finding of the current study is of interest and application to Jordanian geologists. It is hoped that this study will contribute to a better understanding of the petrophysics of oolitic facies and their subsequent exploitation as hydrocarbon reservoirs, building and industrial materials, as well as water aquifers. However, the findings of the current study are not applicable to oolitic facies if they lack any evidence of dissolution during their post-depositional history such as vugs or larger scale features. Field investigations, petrography or petrophysics can be employed to gather such evidence. When the cementation exponent (*m*) value is much higher than two, it indicates the existence of secondary porosity in the form of moldic or vuggy porosity. Lucia (1983) considered that the higher the value of *m* above two, the higher the ratio of separate vug porosity to total porosity. An approximation of the uni- or bi-modality of pore-size distribution can be easily determined from plotting modified saturation against total porosity (see Figure 20). Modified Saturation used in the present study is the same as bulk water volume used in petroleum engineering literature (Asquith, 1985). It is worth mentioning that the relationships established in the present work are applicable to vuggy or moldic oolitic limestones (with very little dolomite, quartz or clay) only and are not generalized to other carbonate lithologies without conducting further experimental work. In addition, the database (representing 54 ooidal limestone types and subtypes; each UK sample is the average of two samples) is small and larger data bases are needed to check the validity of conclusions in a larger context. Due to the lack of laboratory facilities to measure cementation exponent *m* and permeability, the study relied on published literature to estimate these parameters. Although it is desirable to make a comparison between measured and estimated values of these two properties, it is believed that such differences are small. The present study is designed to address the problem of estimating petrophysical properties of vuggy oolitic limestones when access to sophisticated laboratory equipment is not possible, as the case in Jordan and other developing countries. This study is significant because it identifies the parameters that correlate strongly with other difficult to measure parameters.

6. Conclusions

Despite the limited size of the present database, the study shows that some easily measured parameters can be used in deriving other parameters with strong correlation coefficients, mostly over 0.9. Thus, bulk density can be inverted to porosity, which is in turn can be used to derive many parameters such as permeability and *Vp*. The latter parameter is used in deriving cementation exponent (*m*) and other porosity types. The results are summarized in Table 3. However, it is suggested to utilize a larger database to check the validity of relationships deduced by the present study and to restrict its use to clean vuggy oolitic limestone. It is also suggested to carry out further research to quantify the differences between estimated values of different parameters to laboratory-measured values of these same parameters.

References

[1] Aguilera, M. S. and Aguilera, R. F. 2003. Improved models for petrophysical analysis of dual porosity reservoirs. *Petrophysics* 44 (1): 21-35.

[2] Ashurst, J. and Dimes, F. G. (eds) 1990. Conservation of building and decorative stone, London: Butterworth/Heinemann, Volume 2.

[3] Asquith, G. B. 1985. Handbook of log evaluation techniques for carbonate reservoirs: AAPG, Methods in Exploration No.5, 47 p.

[4] Brown, E. T. (ed.) 1981. Rock characterizations, testing and monitoring, Pergamon, Oxford.

[5] Chillingarian G. V., Torabzadeh J., Rieke H. H., Metgalchi, M. and Mazzullo, S. J. 1992. Interrelationships among surface area, permeability, porosity, pore size and residual water saturation, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 1, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 30, p. 379-397.

[6] Choquette, P. W. and Pray, L. C. 1970. Geologic nomenclature and classification of porosity in sedimentary carbonates. *AAPG Bulletin* 54: 207-250.

[7] Feazel, C. T. and Schatzinger, R. A. 1985. Prevention of carbonate cementation in petroleum reservoirs, in N. Schneidermann and P. M. Harris, eds, Carbonate Cements: SEPM Special Publ. 36, p.97-106.

[8] Flugel, E. 1982. Microfacies analysis of limestones, Springer-Verlag, Berlin, 633 p.

[9] Focke, J. and Munn, D. 1987. Cementation exponents in Middle Eastern Carbonate reservoirs, SPE Formation Evaluation, June p. 155-167.

[10] Fox, E. F. and Ahlbrandt, T. S. 2002. Petroleum geology and total petroleum systems of the Widyan Basin and Interior Platform of Saudi Arabia and Iraq, USGS Bulletin 2202-E

[11] Hendrickson A. R., Thomas R. L. and Economides M. J. 1992. Simulation of carbonate reservoirs, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 1, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 30, p. 589-625.

[12] Honarpour, M. M., Chillingarian G. V. and Mazzullo S. J. 1992. Permeability and relative permeability of carbonate reservoirs, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 1, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 30, p. 399-416.

[13] Honeyborne, D. B. 1982. The building limestone of France, BRE, Garston, UK.

[14] Howell, J. V., *ed*., 1962. Glossary of Geology and Related Sciences: 2nd ed., Washington, D. C., The American Geological Inst., 325 p.

[15] Jordy, R. L. 1992. Pore geometry of carbonate rocks and capillary pressure curves (basic geologic concepts), in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 1, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 30, p. 331-377

[16] Jorgensen, D.G.1988. Estimating permeability in water-saturated formations, *The Log Analyst*, 29 (6): 401-409.

[17] Leary. A. 1983. The building limestones of the British Isles. BRE Report Z41/42.HMSO, London.

[18] Lucia, F.J. 1983. Petrophysical parameters estimated from visual descriptions of carbonate rocks, *Journal of Petroleum Technology* 35 (3): 629-637.

[19] Mazzullo, S. J. 2004. Overview of porosity in carbonate reservoirs, Kansas Geological Society Bulletin, 79: 412-422.

[20] Mazzullo, S. J. and Chillingarian, G. V. 1992. Diagenesis and origin of porosity, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 1, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 30, p. 199-270.

[21] Mazzullo, S. J. and Chillingarian, G. V. 1996. Hydrocarbon reservoirs in karsted reservoir rocks, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 2, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 44, p. 797-865.

[22] Moh'd, B. K. 1993. The geology of 1: 50 000 Ar Rabba map sheet, Natural Resources Authority, Amman, Jordan.

[23] Moh'd, B. K. 1996. Evaluation of limestone as building stone. PhD dissertation, University of London, (Unpublished).

[24] Moh'd, B. K. 2001. The geology of 1: 50 000 Irbid and north Shuna sheets, Natural Resources Authority, Amman, Jordan.

[25] Moh'd, B. K. 2002. Estimation of some pore-related properties in limestone from bulk density and water absorption, *Electronic Journal of Geotechnical Engineering*, 7 pages.

[26] Moh'd, B. K. 2007. Characterization of the secondary porosity of some Cretaceous-Recent Jordanian building limestones, *Journal of Applied Sciences*, 7(3): 368-373

[27] Moh'd, B. K. and Muneizel, S. 1998. The geology of 1: 50 000 As Salt map sheet, Natural Resources Authority, Amman, Jordan.

[28] Newell, K. D., Watney, W. L., Ching, S. W., and Brownrigg, R. L. 1987. Stratigraphic and spatial distribution of oil and gas production in Kansas, Kansas Geological Survey, subsurface Geology Series 9, 86 p.

[29] Nugent, W. 1983. Letters to the editor, *The Log Analyst*, 24 (4): 2-3.

[30] Powell, J. H. 1988. The geology of 1: 50 000 Karak map sheet, Natural Resources Authority, Amman, Jordan.

[31] Rasmus, J. 1983. A variable cementation exponent, M, for fractured carbonates, *The Log Analyst*, 24 (6): 13-23.

[32] Ross, K. D., and Butlin, R. N., 1989. Durability tests for building stone, Building Research Establishment, Garston.

[33] Spry, A. H. 1982. Principles of cleaning masonry buildings, Melbourne: Australian Council of National Trusts, and National Trust of Australia (Victoria), p.25.

[34] The Building Research Station 1983. Cleaning external surfaces of buildings, Digest 280, Garston: HMSO, p.6.

[35] Wardlaw, C. N. 1996. Factors affecting oil recovery from carbonate reservoirs and prediction of recovery, in G. V. Chillingarian, S. J.Mazzullo and H. H. Rieke, eds, Carbonate reservoir characterization: a geologic engineering analysis, Part 2, Elsevier Publ. Co., Amsterdam, Developments of Petroleum Science 44, p. 867-903.

[36] Yousef, S. and Norman, G. 1997. Jurassic geology of Kuwait: GeoArabia, v.2, p. 91-110.

JJEES
Volume 1, Number 1, Mar. 2008
ISSN 1995-6681
Pages 33 -44
Jordan Journal of Earth and Environmental Sciences

Developing Reference Crop Evapotranspiration Time Series Simulation Model Using Class a Pan: A Case Study for the Jordan Valley /Jordan

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Abstract

The greatest environmental challenge that Jordan faces today is the scarcity of water resources. Evapotranspiration (ET) affects water resources and it is considered an important process in aridic hydrologic systems. The estimated long-term average of ET in Jordan is over 90% of the total precipitation; nevertheless, there have been no attempts to model reference crop evapotranspiration using a time series approach in Jordan. In this study, a seasonal time series Autoregressive and Moving Average (ARIMA) mathematical model is described. It is used for forecasting monthly reference crop evapotranspiration (ET_o) without using weather data based on past historical records (1973-2002) of measured pan evaporation at Central Jordan Valley: an arid to semi-arid region. The developed ARIMA (1, 0, 0) (0, 1, 1)$_{12}$ model provides reasonable and acceptable forecasts, comparing its performance with a computed reference evapotranspiration from measured pan evaporation parameter. The forecasting performance capability of three tentative ARIMA models was assessed using Root Mean Squared Forecasting Error, Mean Absolute Forecasting Percentage Error, and Maximum Absolute Forecasting Percentage Error. The developed model allows local farmers and water resource managers to predict up to 60 months with a percentage error less than 11% of the mean absolute forecasting. The potential to make such predictions is crucial in optimizing the needed resources for effective management of water resources. Furthermore, the developed model offers a simple, accurate, and an easy short and long-term forecasting in the valley. This would develop a robust strategy for irrigation water management including successful planning, designing, managing, and operating of water resources systems. It also would increase the positive intended outcomes projects conducted by many governmental and nongovernmental organizations. In addition, it would heighten the efficiency of local and national water resources policies.

Keywords: Seasonal reference evapotranspiration modeling; ARIMA model; pan evaporation; Jordan;

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1. Introduction

The Hashemite Kingdom of Jordan (HKJ) is located about 100 km from the south-eastern coast of the Mediterranean between latitudes 29º 11’ - 33º 22’ N and longitudes 34º 59’- 39º 12’ E. The neighboring countries to Jordan are Iraq, Palestine, Syria, and Saudi Arabia (Figure 1). The total land area of HKJ is approximately 89 342 km^2, of which, about 40% is irrigated land. The population of HKJ was estimated to reach 5, 329, and 000 in 2004, of which 30% reside in rural areas (DOS, 2006). The statistics indicates that the population of HKJ is increasing rapidly, with an estimated annual growth rate of 2.6% (DOS, 2006).

ETo : reference crop Evapotranspiration

Figure 1. Map of Jordan shows Deir-Alla Weather Station

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The irrigation water for agriculture sector represents about 68% of the total water demands in HKJ. Due to natural and non-voluntary migration, demands on the domestic water supply increased and accordingly, the per capita share of freshwater decreased. Although the population growth rates are declining (DOS, 2006), the increasing population continue to place enormous pressure on decision makers to find new water supplies and develop an updated water conservation policy. The main water supplies in HKJ are groundwater and surface water. However, HKJ shares most of its surface water resources with neighboring countries, which makes it one of the world's hot spot in regards to water disputes. The groundwater resources represent about 65% of total available water in HKJ. Because of the shortages of the surface water resources, groundwater has been extensively used in the last twenty years; it is overdrafted and becomes susceptible to salt water intrusion. This immense water consumption leads to a decline in water accessibility over the last few decades and is considered one of the most important environmental problems facing decision-makers in HKJ. The extraction of groundwater and contaminants problems comprises a major deterrent to sustain a progressive economy in the region. It may lead to severe limitations in the agricultural and industrial progress in Jordan

Jordan Valley has long been used for agriculture and is one of the main irrigated agricultural areas in the HKJ. The irrigated area is more than 34,000 ha, and the agricultural sector consumes about 68% of Jordan's water resources. This percentage embodies the largest use of water in Jordan. In agriculture, water requirements are linked to irrigation use (Allen et al., 1998). Due to Jordan’s scarcity of water, the efficient utilization of water resources including the use of irrigation water is a major national concern. There are three types of irrigation methods in HKJ. These methods are surface irrigation, sprinkler irrigation, and drip irrigation. Irrigation efficiency is a significant dimension of the water preservation issue that needs to be investigated to reach a better water resources management in HKJ. For example, irrigation efficiencies of the drip irrigation system in the Central Jordan Valley varied from 34% to more than 90% (DAI report, 1995). Furthermore, irrigation water is wasted through runoff, and evaporation; the latter lose about 67% of applied irrigation in the Jordan Valley. In spite of the significance of evaporation as a component in the irrigation efficiency, it was not given a well-deserved attention. Most often, applied irrigation in agricultural is based on farmer experiences. Evaporation can either measured or estimated. Pan A Class can be used for measuring daily evaporation. Evaporation can be predicted by using simulation models. These models ranges from simple to more sophisticated such as ARIAM. The evaporation component should be included in the development of any irrigation water management plan in Jordan Valley. Potential evapotranspiration (ET_p) is defined as the rate at which evapotraspration would occur from a large area completely and uniformly covered with growing vegetation which has access to an unlimited supply of soil water and without advection or heat storage effects (Dingman, 2002).

Modeling and predicting the evapotranspiration rate is required for reliable and effective planning, design, managing, and operation of water-resource projects; managing water quality, determining safe yields from aquifers, planning for flood control and forest fire prevention, proper irrigation scheduling, economics of building water-supply reservoirs, determining the water budget at field scale, assessing soil moisture, predicting climate change and ecosystem responses to climate change, estimation of water available to human use and its management as well as playing an important role in other environmental issues and concerns (Jensen, et al., 1990; Singh and Jaiswal, 2006; Fardous et al., 2001; Mazahrih et al., 2001).

Irrigation scheduling for crops in Jordan Valley is quite empirical and could lead to a great loss of irrigation water and low irrigation efficiencies. Evapotranspiration is the most important variable subsequently to rainfall in the context of irrigation to crops and it is a multivariate phenomenon as it is affected by many hydrological variables (Mohan and Arumugam, 1996). Evapotranspiration includes evaporation from open-water, bare wet soil near the plants, transpiration from within the leaves of plants, the use of water by the vegetation to build new plant tissue, evaporation from the moist membrane surfaces of the vegetation as well as sublimation from ice and snow surfaces (Blaney and Hanson, 1965).

The objective of this study is to develop a time series model to simulate the Reference Crop Evapotranpiriation for the Jordan Valley. Specifically, the objectives are to use historical information of ET_o to calibrate the developed model, and generate a simulation projections for ET_o for the next five years. If the calibrated model will, approximately duplicates measured ET_o, then, the local farmer communities and other water authorities will use it to predict evapotranspiration, which will improve water resources management in the Jordan Valley. This can be done by means of the Box-Jenkins parametric modeling to identify seasonality effects and conduct trend analysis and forecasting as well as to develop a seasonal forecast for future events in the time series. Furthermore, using autoregressive integrated moving average (ARIMA) model (Box and Jenkins, 1976), this study meant to develop the ARIMA model for forecasting the monthly values of ET_o and to analyze the predictability and the performance of these models.

In Jordan, there have been no attempts to model reference crop ET data using a time series technique. This is the first study of its kind conducted in Jordan, thus the scarcity of available data was a challenge. The focal point of this paper is restricted to improving the long-term predictions using past E_{pan} data that was converted to ET_o. With this objective, the Jordan Valley was selected for the study as it contributes the largest proportion of irrigated area; irrigated area being 32.4% of the total cultivated area in Jordan (DOS, 2006).

1.1. Climate and Topographic Features of the Study Area

Jordan is located at the eastern margins of the Mediterranean climatic zone with highly variable and irregular rainfall. This climate is characterized by hot, dry summers and cool, wet winters. The estimated long-term average of ETmight reaches 93% of the total precipitation (Taha, 2006; MWI, 2004). During 2004, it was estimated that 7334 MCM were returned to the atmosphere by evaporation and transpiration from the surface of Jordan (MWI, 2004). However, the estimated long term average potential ET in the Jordan Valley ranges between 1289 mm/yearn in the north at Baqoura and increases in the south at Ghor Al-Safi to reach 1545 mm/y (DOS, 2006)(Figure 1).

Jordan valley lies between 200-400 m below sea level, extending from Lake Tiberia in the North to the Dead Sea, with a length of 104 km and a width of between 4-to16 km; it is surrounded in the east and west by high mountains. The Jordan Valley consists of the Northern Ghor (11 586 ha), Middle Ghor (7875 ha) and the Southern Jordan Valley (11 500 ha). Jordan Valley produces 80% of the national agricultural production and is considered the most important agricultural area, as there is a permanent source of water from the Yarmuk River and side dams for the Jordan River.

In the Jordan Valley, rainfall decreases from approximately 300 mm in the north to 102 mm in the south. The climate of the valley is characterized by very dry, hot summers with average temperature of 31.5 ^{o}C and cool, wet winters with average temperature of 14 ^{o}C. The relative humidity ranges between 64% in the winter to 27% during the summer. Due to its position below sea level and high temperatures (microclimate), Jordan Valley is considered the most important winter vegetable producing area (85%), with citrus and banana production (10%), because of its tropical climate and the limitation of irrigation water. Forage crops (5%) are grown on a very limited scale (Abu-Zanat, 1995). These crops and vegetables are exported abroad to Europe and other countries. Therefore, the valley is considered a food basket for all riparian countries due to its unique climate and agricultural environment. Most cultivable lands in Jordan Valley are irrigated where 73% of the total irrigation sector exists. The majority of holdings are between (3-4 ha). Farmers use modern agricultural techniques in irrigation, production, and marketing.

2. Methodology and Assumptions

It is essential for a successful water resources management in HKJ to evaluate crop water requirements on monthly bases because it is included in any long-term water management operation of water supply and storage systems. The crop water requirement is related to crop evapotranspiration, ET_c, of the crop being grown. Therefore, it is realistic to provide one forecast of a reference crop evapotranspiration rate, ET_o, for a region. Subsequently the ET rate for each crop growing in the region can be forecasted. A time series is a set of measurements of a variable taken over time at equally spaced time intervals. Additional valuable information could be offered during time series analysis. Analysis of time series involves analysis of the statistical manners of a series of data over time, giving that the record is complete, and continuous along with assumption of negligible variability of physical conditions over the period of analysis. If changes of these conditions occur over a long time, one should consider it prior to the analysis.

Reference crop evapotranspiration is the rate of evapotranspiration from an extended surface of 8 to 15 cm tall, with green cover of uniform height, actively growing, completely shading the ground under, and no deficiency of water. Although the estimation of ET_o can be done easily, but the objective of the study is to forecast the ET_o, i.e., to predict future values to be able to improve planning and managing of the water resources and to test the predictability of the developed model. To forecast the ET_o rate, one can use either relationships that rely on forecasts of physical weather parameters or one can consider a mathematical method that seeks to predict future ET_o rates based on the past history of the ET_o rates in a certain region. In this manuscript, we will focus on the latter case.

Pruitt developed different methods and Doorenbos (1977) for estimating ET_o in a region using relationships relating physical parameters incorporated in the ET process. Of these relations are the Blany-Criddle equations; the Penman equation, the Radiation equation; or the Pan Evaporation method. Pans provide a measurement of the integrated effect of radiation, wind, temperature, and humidity on the evaporation from an open water surface. They concluded that mistaken forecasts of the mean wind speed are the main source of difference between the predicted and measured reference crop ET. Moreover, the physically based relationships for forecasting evapotranspiration have some limitations. However, in 1990, the International Commission adopted the Penman-Monteith combination method as a standard for Reference crop Evapotranspiration for Irrigation, Drainage, and World Meteorological Organization. A direct measurement of Evapotranspiration is costly and is not easy; therefore, using historical information of ET_o, time series can be an alternative method for forecasting $ET_{o.}$

Pan Evaporation (E_p) data was recorded at Deir-Alla Weather Station and obtained from Applied Meteorological (Division Jordan Department of Meteorology, 2006). The Station is located in the Central Jordan Valley, at latitude of 32^{o} 13' N, 35^{o} 37' East-longitude with an elevation of 224 meters below the sea level. ET_o was predicted using 30 years of past records of weather values of pan evaporation from the Station. The values of ET_o for this period were produced by pan evaporation method (E_p). In spite of the difference between pan evaporation and the evapotranspiration of cropped surfaces, the use of pan evaporation may be warranted to predict ETo for periods of 10 days or longer (Allen et al., 1998; Abdo, F., 2007. Personal communication. Senior Agronomist, Jordan Department of Meteorology, Amman, Jordan). Using pan evaporation to predict ET_o for periods of 10 days is an international convention that has been reliably put into practice due to the fact that a 10 days is a reasonable time to put any agricultural activity or problem that might occur into operation to be benefited or corrected by the farmers easily and satisfactorily.

Past ET_o data is used to get the long-term ET_o estimates by modeling the time series using suitable ARIMA techniques known as Box–Jenkins model which is very popular type of time series models used in hydrological forecasting. The longest available data set was used to avoid misleading results when using ARIMA procedure (Box and Jenkins, 1976). The data set was divided into two sections: the first section, composed of twenty-five years (1973-1997) (300 months) of data that was used for calibration to identify and develop a univariant seasonal ARIMA model, the second, composed of five years (1998-2002) (60 months) was used to validate and test the model performance and its predictability. Various time series models were developed and tested using monthly averaged ET_o for the study area for the period1973 to 2002.

The pan has proved its practical value and has been used successfully to estimate reference evapotranspiration by observing the evaporation loss from a water surface and applying the pan coefficient to relate pan evaporation to ET_o (Allen et al., 1998). Mazahrih et. al (2001) shows a good relationship (R^2=0.72) between evaporation from class-A pan and the measured crop evapotranspiration of pepper inside a plastic house. In this manuscript, the variable K_p method to derive the 30-year reference evapotranspiration from E_p data was used. The pan coefficient (K_p) was calculated from class-A pan located at Deir-Alla using tabulated values (table 5 in FAO Irrigation and Drainage Paper 56) or table 7 (regression equation) of the method described by Allen et al. (1998) in chapter 4. Then the ET_o was calculated using the following relation (Allen et al., 1998)

$$ET_o = K_p E_p \qquad (1)$$

Where ET_o is reference crop evapotranspiration (grass) [mm/day], K_p is pan coefficient [-], and E_p is pan evaporation [mm/day].

2.1. Models and ARIMA Development

The most common approaches to forecasting evapotranspiration is extrapolation or the prediction method which is based on an inferred study of past data behavior over time. In time series analysis, the observations taken at a constant interval of time are considered random variables. Any particular observed series is supported to be the only realization of all possible series that could be generated under the same set of conditions. ARIMA models in time series analysis can satisfactorily explain such processes according to Box and Jenkins (1976). The Box–Jenkins model authorizes us not only to expose the hidden patterns in the data but also to generate forecasts of the future based exclusively on historical values of the dependent variable. Moreover, the accuracy of forecast of time series models are good, convenient to use when seasonal or monthly patterns must be taken into account, supple enough to be modified when strategy changes occur, the least data-intensive compared to many other models, and easily developed by means of various standard software packages. In addition, seasonal ARIMA models allow for randomness in the seasonal pattern, unlike the classical method approach based on linear regression. However, they are inaccurate when considerable changes in determining variables occur in the future and can be susceptible to their starting values, when carrying the greatest weight in the forecast.

A general ARIMA model contains autoregressive (AR) and moving average (MA) parts. The AR part describes the relationship between present and past observations, whereas the MA part characterizes the autocorrelation structure of the error or disturbance series. In this paper, time series analyze; reference crop evapotranspiration (ET_o) or $\{Y_t\}$ for forecasting and modeling as a function of time. A time series is usually represented by $\{Y_t\}$ where the dependent series $\{Y_t\} = Y_1, Y_2, Y_3 \ldots Y_t$. When t=1 the observation is Y_1 and so on. Then the ARIMA model of Y_t can be represented by ARIMA (p,d,q), where p is the order of non-seasonal autoregressive operators; d is the order of the non-seasonal difference passing operators and typically have a value of 0 or 1, and seldom greater than that; q is the order of non-seasonal moving average operators applied in non-seasonal modeling process.

If we can express the variable Y at time t as the sum of residuals at previous times, then the moving average model can be written as:

$$Yt = C + \theta q\ (B)\ \varepsilon t \qquad (2)$$

Where C is a constant term; θ_q (B) = 1-θ_1(B) - θ_2(B^2)-…..- θ_q (B^q) is the moving average operator of order q; B is backward shift operator ($By_t = y_{t-1}$ and $B^s y_t = y_{t-s}$, y_t is the current value of the time series examined). q is the order of moving average operator which considered the number of lagged periods correlated to present value of the time series. The value of q can be determined from the characteristic of the series of Autocorrelation Function (ACF). The ACF values should be reduced gradually and disappeared after a time lag of q. If the variable Y at time t can be written as the sum of the weighted variables of previous time, then the auto regression model can be expressed as:

$$\phi p\ (B) Yt = C + \varepsilon t \qquad (3)$$

Where ϕ_p (B) = 1-ϕ_1(B) - ϕ_2(B^2)-…..- ϕ_p (B^p) is the autoregressive operator of order p (the number of lag periods where the error term is correlated to the time series). Gradually reducing ACF values and disappearing of the PACF after a time lag of p.

The combined models can be written as:

$$\phi p(B) Yt = C + \theta q(B) \varepsilon t \qquad (4)$$

For a seasonal time series to be modeled, the relationships at the seasonal lag must be incorporated. The lag in this study is 12 for the monthly data collected monthly. These relations can be represented by including of AR and MA parts at that lag. The same procedure is applied to determine the tentative values of P, D, and Q, where P is the order of seasonal autoregressive operators; D is the order seasonal difference passing operators and typically have a value of 0 or 1, and seldom greater than that; Q is the seasonal moving average operators applied in seasonal modeling process. In this case, the time series regarded as non-stationary. Differencing techniques (the integration component of ARIMA) are often used to transform a non-stationary time series into a stationary time series. Visual inspection of the plot of ET_o time series point out a periodic trend (Figure 2).

Now considering that y_1, y_2... y_t are the differenced values of ET_o of time series data, using the backshift operator "B" shifting the subscript of a time series observation backward in time by one period gives:

$$By_t = y_{t-1} \qquad (5)$$

Then the seasonal operator will be:

$$\nabla_s = 1 - B^s \qquad (6)$$

Where "s" is the periodicity or seasonality of the series (12 in this study), Using the general stationary transformation, the transformed time series explained as:

$$Z_t = \nabla^D_s y_t \qquad (7)$$

Where $\nabla^{(D)} y_t$ is the lag-12 difference operator

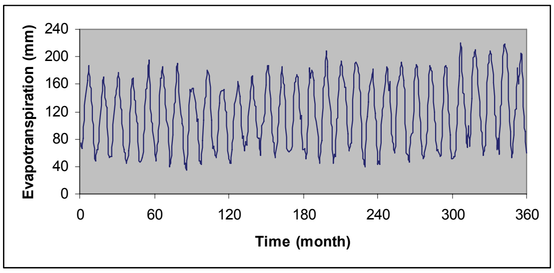

Figure 2. Time series of reference crop evapotranspiration of the studied area between 1973 and 2002

Therefore, the general full general multiplicative seasonal and non-seasonal ARIMA Box-Jenkins model using backshift operator is (Pankratz, 1983):

$$\begin{aligned}\varphi_P(B)\varphi_P(B^s)(1-B)^d(1-B^s)^D Z_t \\ = C + \theta_q(B)\theta_Q(B^s)\varepsilon_t\end{aligned} \qquad t = 1, 2, n \qquad (8)$$

This can be summarized as ARIMA (p, d, q) (P, D, Q) $_{12}$, where p, d, q, P, D, and Q as defined earlier. It is worth noting that the polynomials Φ (B^s) and Θ (B^s) capture the seasonal behavior of the series (P- and Q-order seasonal AR and MA operators, respectively) and C is constant with no specific meaning. Besides, the stationary and invertibility (stationary condition for the MA part of the ARIMA model) conditions demand that all the roots of the characteristics equation Φ (B^s) =0, φ (B) = 0, Θ (B^s) =0, θ (B) =0, lie outside the unit circle in the complex plane (Box and Jenkins, 1976).

The following operators can be used to describe Box-Jenkins models as non-seasonal and seasonal autoregressive operator of order *P* and moving average operator of order *Q* respectively.

$$\phi_P(B) = (1 - \phi_1 B - \phi_2 B^s - \ldots - \phi_p B^p) \qquad (9)$$

$$\phi_P(B^s) = (1 - \phi_{1,s} B^s - \phi_{2,s} B^{2s} - \ldots - \phi_{P,s} B^{Ps}) \qquad (10)$$

$$\theta_q(B) = (1 - \theta_1 B - \theta_2 B^2 - \ldots - \theta_q B^q) \qquad (11)$$

$$\theta_Q(B^s) = (1 - \theta_{1,s} B^s - \theta_{2,s} B^{2s} - \ldots - \theta_{Q,s} B^{Qs}) \qquad (12)$$

Where Φ and θ are unknown parameters, which represent the autoregressive and moving average coefficients at different lags of t time. In this study, ET_o is considered a seasonal time series. The seasonal time series have relationships at a definite lag s (12 for the data collected monthly).

To develop a suitable model for forecasting ET_o, an iterative procedure involving a four-step modeling procedure is conducted. These steps are identification of a tentative model, estimation of model parameters by Maximum Likelihood (ML) Technique, diagnostic checking, and testing the adequacy of this model and providing necessary modification of the model if the tentative model is poor. The final model is then used for forecasting purposes at the fourth stage. This iterative procedure necessitates visual assessment of intermediate statistical results, and the model is ultimately developed based on the expert judgment of the authors.

2.2. Preparing Data for Analysis and Model Identification

The Model identification step in the Box-Jenkins iterative modeling proves to be the most complicated and hard task, particularly if the time series is seasonal or periodic. Seasonal time series might be caused by the nature of the annual weather cycle as in the case of the ET_o time series data of this study (Figure 2). Since Box-Jenkins assumes a stationary time series, therefore stationary nature of the process that generated the time-series is one of the most considerable conditions that have to be imposed on the development of an ARIMA model in order to improve the forecasts.

The first part of this step consists of checking whether the variation in the time series is unstable with time. Transformation must be done on unstable series. If the data fluctuates with increasing variation, a pre-differencing treatment (e.g., logarithmic or square root transformations) is required to stabilize the variance of the time series. Moreover, a trend existing in time series data requires differencing. A time series may be considered stationary if the mean, variance, and its covariance of the time series are constant through time (Box and Jenkins, 1976). Box-Jenkins time series analysis was applied to the monthly ET data sets. The plot of autocorrelation function (ACF) for the overall data sets is presented in Figure 3. The continuous lines in the graphs represent the confidence limits. Values of the ACF within these limits are not significantly different from zero.

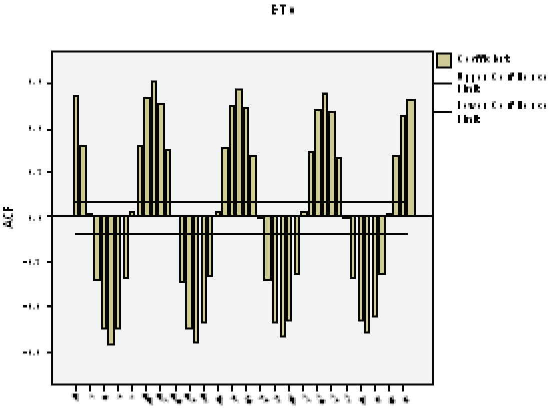

Figure 3. Autocorrelation function of the monthly averaged reference crop evapotranspiration between 1973-2002

By visual inspection of the sample ACF of the original ET_o time series plot, an evidence of periodicity or seasonality exists indicating strong seasonal serial dependencies and some correlation at lags up to 12. In order to remove the serial dependency and to model/forecast the $ET_o(Y)$, time series analysis begins by transforming Y to ensure it being stationary. Examining the characteristics and statistics of both ACF and PACF (PACF not shown to reduce the size of the manuscript) of the transformed series is the second part of step one. The purpose of this part is to determine if the series need additional differencing to remove the trend or seasonality to make the series stationary by eliminating seasonal and non-stationary behaviors of the ET time series. The ACF of a stationary time series shows a quick decay for moderate and large lags. A distinctive feature of the data that suggests the convenience of differencing the original time series is a slowly decaying positive ACF.

The plot above illustrates this behavior, which clearly indicates seasonal periodicity in the studied data. To eliminate this periodicity trend, the time series must be differenced until a rapidly decaying ACF (Brockwell and Davis, 1996). The ACF plot of the overall time series shows that the data are seasonal due to the peaks of the ACF at lags that are multiples of 12. The peaks presented in the plot show a correlation in the data every 12 lags. This means that the order of the seasonal differencing is one (D=1). Removing this seasonal component of period 12 from the series Y_t, the transformed series $Z_t = Y_t - Y_{t-12} = (1-B^{12})\, Y_t$ was generated where B is the backward shift operator as indicated earlier (Box and Jenkins, 1976). In this study, various types of differenced series for both non-seasonal and seasonal patterns are plotted and examined until most of serial dependencies have disappeared.

Differencing creates a new data series, $\{Z_t\}$, which becomes input for the Box-Jenkins analysis; the ARIMA (Figure 4 and 5). Then, the transformed time series is fitted with an ARIMA model where the current value of the time series, $\{Y_t\}$, is expressed as a linear combination of p earlier values and a weighted sum of q earlier deviations (original value minus fitted value of previous data) plus a stochastic random process or error, ε_t that are independently and identically distributed with a normal distribution $N(0, \sigma_a^2)$.

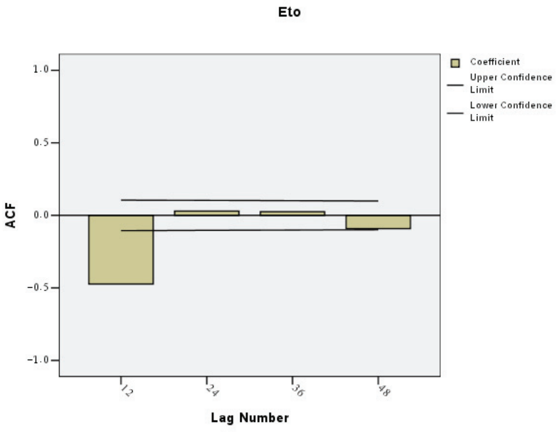

Figure 4. Sample autocorrelation function of transformed reference crop evapotranspiration time series (D=1).

A verification of seasonal removal, is conducting by re-plotting the ACF to see the elimination of the peak. After the elimination of seasonal and/or cyclical components, the resulting time series $\{Y_t\}$ could be non-stationary. Thus, the time series can be transformed into a stationary one, $\{Z_t\}$, differencing recursively D times until the ACF reduced significantly (Brockwell and Davis, 1996). The sample time series ACF, Figure 3 already shows decay for moderate lags, being no necessary more differencing is required. We now have a stationary and seasonal time series, $\{Z_t\}$, and the identification of the ARIMA (p, d, q)*(P, D, Q) $_{12}$ model orders should be undertaken.

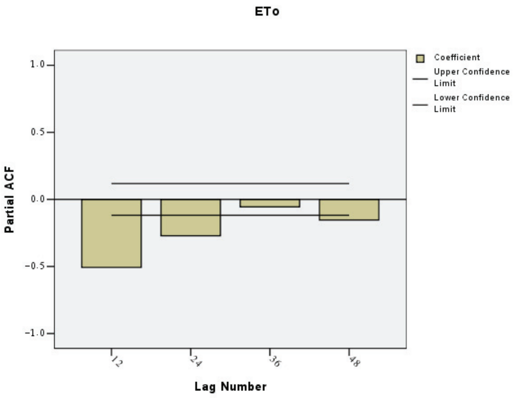

Figure 5. Sample partial autocorrelation function of transformed reference crop evapotranspiration time series (D=1)

3. Results

3.1. Parameter Estimation of the Model

Before we can specify the parameters to be estimated, the formulation of ARIMA model has to be identified based on the transformed ET_o time series data. Here we determine the values of the parameters (θ and ϕ) of the proposed model of both seasonal and non-seasonal time series after determining the type of a tentative ARIMA model, i.e. p, d, q; P, D, and Q using statistics interpretation and plot of ACF and PACF. The parameters are estimated using maximum likelihood approaches. These methods are frequently used and would yield efficient parameter estimates compared to other approaches. Furthermore, ML can tolerate missing data in the series in spite of no missing values in our ET_o data (Shumway and Stoffer, 2000). In this manuscript, the computations were done using SPSS computer software (SPSS, 2005).

In general, sample autocorrelation function and the sample partial autocorrelation function are used for the detection of various types of autocorrelation. This was done by using the behavior of both functions at the non-seasonal level to tentatively identify non-seasonal and seasonal models describing the time series values (Brockwell and Davis, 1996). Then, the parameters of the proposed tentatively identified models are estimated followed by estimating t values for diagnostic and adequacy checking of those models and, if required, to suggest an improved model. The judgment of model selection entails not only knowledge but also a good deal of experimentation with alternative models as well as the technical parameters of ARIMA (Bowerman and

O'Connell, 1993). In the parameter estimation step using the iterative ML method, the optimization criterion is based on the minimizing of residual sum of the squared between the observed data and the estimated one. Besides, the estimation was conducted using 0.001 as a minimal iteration value and 0.0001 as a minimal change between iterations for the sum of the squared residuals. Many models were identified for detailed assessment. Three candidate models were selected for diagnosis; ARIMA (2,0,0) (0,1,1), ARIMA (1,0,0) (2,1,1) and ARIMA (1,0,0) (01,1).

3.2. Diagnostic Checking of the Model

Two objectives should be fulfilled in this step. The first is to test hypothesis process by checking the significant of the parameters for each proposed model. Checking the normality of the residual distribution is the second task. In addition to the visual inspection of the residuals, various diagnostics (i.e., t-ratios, Q stat, Akaike Information Criteria"AIC," etc) are used to check the adequacy of the tentatively identified models and, if necessary, to propose an enhanced model.

Between competing models, the model that produces residuals with ACF that are not significantly different from zero at all lags and have smaller standard error will be selected. The model (1,0,0)(0,1,1) has the smallest error magnitudes, and the autocorrelation coefficients of the prediction errors were not statistically significant, i.e., all values of residual correlations were close to 0 and inside the confidence limit to 95%; there was no serial dependency between residuals.

Moreover, correlation analysis of the residual in the plot of the ACF and the goodness of fit using chi square test is conducted. If the model does not show a correlation in the residuals, then the residuals are white noise indicating the adequacy to represent the time series. ACF of Residuals of the three selected tentative models is shown in Figures 6, 7 and 8. The time series of errors associated with the initial model forecasts was analyzed using the ACF analysis tool. This procedure was repeated until the errors of the forecasting model were reduced to white noise with no significant correlations. Figures 6, 7, and 8 indicate that no significant sample autocorrelations of the residual series are found based on the values of ACF residuals. Based on Box-Pierce chi-square statistics, all the values can be considered negligible and residuals are not correlated. Therefore, the selected two candidate ARIMA models are adequate and the ET$_o$ time series is the white noise.

The results for detailed evaluation and verification of these three models are presented in Table 1. Based on Box and Jenkins (1976), a good model should require the smallest possible number of estimated parameters of an adequate representation of the patterns in the available data. The overall time a seasonal model that includes one non-seasonal autoregressive and one seasonal moving average terms of order1 describes series.

Table 1 also presents the results of parameter values of the tentative models, Box-Pierce and, Box-Pierce chi-square and standard errors. The Box-Pierce is based on the computation of ACF residuals. All ACF lie within the limits indicated by the upper and lower horizontal lines shown in Figure 6, 7 and 8 which reveal that the residuals are not correlated and all the ACF values can be neglected.

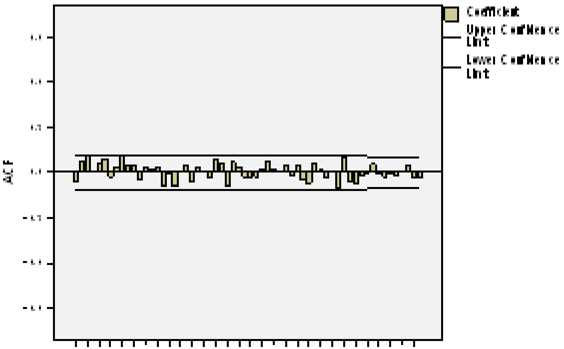

Figure 6. Autocorrelation function of residuals of ARIMA (1, 0, 0) (2, 1, 1)12

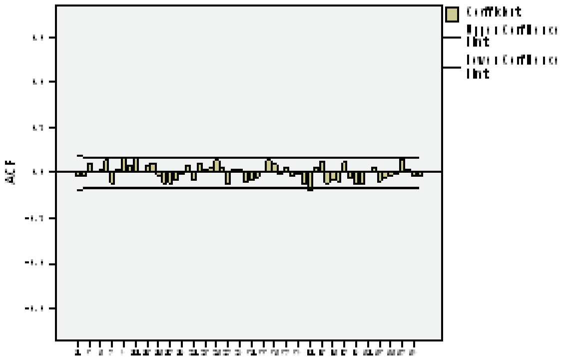

Figure 7. Autocorrelation function of residuals of ARIMA (2, 0, 0) (0, 1, 1)12

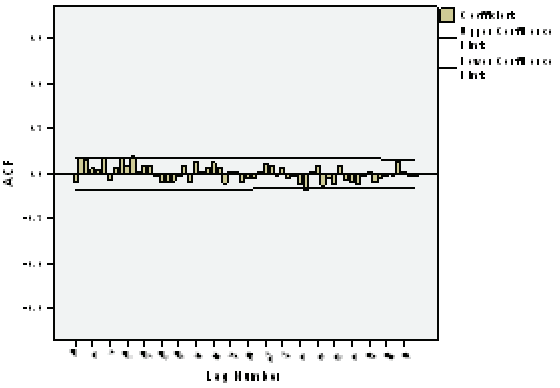

Figure 8. Autocorrelation function of residuals of ARIMA (1, 0, 0) (0, 1, 1)12

A high standard error corresponds to a higher uncertainty in parameter estimation, which queries the stability of the model. If the result of the ratio between the parameter values to the standard error is larger than two, then the model is adequate. The Akaike Criteria (AIC) and the residual variance are additional helpful parameters in selecting the best models.

Table 1. Results of Model Estimation and Verification

Tentative Models	ARIMA Model I (200)(011)12			ARIMA Model II (100)(211)12				ARIMA Model III (100)(011)12	
	Parameter			Parameter				Parameter	
Tests	AR(1)	AR(2)	SMA(1)	AR(1)	SAR(1)	SAR(2)	SMA(1)	AR(1)	SMA(1)
Parameter value	0.30	0.148	0.91	0.34	0.065	0.088	0.96	0.35	0.914
Standard error	0.052	0.052	0.041	0.05	0.067	0.064	0.081	0.05	0.041
t-ratio	5.708	2.833	22.366	6.761	0.983	1.371	11.877	7.027	22.363
Q-value	24.732			34.921				24.726	

Although the models 1, 2, and 3 have no major differences in terms of the parameters shown in table 1, model No 3 is preferable. Based on the lower values of Q, lower number of parameters, t value and other verification results, model 3 is recommended and is therefore more suitable than model 1 and 2 in forecasting. Furthermore, model 2 does not meet the t-stat condition, unlike model 1 and 3. Table 2 shows simple statistics for both the original time series of the evapotranspiration and the predicted time series using the best-diagnosed models. The values of Model III are closest to those statistics that we selected: mean variance and skew ness.

Table 2. Simple statistics of the best-diagnosed model

Model	Mean	Variance	Skewness
Original ETo Time Series	118	2310	0.08
Predicted ETo Time Series, Model I (2,0,0)(0,1,1)	117	1932	-0.002
Predicted ETo Time Series, Model II (1,0,0)(2,1,1)	117	1936	0.000
Predicted ETo Time Series, Model II (1,0,0)(0,1,1)	115	2016	0.031

3.3. Model Forecasting

We fitted on the first 300 data points, using the Q-stat, t ratio, AIC criterion, and standard error. The best obtained model is for p = ١, d=0, q = 0, P = ٠, D=1, Q = 1. The final model can be written in the following form:

$$ET_{o,t} = 0.35ET_{o,t-1} + ET_{o,t-12} \\ -0.35ET_{o,t-13} - 0.914\varepsilon_{t-12} + \varepsilon_t \quad (13)$$

This model is used to forecast future values of the transformed time series. Lastly, the previous transformations are undone, in order to obtain the future values of the original time series, $\{Y_t\}$. All the steps were done in an iterative fashion. The process of forecasting usually requires a great deal of experience and testing alternative models. The resulted forecasts are shown in Figure 9.

Once a final satisfactory ARIMA model was selected, the tentative models were used to forecast monthly values of ET_o. The forecasting period was 1 month ahead for 60 months that covers the period 1998 to 2002 based on the previous 300 months. The forecasting performance capability for the post sample period of the tentative ARIMA models was assessed using Root Mean Squared Forecasting Error (RMSFE), Mean Absolute Forecasting Percentage Error (MAFPE), and Maximum Absolute Forecasting Percentage Error (MXAFPE). By examining the mean and maximum across all models, we can get an indication of the uncertainty in the predictions.

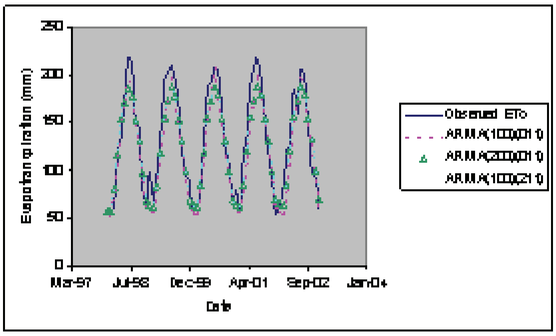

Figure 9. Comparison of predicted to actual reference crop evapotranspiration of the two tentative ARIMA models

Typically, the RMSFE is defined as the error accumulated in the forecasted observations.

$$RMSFE = \sqrt{\frac{1}{N}\sum_{t=1}^{N}(Y_t - \hat{Y}_t)^2} \quad (14)$$

The mean percentage absolute forecasting error is the absolute error in the desired prediction length, which considered a measure of how much a dependent series varies from its model-predicted level. The mathematical representation of this measure is:

$$MPAFE = \frac{1}{N}\sqrt{\sum_{t=1}^{N}\frac{|e_t|}{Y_t}} * 100 \quad (15)$$

Where e_t is the absolute error between observed and estimated ETo, Yt based on an estimated model at time i and *N* is the number of forecasts used for this purpose.

The Maximum Absolute Forecasting Percentage Error is the largest forecasted error, which is considered a measure useful in imagining a worst-case scenario for the forecasts. Assuming that the estimated model is representative of the forecasting period, the post-sample RMSFE should be consistent with the residual standard error of the estimated model. As a result, comparisons of forecast performance based on the RMSFE, MAFPE, and MAXAFP are made.

It is worth mentioning that for evaluation intentions, the post-sample period is employed to provide reasonable cross-validation and to shun the potential misleading idea that the fit is better than it really is due to over-fitting the training series. The out-of-sample error indicators for both candidate ARIMA models are presented in table 3. In general, the best forecasting for the overall time series came from the ARIMA model 3. Overall, the ARIMA approach in forecasting reference evapotranspiration gave very good results for monthly data (Mariňo et al. 1993: Hameed et al., 1995; and Trajkovic, 1999) which can be easily implemented following the aforementioned steps.

Table 3. Sample error indicators for the three candidate ARIMA Models

#	ARIMA	RMSFE	MXAFPE	MAFPE
I	Model (200)(011)	12.88	64.68	10.89
II	Model (100)(211)	12.98	68.52	10.99
III	Model (100)(011)	12.75	61.20	10.75

4. Discussion

After a complete evaluation of model identification, estimation, diagnostic checking, and forecasting, time series analysis is eventually established for reference crop evapotranspiration. ACF and PACF, as elements in time series analysis play an important role in this matter. Both functions were tested to calculate the significant autocorrelation existing in the reference crop evapotranspiration data and to identify the components of the ARIMA models. The application of ARIMA model on a time series should obey stationary criterion. A periodic ET_o time series as shown in Figure 2, mandates transforming the data to be stationary by differencing once, reducing ACF of the time series significantly. Throughout the discussion of this data set, 5/6 of the total data is used to established and identify the model, and the remaining 1/6 of the total is used to validate the models.

Twelve different types of ARIMA models are sequentially tested for the ET_o time series data. Based on the exploration of the nature of the time series data (i.e., the identification phase of ARIMA), a seasonal ARIMA and non-seasonal ARIMA with lag 12 are run on the data and both autoregressive and moving average ARIMA parameters are estimated. Table 3 lists three final models prepared for the studied area. To select the best-developed model for forecasting of the crop evapotranspiration, an assessment of the performance of these models was conducted as measurement of how closely two independent data sets match. This evaluation was done using Root Mean Square Forecasting Error as a deterministic approach in addition to the Mean Absolute Forecasting Percentage Error and the Maximum Absolute Forecasting Percentage Error.

The results of this evaluation are shown in Table 3. The three candidate models demonstrated good performance. The seasonal ARIMA model $(1,0,0)(0,1,1)_{12}$ fits slightly better and gives a smaller confidence interval than the models $(1,0,0)(2,1,1)_{12}$ and (2,0,0)(0,1,1). The model diagnostic shows that the residuals do pass the test for normality (not shown). The finest ARIMA model was identified calculating the t statistic and other statistical tools. The RMSFE, MAXAFP, and MAFPE were minimum for the case of the model $(1, 0, 0)\ (0, 1, 1)_{12}$. The selected ARIMA model with two parameters seems to forecast the time series data very well (Figure 9). This result is supported by the work done by Mariño et al., 1993; Hameed et al., 1995; and Trajkovic, 1999. These investigators have obtained good results when ARIMA model was compared with different time series and conventional methods of evapotranspiration estimation.

Figure 9, however, shows that predicted ET_o gave reasonable agreement for the ARIMA $(1, 0, 0)\ (0, 1, 1)_{12}$ up to rates of 200 mm $month^{-1}$ but insignificant underestimation at higher rates. Yet, the ARIMA (1, 0, 0) (0, 1, 1) model forecasts ET_o better than model I and II. To reflect the uncertainty in the forecasts, this analysis therefore follows that an approximate 95% prediction interval for the historical and forecasting values may be made in the same manner as in general least-square regression issues. Furthermore, the model produces similar ACF when predicts the ET_o during the period 1998 to 2002 as indicated in Figure 10. For the same period, by visual inspection, Figure 11 showed an excellent correlation between the observed and the forecasted (calculated) values of ET_o which supports our results.

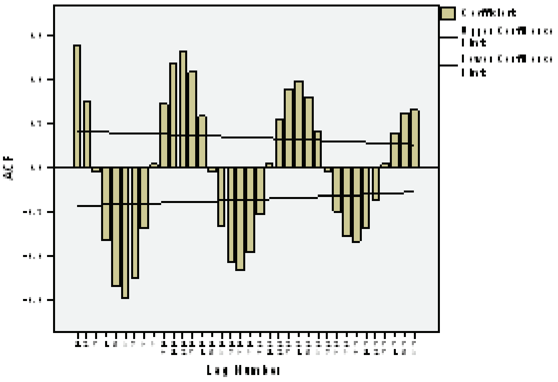

Figure 10. Autocorrelation function of the predicted reference crop evapotranspiration using ARIMA (1, 0, 0) (0, 1, 1)

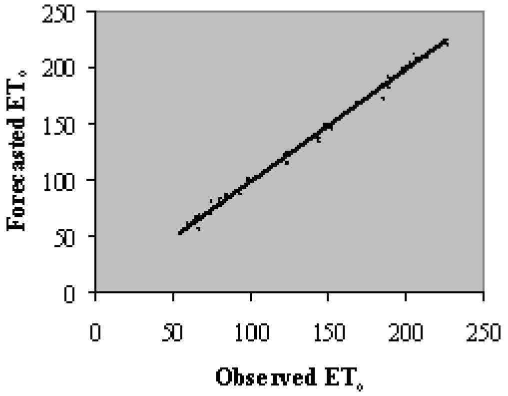

Figure 11. Observed versus forecasted reference evapotranspiration between 1998 and 2002

It must be pointed out that the predicted time series values of reference crop evapotranspiration are relatively lower than the observed values obtained from the Deir-Alla weather station on the year 1998. This might be due to a drought period. Drought periods might lower the performance of the forecasting techniques. To examine the drought periods, ET_o estimation for the 1998 drought year was at relatively higher variance with the reported ET. This variation contributed significantly to increasing the RMSFE and, in turn, lowering the forecasting performance. Moreover, the reference crop ET relating to the severe drought year acts as an outlier and influences the characteristics (e.g. being stationary) of the series. Therefore, we expect a longer series would lead to improved forecasts. This is due to enduring the negative effect of drought periods on the performance of a forecasting technique.

The lack of water in arid and semi-arid regions constitutes a major deterrent to sustainable development of these areas. To meet demands for water for a multitude of uses, there is a continuing struggle. Insufficient water at the right place, at the right time, and with the right quality requires more than ever before improved management, efficient utilization, and increased conservation of limited freshwater resources. This manuscript aims at providing a time series forecasting approach presentation, which can identify the needs for future developments associated with water resources development, utilization, management, and conservation in arid and semi-arid regions. This would reflect into the real world application where time series modeling may serve as a convenient tool for the prediction of ET_o when water resources are of a paramount importance as in the case of Jordan.

Successful forecasting of evapotranspiration would play a vital role in the irrigated agriculture sector. This will help in water resources management, which will contribute in strengthening Jordan's economy. Therefore, adequate estimations and forecasting of evapotranspiration are required especially in irrigated agriculture. Evapotranspiration is one of the most significant hydrologic processes affected by human activities that alter the type and extent of vegetative cover. Moreover, knowledge of ET on not only a local but also a regional scale enables hydrologists to perform water balance calculations and understand hydrological cycles. ET forecasting shall be useful in irrigated agriculture, i.e., for water and agricultural planners: it will allow agronomists and farmers to assess crop water requirements in Deir-Alla

Irrigated agriculture is a trade of Jordanian lineage practiced in the Jordan Valley, which contributes to the production of food and job opportunities in direct and indirect agricultural employment and supporting services. It also augments the environment and helps apprehend desertification indirectly. This enhances and helps in increasing on-farm irrigation efficiency and maximizing the agricultural output of a unit of land area per unit flow of irrigation water. In addition, in order to determine the volume of replenishment water that is needed for irrigation, evapotranspiration rates need to be forecasted to wet root zone and to sustain a low drainage rate.

ET information is needed for drainage design and drains networking to be help in installing drainage system in the valley where natural drainage is not sufficient to serve this purpose. This encourages community farmers who usually need additional water for soil leaching from salts in the studied area to set up a drainage system in their farms. Forecasting ET would help in that prospective and through minimizing the reuse of treated water as supplement water in irrigation. Therefore, the water surplus that can be saved by knowing ET priori can be used to either irrigate extra arable land to maximize productivity and increasing cropping intensities or use it wherever shortages occur in any of the other water-consumed sectors: municipality and industry.

It is worth mentioning that irrigation water consumes about three-fourths of the available fresh water resources in Jordan. Managing the irrigation water use under geographic, socio-economic, and demographic constraints is of a vital importance to Jordan. This case study shows that forecasting ET can be incorporated in irrigation water management by proper choice of crops and farming patterns. Furthermore, managers who manipulate soil-plant systems in the Jordan Valley should have a good fundamental understanding of the process of ET and the factors that influence its magnitude.

Controlling the fate of water and achieving a proper management of the scarce water resources in Jordan would diminish the exploitation of water resources, which is considered a real threat to peace and future development process in the region. Possible conflict over water in the region might retard any integrated and sustainable development plans. Moreover, improved and efficient water resources management could help in sustaining the tourism since the Jordan Valley contains many tourism attractions and places like the Dead Sea, Jordan River and many others. It has been demonstrated by many studies in the world that the tourism water use produces higher net revenue compared to irrigation use (The PRIDE Report, 1992).

Potential evaporation is extremely high in the studied area. Evapotranspiration is considered on of the most important factor in managing water resources in the Jordan Valley. Poor water management can result in disease-causing pollution, loss of topsoil from erosion, damage to animal habitats and to forests and others. Worst of all is the damage to irrigated agriculture that now provides Jordan's food supply and must be relied upon to provide more since rainfed agriculture has reached a ceiling and can produce little more than it already is producing.

5. Conclusions

On a per capita basis, Jordan is one of the lowest ranked countries in water resources with the per capita share of water being less than 175 for all uses. This places Jordan at only 20 percent of the water poverty level, which reflects the doughtiness level. Evapotranspiration is one of the most important indices in the drought equation, which exceeds 90% in Jordan. Therefore, time series forecasting of evapotranspiration was conducted to help the decision makers and water system mangers establish appropriate strategies to sustain and manage water resources. Time series assume that "history repeats itself," so that by studying the past, better decisions, or forecasts, can be made for the future.

In this paper, an endeavor is made to obtain a long-term forecast of monthly averaged reference crop ET without using weather data. Thirty years of ET data was used in this study to ensure a satisfactory estimate of monthly values. Nevertheless, the change of inherent characteristics in the ET_o may occur very slowly and time-series models may be useful for long-term planning of water resource management.

Modeling was done using deterministic measures such as RMSFE for evaluating the performance of a forecasting technique. ARIMA model has demonstrated good results for monthly data in terms of accumulative error and performing 5-year predictions within an established reasonable accuracy level. This could be put into practice without difficulty following the previously mentioned procedure.

Moreover, the forecasting techniques presented in this paper allow water resource managers to predict up to 60 months within a mean absolute forecasting percentage error less than 11%, making these predictions very useful to optimize the resources needed for effective water resources management. Predictions can also be made for longer periods. These findings guarantee a dependable planning, design and operating of irrigation projects. On the long term, these findings can help enhance both local (Deir-Alla) and national water resources policies and strategies for irrigation water management in addition to assisting in planning a more effective management of these vital resources. This could reflect on the water quality, which has worsened in the last two decades because of the increasing consumption of the groundwater and the usage of treated wastewater. Moreover, it is likely that forecasting models based on arid and semi-arid conditions would be suitable for other similar regions.

Finally, although these conclusions are strengthened by analyzing a longer reference crop ET series, the long-term forecasts with relatively less reliability may still be needed in system planning and analysis. The findings of this study could lay the grounds for further investigations and studies that could lead to the establishment of a complete and reliable weather database and proper ET prediction in the Jordan Valley region using a dynamic programming approach. Future research should be addressed to extend the validation data set and to check the validity of our results on other regions. It should also explore how to improve forecasting as well as exploring intervention models to estimate various types of environmental impacts for a long time.

References

[1] Abu-Zanat, M., 1995. Production systems of small ruminants within the different agro-ecological zones of Jordan. Working paper submitted to livestock research priorities workshop, Amman, 9-10/11/1995.

[2] Al-Jaloudy, M. 2001. Country Pasture/Forage Resource Profiles-Jordan. FAO Publication. (http://www.moa.gov.jo)

[3] Allen R.G., Pereira, L.S., Raes, D. and Smith, M., 1998. Crop Evapotranspiration. Guidelines for Computing Crop Water Requirements. FAO Irrigation and Drainage Paper No. 56. FAO, Rome, Italy.

[4] Blaney, H.F. and. Hanson, E. G, 1965. Consumptive use and water requirements in New Mexico. Technical Report 32. Santa, Fe, NM: New Mexico State Engineer.

[5] Box G., and Jenkins G., 1976. Time series analysis forecasting and control. Second Edition. Holden-Day, San Francisco, California.

[6] Bowerman, B. L. and O'Connell, R. T., 1993. Forecasting and Time Series: Application Approach. Wadsworth, Inc., Belmont, CA.

[7] Brockwell P.J, and Davis, R. A., 1996. Introduction to Time Series and Forecasting. New York: Springer-Verlag.

[8] Development Alternatives Incorporation (DAI), 1995. Information and Management Systems for Irrigation (IMSI). DAI_Report. Amman, Jordan.

[9] Department of Statistics (DOS), 2006. Annual report. Amman, Jordan.

[10] Dingman, S. L. 2002. Physical Hydrology, 2nd Edition, Prentice Hall, USA.

[11] Doorenbos, J., and Pruitt, W.O. 1977. Crop water requirements, FAO Irrigation and Drainage Paper No. 24. FAO, second Ed., Food, and Agricultural Organization of UN, Rome, Italy.

[12] Fardous, A.N., Taimeh, A., Serpekain, A., Jitan, M., Hatter, M., and. Shrouf, A.,2001. Irrigation Management Information System Project in the Jordan Valley. Unpublished Report. National Center for Agricultural Research and Technology Transfer (NCARTT), Jordan.

[13] George, W., Pruitt, W.O., and Dong, 1985. Evapotranspiration Modeling. Final Report. , III-36-61, California Irrigation Management. Information System, University of California, Davis, CA.

[14] Hameed, T., Marino, M.A., and Shumway, R. H., 1995. Evapotranspiration transfer-function-noise modeling. *J. Irrig. and Drain.Eng. ASCE*, 121(2),159-169.

[15] Jensen, M.E., Burman, R.D., and Allen, R.G., 1990. Evapotranspiration and irrigation water requirements. ASCE Manuals and Reports on Engineering Practice No. 70. New York: *Amer. Soc. Civil Eng*., pp332.

[16] Jordan Department of Meteorology, 2006. Annual report. Amman, Jordan.

[17] Mariño, M.A., Tracy, J.C., and Taghavi, S.A., 1993. Forecasting of reference crop evapotranspiration, *Agricultural Water Management*, 24, pp.163-187.

[18] Mazahrih, N., Shatanawi, M.R., Abu-Awwad, A., Battikhi, A., Suwwan, J., and Fardous, A., 2001. Evapotranspiration measurement and modeling for Bermuda Grass and Hejazi Alfalfa, Cucumber, Cucumber, and Tomato grown under protected cultivation in the Central Jordan Valley. University of Jordan, Amman. Unpublished Ph.D. Thesis.

[19] Ministry of Water and Irrigation (MWI), 2004. Annual Report. Amman, Jordan.

[20] Taha, Suzan. 2006. Country paper Presented to the Conference of the Water Directors

[21] Of the Euro-Mediterranean & South Eastern European Countries. *Ministry of Water and Irrigation*

[22] Athens, Greece (http://www.minenv.gr/medeuwi/meetings/conference.of.the.water.directors.athens.6&7-11-06_en/00/JordanCountryeport.doc)

[23] Mohan, S. and Arumugam, N., 1996. Relative importance of meteorological variables in evapotranspiration: Factor analysis approach, *Water Resources Management*, 10(1), 1-20.

[24] Pankratz, A., 1983. Forecasting with Univariant Box-Jenkins Models: Concepts and Cases. John Wiley, New York.

[25] Pruitt W. O. and Doorenbos, J., 1977. Empirical calibration, a requisite for evaporation formulae based on daily or longer means climatic data, ICID conference on evapotranspiration, Budapest, Hungary, 26-28 May 1977, International Commission on Irrigation and Drainage.

[26] Shumway, R. H. and Stoffer, D. S., 2000. Time Series Analysis and its Applications. Springer, USA.

[27] SPSS Inc., 2005. SPSS Inc. Headquarters, 233 S. Wacker Drive, 11th floor Chicago, Illinois 60606.

[28] Surjeet Singh and Jaiswal, C. S., 2006. Numerical Solution of 2D Free Surface to Ditch Drains in Presence of Transient Recharge and Depth-Dependent ET in Sloping Aquifer, *Water Resources Management*, 20(5),779-793.

[29] The PRIDE Project, 1992. ‘A Water Management Study for Jordan’ PRIDE Technical Report # 4,
[30] Washington DC.
[31] Trajković, S., 1998. Comparison of prediction models of reference crop Evapotranspiration. The Scientific Journal FACTA UNIVERSITATIS, Architecture and Civil Engineering, 11(5), 617-625.

JJEES

Jordan Journal of Earth and Environmental Sciences

Volume 1, Number 1, Mar. 2008
ISSN 1995-6681
Pages 45 -52

Rare Earth Elements Geochemistry of the Cambrian Shallow Marine Manganese Deposit at Wadi Dana, South Jordan

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Abstract

The Cambrian manganese deposits of Wadi Dana were investigated for their REE geochemistry, contents and patterns. Compared with other manganese ore types the studied ore is REE depleted. However, such depletion can be applied to the high-grade ores, while the low-grade ores bears higher REE due to the detrital contribution. The horizontal variation throughout the basin is insignificant, while, the vertical variation is pronounced. Vertically. The ∑REE and many individual REE's are increasing upwards except for Yb and Eu. Moreover, Ce/∑REE and Eu/Sm vertical behavior shows inverse relationship that reflects the increase of oxic diagenetic conditions upwards. The normalization pattern shows that the ore exhibits a high positive Eu and no or small positive Ce anomalies. The REE pattern and content is comparable to similar worldwide diagenetic manganese ores.

Keywords: REE; Spatial variation; Mobilization; Diagenesis; Ce and Eu-anomalies;

1. Introduction

Manganese deposits were known to form since the Archean and are being formed at the present day. It formed in various environments e.g. lakes, internal seas, pelagic, archipelago, shallow marine, deep marine, as well as terrestrial mineralization. This is due to the fact that manganese can be formed by hydrothermal, sedimentary, and supergene processes. Manganese diversity in time and environment of deposition can be of great importance for better understanding of the geochemical processes responsible for its deposition. Furthermore, it can contribute to the on going investigation of the Earth's evolution history, and help in explaining the worldwide phenomena such as the Banded Iron Formation (BIF) (Kimberely, 1989). Huge deposits were discovered around the world (e.g. Nikopol of Ukrania, and at Chiatura of Georgia, and the Groote Eylandt deposit of Northern Australia, (Varentsov, 1982; and Frakes & Bolton, 1992), Hokkaido manganese deposits of Japan (Miura and Hariya 1997) and Thrace deposits of Turkey (Ozturk and Frakes 1995) and Orissa, manganese deposits of India (Nicholson et al. 1997).

The REE geochemistry as a tool and tracer for marine environment and sedimentary processes has been used by many authors (e.g. Elderfield et al. 1981; De Baar et al. 1983; Alpin, 1984; Klinkhammer et al. 1983; Michard et al. 1983; Calvert et al. 1987; Glasby et al. 1987; De Baar et al. 1988 and Rolland et al. 2003). Slight change in REE contents or their patterns may reflect a change in redox potential (Piper, 1974; Elderfield, 1988; and De Carlo, 1991), and might be due to the change in sorption properties of solid phases (Alpin, 1984; Byrne & Kim 1990; De Carlo & Koeppenkastrop 1990; and Koeppenkastrop & De Carlo 1990). Also it can be caused by complexation with major anions of seawater (Byrne & Kim 1990; Cantrell & Byrne 1987; and De Carlo & MaMurtry 1992). Hence the REE mobility is controlled mainly by the redox potential of the environment, therefore REE patterns can be used in tracing out the post-depositional processes (i.e. diagenesis) (Ozturk and Frakes 1995; De Carlo, 1991; and Dymon et al. 1984). Dubinin & Volkov, (1986) found that low Ce/La ratio was found to be indicative for ore deposition by direct precipitation or adsorption from seawater. Moreover, Glasby et al. (1987) found Ce/La ratio a useful redox indicator, when they noticed the increasing trend in Ce/La ratio from the SW Pacific towards the equatorial Pacific; due to the passage of the Antarctic Bottom Water. Ponater (1988) have measured a higher Ce/La ratio (2.5-3.2) in the Urkut manganese deposit of Hungary and used it as an indicator for a terrigenous source of REE, which causes also a

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positive Ce anomaly. Furthermore, conditions that are more oxic would lead to REE enrichment (Ingri, 1985; Ingri & Ponater 1987; Shokoriviz et al. 1992). Additionally, Varentsov (1995) has used Eu/Sm ratio as indicator for supergene ore formation.

Enlightened by these observations the geochemical characteristics of REE were investigated in the Cambrian shallow marine manganese mineralization of Wadi Dana. Cambrian manganese deposits in Jordan were targeted by many previous investigations regarding their petrology, mineralogy, and genesis using trace element geochemistry (G.G.M., 1965; Basta and Sunna, 1970 & 1972; Khoury, 1986; and Shaltoni, 1988). Recent studies reveal that the ore was formed through three genetic stages each of which has its mineralogical and geochemical signature (El-Hasan, 1999; and El-Hasan et al. 2001). However, the REE geochemical signature was not yet been investigated.

2. Objectives

The aim of this work to investigate the behavior of REE with regard to these genetic stages, and to test the reliability of REE in determining the different evolution history of ore formation of the study area as indicated by the trace element geochemistry (El-Hasan et al. 2001)

2.1. Geologic Setting

The investigated area occupies the north of central Wadi Araba region, where the main manganese outcrops in Jordan are located (Fig. 1). The manganese mineralization is hosted within the Lower and Middle Cambrian formations. The Lower Cambrian consists of bedded arkosic sandstone unit (Saleb Formation) (BASU); is a 20-35 m thick, consisting of vary-colored arkosic sandstone layers, with quartz pebbles and cross-beddings. Clay and shale layers are intercalated within the sandstone beds. The stratigraphic features indicate that it was formed under shallow marine to braided river environment conditions (Bender, 1974; Amireh, 1987 and Rabba', 1994). The manganese mineralization occurs in the form of lenses, concretions, and encrustation (El-Hasan, 1999). The Middle Cambrian dolomitic limestone shale unit (DLSU) or (Burj Formation) consists of three parts, the lower sandy, middle is carbonaceous and the upper is shaley (Amireh et al., 1994). The middle part is composed of dolomite and dolomitic sandstone layers, intercalated with clay and shale beds, whereas the upper part consists of brown – red sandstone with ripple marks and cross-beddings intercalated with red shale. The manganese hosted in this formation was found as disseminations, thin intercalations, lenses, concretions, and bands (El-Hasan, 1999 and El-Hasan et al. 2001).

2.2. Mineralogy of the Studied Horizons:

The mineral assemblage is cryptomelane, psilomelane, pyrolusite, hollandite, todorokite, and coronadite. Rarely manganite and birnessite were detected. Hematite is found as minor mineral in all sites; however, at Wadi Dabah it is a major constituent. Such mineral assemblage usually found in supergene enrichment (Ozturk and Frakes 1995 and Varentsov, 1995).

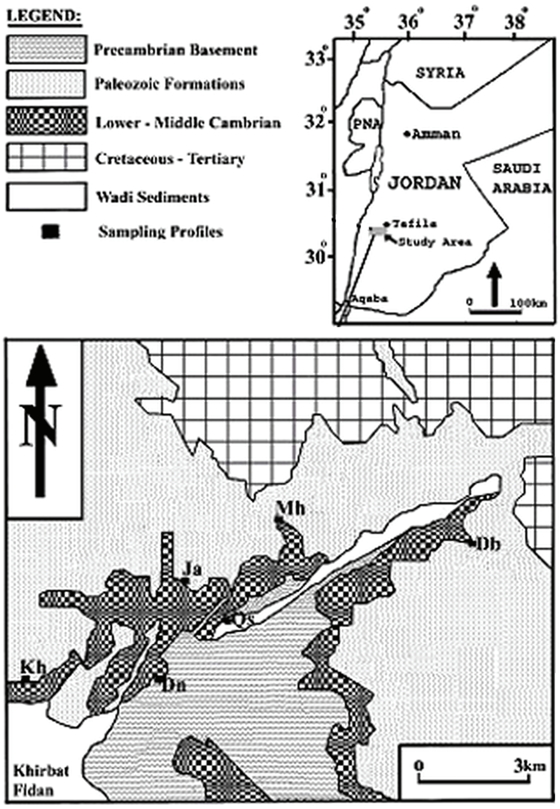

Fig. (1). Geological map of the study area showing the location of the six sampling profiles. The sites are from West to East:- Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.

Detailed mineralogical investigation carried out by (El-Hasan, 1999; and El-Hasan et al. 2001) showed that the ore had been evolved through three stages. First is the primary sedimentary ores, which characterized by the presences of todorokite and birnessite in the form of oolites found as remnants in the lower Cambrian BASU (Saleb Formation). Secondly the supergene-enrichment ores, which characterized by the presence of cryptomelane, psilomelane, hollandite, pyrolusite and hematite. It is the dominant phase of the middle Cambrian (Lower Burj Formation). Finally, the epigenetic ores that most likely formed as result of lateritization; its main mineral phases are coronadite, hollandite-coronadite solid solution, barite and geothite. This phase is confined to the upper most portions of Middle Cambrian DLSU (i.e. Middle Burj Formation). The tentative paragenetic sequence of the three ores is shown in Fig. (2). Moreover, the distribution of these ores within the lithilogical columnar section was illustrated in Fig. (3).

	Primary Sedimentary	Secondary Supergene Early Diagenetic	Secondary Supergene Late Diagenetic	Epigenetic Lateritization
Quartz	---------------			
Dolomite	---------------			
Kaolinite	--------------			---------
Smectite-Illite				-------------
Todorokite	---------			
Birnessite	--------			
Manganite	----------			
Apatite	-------------			-------------
Cryptomelane		------------	-------------	
Psilomelane		-----------	-----------	-------------
Hollandite		-----------	-----------	
Pyrolusite		-----------	----------	
Hematite		-----------	-----------	------
Goethite			-----------	----------
Barite			----------	----------
Calcite		-----------	----------	-----
Kutonahorite		--------		
Ankerite		----------		
Coronadite				-----------
Chrysocolla				-----------

Note: Number of dots in dotted lines shows the degree of abundancy of the mineral phases in each stage

Fig. (2). Paragenetic sequence of Wadi Dana manganese ore deposits, including the gangue minerals *(After El-Hasan et al., 2001).*

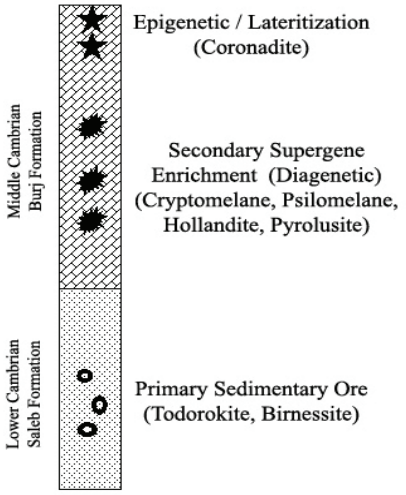

Fig. (3). Schematic lithological columnar cross section showing the distribution of ore types and their correspondent mineral phases within the studied area.

3. Analytical Methods

Thirty-six selected ore samples from six profiles along Wadi Dana mineralized area were analyzed for their content of REE using ICP-MS (Yokogawa, PMS-2000) at the Analytical Center of the University of Tsukuba. Because high REE content was expected, the samples were not pre-concentrated. The powdered samples were dried in the oven for at least 6 hours, and digested following the procedure of mixed acid (Yamaguchi, 1994). 0.05 g of the sample powder was treated with acid mixture of 0.2 ml $HClO_4$, 0.6 ml (1:1) HNO_3, and 1 ml HF. The Teflon beaker was closed tightly and kept overnight at 105 °C. In case of incomplete decomposition, samples were treated again with the same acid mixture. After total digestion was achieved, 5 ml of (6N) HCl were added to the residue and the beaker was closed tightly again and heated for at least 8 hours. The samples solutions were completed up to 100 ml with de-ionized water and transferred into polyethylene bottles. Solutions with different concentrations were prepared in order to match the standardization of the ICP-MS machine. JMn-1, JR-1, JB-1a, and JLK-1 of the Geological Survey of Japan (GSJ) standards were used. These standard samples were repeatedly analyzed every 10 samples to monitor any shift or change in the setup. The calculated error was less than ± 2% range. The results were then normalized against the North American Shale Composite (NASC) (Haskin and Haskin 1968). Detailed mineralogical investigation was conducted for selected samples using the SEM-EDS (JOEL-JSM 5400), at the Geosciences Institute; University of Tsukuba.

4. Results

The analytical results of all selected ore samples from all studied profiles are listed in Table. (1).

In this table the total REE (∑REE) is slightly decreasing from west to east, in other words from low-grade towards high-grade ores. The high-grade ore mineralization especially at Wadi Mahjoob and Wadi Dabah is relatively depleted in REE, particularly in Ce and La, but they are relatively enriched in Eu.

Although ∑REE is decreasing from low to high-grade ores, the overall spatial distribution for some individual REE's shows slight horizontal variation Fig. (4). As an example La shows insignificant horizontal variation, in spite it is considered as the most mobile REE and used to measure the degree of differentiation between light REE (LREE) and heavy REE (HREE) (Varentsov, 1995). Similarly, Ce and Yb exhibit a steady increase from west to east. Only at Wadi Khaled Ce shows higher values. At Wadi Dabah, Yb shows slightly higher values. On the other hand, Eu is steadily increasing towards the east until it reaches its highest value as at the ore body of Wadi Dabah as reflected by the highest Eu/Sm ratio. Moreover, Ce/La and Ce/∑REE show insignificant changes horizontally, but the values are relatively higher at the western most sites at Wadi Khaled. The La/Yb ratio shows no change up to Wadi Mahjoob, and then it drops towards the ore body of Wadi Dabah, (Fig. 4).

Table (1). REE analytical results for selected Mn-ore samples from all studied profiles along Wadi Dana mineralized area, all are in ppm. *Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.*

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Kh2	39.24	348.38	9.91	38.85	7.67	2.16	6.33	0.97	5.37	1.07	2.86	0.5	2.63	0.5
Kh4	26.31	80.61	4.43	15.94	2.94	2.02	2.37	0.37	2.24	0.51	1.36	0.22	1.37	0.25
Kh5	15.4	40.05	2.67	9.2	1.68	0.91	1.35	0.21	1.17	0.27	0.74	0.17	0.83	0.16
Dn2	47.7	81.81	10.94	46.11	8.44	1.32	5.77	0.89	5.13	1.11	2.73	0.45	2.89	0.45
Dn5	11.03	19.14	2.48	10.85	3	0.48	2.65	0.42	2.09	0.44	1.02	0.17	0.94	0.13
Dn7	14.44	25.03	2.78	10.88	2.35	0.37	1.97	0.32	2.33	0.48	1.14	0.23	1.27	0.2
Dn10	19.48	43.55	4.67	19.24	3.92	1.37	2.58	0.39	2.05	0.45	1.03	0.16	0.98	0.18
Dn11	19.08	39.88	4.04	15.86	3.26	2.61	2.19	0.33	1.74	0.37	0.95	0.14	0.96	0.15
Dn13	20.04	63.53	5.14	22.31	6.23	5.25	3.82	0.54	2.54	0.5	0.97	0.13	0.87	0.16
Dn14	2.99	8.88	0.72	3.11	0.76	0.38	0.98	0.15	0.94	0.24	0.56	0.08	0.4	0.08
Ja6	14.06	62.82	2.98	11.19	1.9	2.21	1.76	0.25	1.43	0.36	0.81	0.16	0.85	0.14
Ja8	1.64	1.75	0.3	1.09	0.28	3.84	0.32	0.06	0.33	0.12	0.29	0.05	0.34	0.09
Ja16	20.53	44.38	5.05	20.61	5.22	1.2	3.67	0.55	2.62	0.51	1.09	0.2	0.92	0.15
Qs4	32.66	117.05	9.11	44.88	11.85	4.21	10.51	1.42	6.95	1.29	2.75	0.39	1.81	0.29
Qs5	29.23	68.06	7.22	29.08	4.65	0.99	2.83	0.38	2.17	0.47	1.13	0.22	1.19	0.19
Qs7	19.78	55.89	5.87	26.68	6.77	1.21	5.18	0.85	4.23	0.82	1.9	0.34	1.86	0.28
Qs8	15.66	36.82	3.43	14.28	2.72	0.7	2.27	0.3	1.81	0.36	1.09	0.17	1.04	0.18
Mh1	9.9	25.91	3.29	14.55	3.78	1.47	3.9	0.51	2.6	0.55	1.12	0.17	0.96	0.14
Mh3	10.72	33.32	3.17	12.69	2.9	1.14	1.75	0.28	1.51	0.29	0.71	0.12	0.77	0.11
Mh4	17.3	31.72	3.66	14.25	2.68	0.83	2.21	0.33	1.79	0.37	0.98	0.16	0.98	0.16
Mh6	23.44	44.59	6.19	26.34	4.93	1.81	3.46	0.51	2.47	0.47	1.04	0.15	0.94	0.16
Mh7	51.62	97.84	9.24	35.42	8.38	7.79	10.79	1.97	10.63	2.19	5.51	0.84	5.08	0.83
Mh8	12.89	34.88	2.85	11.08	2.09	1.42	1.91	0.36	2.11	0.16	1.13	0.17	1.17	0.15
Mh9	29.1	61.83	4.98	20.41	3.8	2.69	3.11	0.42	1.96	0.4	0.93	0.14	0.71	0.13
Mh10	21.99	53.73	5.28	17.94	3.14	4.09	2.54	0.41	2.41	0.5	1.43	0.18	1.14	0.18
Mh11	18.63	42.18	4.15	13.42	2.64	6.27	2.19	0.41	2.3	0.52	1.33	0.18	1.23	0.21
Mh13	9.47	22.57	2.12	8.87	2.1	2.81	2.51	0.45	2.44	0.49	1.19	0.19	1.4	0.23
Mh14	11.89	24.41	2.49	9.2	1.68	1.45	1.61	0.3	1.61	0.37	0.93	0.14	0.99	0.15
Db8	10.2	20.3	2.89	14.26	3.58	2.13	5.58	0.93	5.41	1.29	2.92	0.37	1.7	0.32
Db9	9.34	24.49	2.18	9.84	2.1	1.76	2.93	0.46	2.88	0.63	1.42	0.17	0.91	0.16
Db10	15.71	39.26	4.93	22.87	6.26	3.18	6.7	1.12	5.72	1.2	2.78	0.37	1.99	0.32
Db12	7.68	22.36	1.9	8.52	2.17	1.84	2.97	0.46	2.59	0.62	1.36	0.15	0.83	0.14
Db13	3.36	7.66	0.83	4.14	1.05	1.9	1.52	0.24	1.51	0.4	0.8	0.1	0.47	0.09
Db14	10.69	22.09	2.42	10.14	2.32	5.22	1.95	0.36	2.24	0.45	1.25	0.21	1.58	0.3
Db16	9.78	19.03	2.13	7.75	1.13	0.23	0.97	0.22	1.22	0.32	0.74	0.15	1.01	0.17

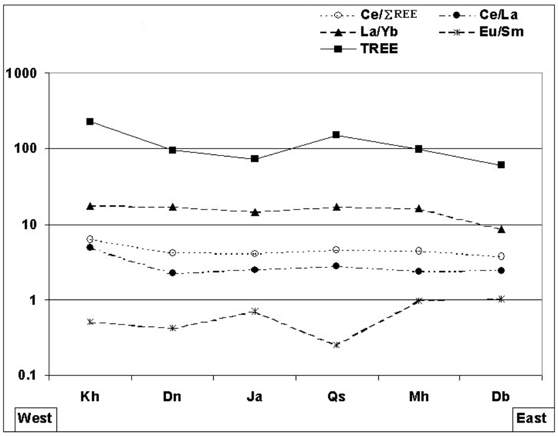

Fig. (4). Plot showing the spatial REE variations (in ppm) along the course of the study area. *(Same abbreviations as in Fig. 1).*

4.1. Normalization

The NASC normalized patterns for all mineralized sites are shown in (Fig. 5).

The quantitative anomalies were calculated using the following equations:

$$Ce\ anomaly = Ce^{*} - (2/3La^{*} - 1/3Nd^{*})$$

$$Eu\ anomaly = Eu^{*} - (1/2Sm^{*} - 1/2Gd^{*})$$

Where Ce*, La*,Nd*, Eu*, Sm* and Gd* are the North American Shale Composite (NASC) normalized value of Ce, La, Nd, Eu, Sm and Gd. All sites exhibit a positive Eu anomaly; its highest values are at high-grade ore sites of Wadi Mahjoob and Wadi Dabah. Meanwhile, Ce shows weak positive anomaly; only at Wadi Khaled it has high positive anomaly. This might be due to that samples of Wadi Khaled contain higher detrital material and it is highly affected by the epigenetic solutions. The Eu positive anomaly is clearly found in all sites, and it increasing toward the high-grade ores (Fig. 5) and (Table 2). This was reflected from the positive correlation between Eu and Mn (Table 3).

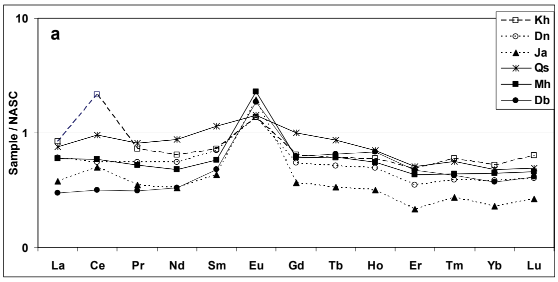

Fig. (5). REE normalizations for all samples from the three ore types for each studied sites relative to NASC (Haskin et al. 1968), *(Same abbreviations as in Fig. 1).*

Table (2). Quantitative Ce and Eu anomalies in all mineralized sites of Wadi Dana area.

	Ce Anomaly	Eu Anomaly
Kh	1.36	0.69
Dn	-0.03	0.73
Ja	0.14	1.55
Qs	0.15	0.36
Mh	0.03	1.7
Db	0.01	1.31

Kh: Wadi Khaled; Dn: Wadi Dana Camp; Ja: Wadi Al-Jamal; Qs: Ain Quseibeh; Mh: Wadi Mahjoob; Db: Wadi Dabah.

Table (3). Average major oxides for each ore type. All values are in wt%.

	Supergene	*Primary*	Epigenetic
SiO_2	37.25	47.05	54.85
Al_2O_3	2.20	1.93	4.89
TiO_2	0.097	0.064	0.19
Fe_2O_3	6.10	15.48	5.74
MnO_2	23.35	10.75	12.56
MgO	2.00	2.08	0.47
CaO	6.86	11.98	2.66
Na_2O	0.31	0.38	0.06
K_2O	1.01	0.75	1.75
P_2O_5	1.60	0.10	0.56

5. Discussion

Recalling the schematic cross section of (Fig. 3) REE content and ratios are changing vertically according to ore genetic types (i.e. primary, supergene and epigenetic). The REE behavior of the primary ores is rather ambiguous due to the small number of samples. El-Hasan et al. (2001) described Fe-rich layers at Dana-camp and Wadi Mahjoob in the lower Cambrian Burj formation and considered them as the remnants of the primary manganese ores after extensive leaching, they have very low Eu/Sm ratios (0.16-0.31). Therefore, primary ores are believed to be rich in Eu, such result was observed in (Komuro et al. 2006). However, in the studied primary ores Eu was removed after extensive diagenetic modifications causing very low Eu/Sm ratio. Beside that, primary ores show low values of Ce/∑REE, Ce/La, and La/Yb (Fig. 6). This type of ore showed somehow contradictory observations due to diagenetic alteration processes, which caused REE pattern to be difficult to use as paleoredox indicator (Girard et al. 2002; and Kato et al. 2006).

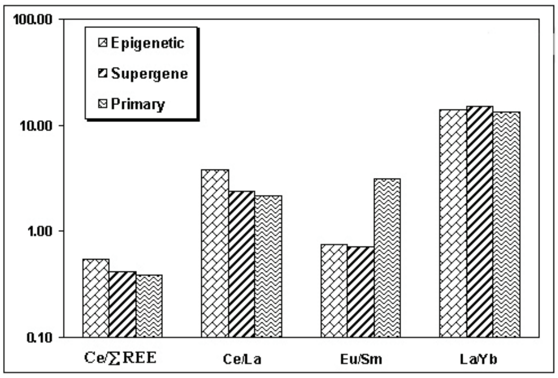

Fig. (6). Histogram showing the REE Ratios behavior among the different genetic stages of the ore.

The supergene ores show relatively high ∑REE; this is due to the upward remobilization from the lower primary ores, and the downward leaching of the upper mineralized horizons by the descending epigenetic solutions. Furthermore, this ore type is characterized by intermediate values of Ce/∑REE, Ce/La, and lower values of Eu/Sm than those of primary ores, and they exhibit the highest La/Yb values (Fig. 6). This might be attributed to higher degree of r modification compared with the primary ores, which have lower La/Yb ratio. The low Eu/Sm values and high La enrichment within this horizon indicate the remobilization of primary ores and their re-deposition under supergene conditions. The lower Eu/Sm was used as an indicator for advanced superegenity of the primary ores and to estimate the degree of alteration of these ores (Wakita et al. 1971; and Varentsov, 1995). Positive Eu anomaly with no distinct Ce anomaly are indicators for oceanic anoxia prevailed through out the early Triassic siliceous claystone from Oritate area southwest Japan (Komuro et al. 2006), Therefore, higher Eu/Sm ratios represent the primary ore then as the alteration proceeds the Eu is removed, causing the Eu/Sm ratio to drop drastically in the Fe-rich layers that is the remnants of the primary ores. Within the supergene horizon, there is a slight difference in Ce and Ce/∑REE between Mh and Db, where it is relatively higher in the former than in the latter. Similar changes between the two sites were recorded in trace elements particularly in Fe content (El-Hasan et al. 2001). This might be attributed to the difference in the environment parameters between them in terms of Eh and pH. El-Hasan et al. (2001); and El-Hasan & Lataifeh, (2001) shows that Db high-grade ores have hematite as main mineral phase together with Mn-oxides and Mn-melane minerals, more than in Mh ores. The presence of Fe-oxides with Mn-oxides would indicate lower Eh and pH (i.e. mildly reducing) values prevailing in Db (Brookins, 1988). Therefore, such mildly reducing environment would cause Ce depletion and Eu enrichment, which is obvious in Fig (4) where Db ores exhibits a remarkable drop in ∑REE and in Ce/REE to lesser extent, meanwhile it shows an increase in Eu/Sm ratio than the adjacent Mh ores. The changing in Eh, pH and temperature was found to be the cause for Eu and Ce mobility (Alderton et al. 1980; Taylor & Fryer 1980; Sverjensky, 1984; and Parcejus et al. 1990).

The epigenetic ore has the highest Ce content, thus high Ce/∑REE and Ce/La ratios. This was clear from the SEM illustration of (Fig. 7). Meanwhile, Eu/Sm is continuing to decrease upward as shown in (Fig. 6), this confirms the oxic diagenetic environment that affected the upper horizons; at the same time it might indicate the involvement of meteoric water in the continuous leaching process downward (i.e. lateritization) (Ozturk and Frakes, 1995). Moreover, the epigenetic ore shows an intermediate La/Yb value relative to other ores. It is slightly lower than in the supergene, which would reflect a lesser degree of differentiations that might be due to the effect of lateritization. Within this horizon, a clear difference between the western Kh site and the eastern site Mh was recognized. At Kh the ∑REE, particularly Ce, and La are much higher than in Mh (Fig. 4). This difference might be due to the detrital contribution in Kh samples (El-Hasan, 1999).

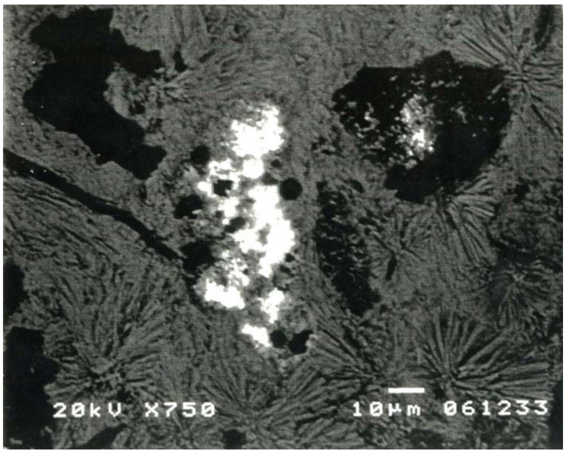

Fig. (7). SEM micro-image showing Ce (White) intergrowth inside the Mn-Oxides radiated crystals (gray).

Generally from the vertical investigation through the three ore types primary, supergene and the epigenetic ores (bottom to top respectively) as shown in Fig. (3), we noticed an upward increase in Ce, Ce/La, Ce/∑REE, in the same time an upward decrease in Eu/Sm ratio, as shown in Fig (6). All these trends are in agreement with each other and would indicate an increasing upward remobilization under oxic conditions, as the upward increase of Ce/La and Ce/∑REE ratios are good indicators for ongoing oxic diagenesis (Glasby et al. 1987; Ingri & Ponater 1987; and Varentsov, 1995). Therefore, it would indicate not only the direction of remobilization, but also the behavior of these REE ratios is in agreement with trace element behavior concluded by (El-Hasan et al. 2001).

The reducing environment that prevailed and affected the primary ores caused the remobilization of Ce upward. Because of the oxidizing environment would facilitate the oxidation of Ce^{+3} to Ce^{+4}, eventually this will develop a positive Ce anomaly. As the repeated oxic diagenesis continues it would enhances the Ce content in the ore more than other REE's (Glasby et al. 1987). Therefore, the oxidation process would lead to REE enrichment (Ingri, 1985; and Ingri & Ponater 1987). Therefore, the Ce anomaly has been used as redox measure of the environment of deposition by many authors (Glasby, 1973; Piper, 1974; De Baar et al., 1983; Ingri, 1985;Glasby et al. 1987; Ingri & Ponater 1987; Shokoriviz et al. 1992; Varentsov et al. 1993; and Varentsov, 1995).

The Oligocene manganese deposits of the Thrace basin (Turkey) exhibits a REE pattern similar to the studied supergene ore samples (Fig. 8). They have relatively moderate REE content and a positive Eu and Ce anomalies. Its pattern shows clear diagenetic features, probably due to fresh water involvement in the ore formation (Ozturk and Frakes, 1995). The similarity between the two deposits indicates that the studies ores are of diagenetic manganese ore type. On the other hand, (Ozturk and Frakes, 1995) noticed higher REE contents in the intercalating clay layers. These clays may have scavenged the REE from the ore layers. The fact that clay is a good and common scavenger of REE was reported by (Dymond et al. 1984; and Grasselly & Ponater 1988). This would explain the relative depletion of REE in the diagenetic manganese mineralization, as the mobilized solutions rich in REE would be adsorbed onto the clay phases during their percolation; eventually this would create a relatively REE-depleted Mn ores.

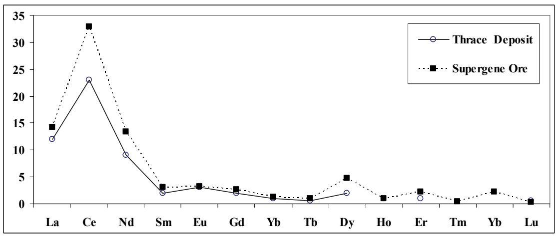

Fig. (8). Plot showing the comparison between the REE-NASC normalized patterns of the studied supergene ore samples of Mh and Db and the Oligocene Tharce manganese deposit of Turkey.

El-Hasan et al. (2001) mentioned that the primary ores characterized by higher Fe_2O_3, CaO and MgO, while supergene ores has the highest MnO_2 and P_2O_5 content beside moderate Fe_2O_3, Al_2O_3, CaO, K_2O, Na_2O and MgO. However, epigenetic ores bears higher SiO_2, Al_2O_3, TiO_2 and K_2O, which might be attributted to higher detrital incrimintation Table (4). Therefore the effect of mineral control on REE enrichment was tested by using a total of 23 high-grade supergene ore samples of Wadi Mahjoob and Wadi Dabah. The correlation coefficient matrix between REE and the possible mineral carriers such as Mn, Fe, P, Ca, Si, and Al are shown in Table (3). There was insignificant correlation between any of the REE's and Fe, P, Ca, Al or Si, and only a slight positive relationship between Mn and Eu. This might indicates that the role of the diagenetic modification is being more effective than the mineralogical control on REE enrichment.

Table (4). Correlation coefficient matrix between the REE and the major and trace elements in the ore samples of Wadi Dana (n=23).

	La	Ce	Nd	Sm	Eu	Gd	Er	Tm	Lu
Mn	-0.28	-0.17	-0.29	-0.28	0.44	-0.14	0.02	-0.13	-0.11
Fe	-0.27	-0.08	-0.17	-0.08	-0.18	0.12	0.24	0.06	0.04
Si	0.15	0.05	0.16	0.16	-0.24	-0.01	-0.17	-0.04	-0.07
Al	0.25	0.37	0.13	0.07	-0.13	-0.03	-0.05	0.04	0.10
Cu	-0.05	0.29	-0.11	-0.13	0.09	0.00	0.19	0.13	0.21
Co	-0.25	-0.11	-0.29	-0.29	0.31	-0.27	-0.26	-0.26	-0.21
Ba	-0.21	-0.21	-0.22	-0.19	0.43	-0.16	-0.16	-0.27	-0.26
Pb	-0.15	-0.11	-0.15	-0.13	0.02	-0.10	-0.12	0.00	-0.03
Zn	-0.08	0.01	-0.15	-0.18	0.43	-0.08	0.11	-0.01	0.04
Ca	0.06	0.02	0.01	-0.02	0.05	-0.09	-0.20	-0.20	-0.20
P	-0.02	0.05	-0.06	-0.10	-0.02	-0.11	-0.14	-0.10	-0.10

At 95% Confidence the significance value is 0.396

6. Conclusions

Generally the REE's content within the studied ore horizons are relatively depleted compared to other manganese ore types. No or weak positive Ce anomaly exist, while a positive Eu anomaly is noticed at all sites. There is a slight lateral variation within REE concentrations; meanwhile vertical variation in REE distribution was more obvious, which was related to the ore genetic evolution. Through genetic ore types; from the primary at the bottom, supergene and the epigenetic at the top, there is an obviuos enrichment of Ce/∑REE which is associated with depletion in Eu/Sm. Mainly due to upward oxic diagenetic process, therefore, high Ce anomaly is commonly associated with supergene ores, while the Eu anomaly is indicative for the primary ores. The REE patterns of the study area indicate the effect of the extensive diagenesis processes on the ore formation. As well it could reflect the different history of ore formation stages.

Acknowledgment

The authors are deeply thankful to the analytical center staff–Tsukuba University for their help in providing the ICP-MS. Thanks are due also to Ms. M. Takazawa for her great assisstance in the analysis. Also thanks are due to Prof. S. Kembe, University of Darmstadt / Germany for his valuable reviewing the manuscript.

References

[1] Alderton, D.H.M., Pearce, J.A., and Potts, P.J., 1980. Rare earth element mobility during granite alteration: evidence from southeast England, Earth Planet Sci. Lett, 49: 149-165.

[2] Alpin, A., 1984. Rare earth element geochemistry of central Pacific ferromanganese encrustations, Earth Planet. Sci. Lett. 71:13-22.

[3] Amireh, B.S., 1987. Sedimentological and Petrological interplays of the Nubian Series in Jordan with regard to paleogeography and diagenesis. Unpublished PhD thesis, Diss. 7, University of Braunschweig. Germany.

[4] Amireh, B.S., Schneider, W., and Abed, A.M. 1994. Evolving fluvial-transitional-marine deposition through the Cambrian sequence of Jordan, Sedimentary Geology 89:65–90.

[5] Barjous, M. O., 1992. The geology of the Ash Shawbak area, map sheet No. 3151 III. Geology Directorate/NRA, Amman. Bulletin 19 P 80. Unpub.

[6] Basta, E.A. and Sunna, B., 1970. Mineralogy and mode of occurrence of copper ores in Wadi Araba, Jordan, Extrait du Bulletin de Institute de Egypte. 11: 197-225.

[7] Basta, E.A. and Sunna, B., 1972. The manganese mineralization at Finan district, Jordan, Bulletin of Faculty of Science- Cairo Univ. 44: 111-126.

[8] Bender, F., 1974. Geology of Jordan. Contribution to the regional geology of the world. Gebrueder Borntraeger, Berlin.

[9] Byrne. R.H., and Kim, K.H., 1990. Rare earth element scavenging in seawater, Geochem. Cosmochem. Acta. 54: 2645-2656.

[10] Brookins, D.G. 1988. Eh-pH diagrams for geochemistry. Springer-Verlag, Berlin, pp 176.

[11] Calvert, S.E., Piper, D.Z., and Baedecker, P.A., 1987. Geochemistry of rare earth elements in ferromanganese nodules from DOMES Site a, northern equatorial Pacific, Geochem. Cosmochem. Acta. 51: 2331-2338.

[12] Cantrell, K.J., and Byrne, R.H., 1987. Rare earth element complexation by carbonate and oxalate ions, Geochem. Cosmochem. Acta. 51: 597-605.

[13] De Baar, H.J.W., Bacon, M.P., Brewer, P.G., 1983. Rare earth element distribution with a positive cerium anomaly in the western North Atlantic Ocean, Nature. 301: 324-327.

[14] De Baar, H.J.W., German, C.R., Elderfield, H. and Van Gaans, P., 1988. Rare earth element distributions in anoxic waters of the Cariaco Trench, Geochem. Cosmochem. Acta. 52:1203-1219.

[15] De Carlo, E., 1991. Paleooceanographic implications of rare earth element variability within a Fe-Mn crust from central Pacific Ocean, Marine Geology. 98: 449-467.

[16] De Carlo, E.H, and McMurtry, G.M., 1992. Rare-earth element geochemistry of ferromanganese crusts from the Hawaiian Archipelago, central Pacific, Chemical Geology. 95: 235-250.

[17] De Carlo, E.H., and Koeppenkastrop, D., 1990. Sorption kinetics and thermodynamics of rare earth elements onto natural and synthetic iron and manganese oxides. Eos. 71: 1417 (abstract book).

[18] Dubinin, A. V., and Volkov, I. I., 1986. Rare earth elements in metalliferous sediments of the East Pacific Rise, Geokhimija. 5: 645-662.

[19] Dymond, J., Lyle, M., Finney, B., Piper, D.Z., Murphy, K., Connard, R., and Pisias, N., 1984. Ferromanganese nodules from MANOP sites H,S, and R. control of mineralogy and chemical composition by multiple accretionary processes1988. , Geochem Cosmochem Acta. 49: 931-949.

[20] Elderfeild, H., The oceanic chemistry of the rare earth elements, Philos. Trans. R. Soc. London, Ser. A, 325: 105-126.

[21] Elderfield, H., Hawkesworth, C.J., Greaves, M.J., and Calvert, S.E., 1981. Rare earth element geochemistry of oceanic ferromsnganese nodules and associated sediments, Geochem. Cosmochem. Acta, 45: 1231-1234.

[22] El-Hasan, T., Al-Malabah, A., Kajiwara, Y., and Komuro, K., 2001. Petrology, Mineralogy, and genesis of Wadi Dana Cambrian Manganese Deposit, Central Wadi Araba Region, Jordan. Qatar Univ. Sci. J., 21:101-117.

[23] El-Hasan, T.M., and Latatifeh, M.S. 2001. Differentiation between various manganese deposits of Jordan using magnetization measurements. Al-Manarah, 7:71-86.

[24] El-Hasan, T.M., 1999. Geology, Mineralogy, and geochemistry of the Cambrian manganese deposits of central Wadi Araba region, Jordan, Ph.D. Thesis, Tsukuba University.

[25] Frakes, L., and Bolton, B., A., 1992. Special Issue devoted to Advances in Manganese Metallogenesis: Effects of Ocean Chemistry, Sea Level, and Climate on the Formation of Primary Sedimentary Manganese Ore Deposits, Econ. Geol., 87: 1207-1217.

[26] Girard, C. and Lecuyer, C. (2002): variations in Ce anomalies of conodonts through the Frasnian/Famennian boundary od Poland (Kowala-Holy Cross Mountains): implications for the redox state of seawater and biodiversity. Palaeogeogrr. Palaeoclimatol.. Palaeoecol., 181:299-311.

[27] G.G.M., 1965. German Geological Mission in Jordan 1961-1965: Final report, Unpubl. Report, Geol. Surv. Of Fed. Rep. of Germany and Natural Resources Authority. Amman. Hannover.

[28] Glasby, G. P., 1973. Mechanisms of enrichment of the rare earth elements in marine manganese nodules, Marine. Chemistry. 1: 105-125.

[29] Glasby, G.P., Gwozdz, R., Kunzendrof, H., Friedrich, G., and Thijssen, T., 1987. The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and S.W. Pacific, Lithos. 20: 97-113.

[30] Grasselly, Gy., and Ponater, Gy., 1988. Rare Earth Elements in the Manganese Deposit of Urkurt (Bakony Mountains, Hungary), *Ore Geol. Rev.,* 4: 115-124.

[31] Haskin, L.A., Haskin, M.A., Fery, F.A., and Wildeman, T.R., 1968. Relative and absolute relative abundances of rare earths. In: L.H. Ahrens (eds): Origin and distribution of elements. Pergamon, Oxford, 889-912.

[32] Ingri, F. and Ponater, C., 1987. Rare earth abundance patterns in ferromanganese concretions from the Gulf of Bothnia and the Barents Sea, Geochem. Cosmochem. Acta. 51: 155-161.

[33] Ingri, J., 1985. Geochemistry of ferromanganese concretions in the Barents Sea, Marine Geology. 67: 101-119.

[34] Kato, Y., Yamaguchi, K.E., and Ohmoto, H. (2006): Rare earth elements in Precambrian banded iron formations: secular changes of Ce and Eu anomalies and evolution of atmospheric oxygen. Geol. Soc. Amer. Mem., 198:269-289.

[35] Khoury, H. N., 1986. On the origin of stratabound copper-manganese deposits in Wadi Araba, Jordan, Dirasat. 13: 227-247.

[36] Kimberely, M., 1989. Echalative origin of origin formation, *Ore. Geol. Rev*. 5: 16-190.

[37] Klinkhammer, G., Elderfield, H. and Hudson, A., Rare earth elements in seawater near hydrothermal vents. *Nature*. 305 (1983) 185-188.

[38] Koeppekastrop, D. & De Carlo, E.H., 1990. Distribution of rare earth elements between seawater and synthetic mineral phases, Eos. 71:1417 (abstract book).

[39] Komuro. K., Agematsu, S. and Sashida, K., (2006): Chemistry of late Triassic siliceous Claystone (Toshi-type Shale) from the Oritate Area, Sambosan Belt, Kyushu, Southwest Japan. Resource Geology. 56(4): 447-455.

[40] Michard, A.F., Alarede, F., Michard, G., Minster, J.F., and Charlou, J.L., 1983. Rare-earth elements and uranium in high temperature solutions from East Pacific Rise hydrothermal vent field (13ºN). Nature. 303: 795-797.

[41] Miura, H. and Hariya, Y., 1997. Recent manganese oxide deposits in Hokkaido, Japan. In: Nicholson, K. et. al. (Ed): Manganese mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, Geological Society Special Publication, 119: 281-300.

[42] Nicholson, K., Nayak, V.K., and Nanda, J.K., 1997. Manganese ores of the Ghoriajhor - Monmunda area, Sundergarh District, Orissa, India: gechemical evidences for a mixed Mn source. In: Nicholson, K. et. al. (Ed): Manganese mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits, Geological Society Special Publication. 119: 117- 122.

[43] Ozturk, H. and Frakes, L.A., 1995. Sedimentation and diagenesis of an Oligocene manganese deposit in a shallow sub basin of the Paratythes: Thrace basin, Turkey, Ore Geol. Rev. 10: 117-132.

[44] Parcejus, B., and Bolton, B.R., Frakes, L.A. and Abboott, M., 1990. Rare-earth element geochemistry of supergene manganese deposits from Groote Eylandt, Northern territory, Australia. In: B.R. Bolton (Eds): Metallogenesis of manganese. V2, Ore Geol. Rev. 5: 293-314.

[45] Piper, D.Z., 1974. Rare earth elements in ferromanganese nodules and other marine phases, Geochem. Cosmochem. Acta. 38: 1007-1022.

[46] Rabba', I., 1994. *The geology of the Al-Qurayqira (Jabal Humrat Faddan)*, Map sheet No. 3051 II , Geology Directorate/NRA, Amman. Bulletin 28.

[47] Shaltoni, S., 1988. Geochemical characteristics of the Mn mineralization at Wadi Dana area/ South Jordan. M. Sc. Thesis. Univ. of Jordan. Amman.

[48] Shokoriviz, E.R. Shaw, T.J., and Schneider, D.L., 1992. The geochemistry of rare earth elements in the seasonally anoxic water column and porewaters of Chesapeake Bay, Geochemica et Cosmochimica Acta, 56: 3389-3402.

[49] Sverjensky, D.A., 1984. Europium equilibrium in aqueous solution, Earth. Planet. Sci. Lett. 67: 70-78.

[50] Taylor. R.P. and Fryer, B.J., 1980. Multi-stage hydrothemal alteration in porphyry copper systems in northern Turkey: the temporal interplay of potassic; porphyritic; and phyllic fluids, Can. J. Sci., 17: 901-926.

[51] Rolland, Y., Cox, S., Boullier, A.M., Pennacchioi, G., and Mancktelow, N. (2003): Rare earths and trace element mobility in mid crustal shear zones: insights from the Mont. Blanc Massif (Western Alps). Earth Planet. Sci. Lett. 214(1-2): 203-219.

[52] Varensov, I.M., Veiman, A.B., Rozhnov, A.A., Shibirk, V.I., and Sokolova, A.L., 1993. Geochemical model of formation of manganese ores of the Famennian riftogenic basin of Kazakhstan (main components, rare earths, trace elements), Lithology and Mineral Resources, 3: 56-79.

[53] Varentsov, I., 1982. Groote Eylandt manganese oxide deposits, Australia, Chem. Erde. 41: 157-173.

[54] Varentsov, I.M., 1995. Manganese ores of supergene zone: Geochemistry of formation, Kluwer Academic Publishers, Dordrecht.

[55] Wakita, H., Rey, P., and Schmitt, R.A., 1971. Abundances of the 14 rare-earth elements and 12 other trace elements in Apollo 12 samples: five igneous and one breccia rocks and four soils. Proc. 2nd. Lunar Sci. Conf. 1319-1329.

[56] Yamaguchi, K., 1994. Depositional process for the Noda-Tamagawa stratiform manganese deposits, Northern Kitakami Mountains. Unpublished. M.Sc. thesis. University of Tsukuba, Japan.

التقديم

بعون من أﷲ وبتوفيقه، يسعدني أن اقدم لكم العدد الأول من المجلد الأول من المجلة الأردنية لعلوم الأرض والبيئة(Jordan Journal of Earth and Environmental Sciences) ، وهي مجلة علمية عالمية محكمة و مفهرسة، تصدر عن اللجنة العليا للبحث العلمي في وزارة التعليم العالي والبحث العلمي في المملكة الأردنية الهاشمية. ويشرف على إعداد و نشر هذه المجلة عمادة البحث العلمي والدراسات العليا في الجامعة الهاشمية.

تحرص هيئة التحرير للمجلة الأردنية لعلوم الأرض والبيئة أن تكون مرجعاً مهماً للدارسين والباحثين، يستنيرون بما ستتضمنه من بحوث أكاديمية أصيلة ودراسات علمية عميقة في شتى موضوعات علوم الأرض والبيئة. وتسعى هيئة التحرير ومن خلال دعم وزارة التعليم العالي والبحث العلمي والجامعات الأردنية كافة المتواصل أن تصل هذه المجلة إلى مرتبة متقدمة ضمن المجلات العلمية العالمية المتخصصة في هذا المجال.

إننا نتمنى أن تشكل هذه المجلة قاعدة أساسية ترفد عملية النشر والبحث العملي في مجالات علوم الأرض والبيئة المتعددة، وتضع ما توصلت إليه الأبحاث العلمية المنشورة في المجلة في متناول أيدي الباحثين والمتخصصين. وتنشر المجلة مقالات الأبحاث العلمية التي تتسم بالجدة والأصالة، إضافةً إلى الملاحظات الفنية و التقنية ومقالات المراجعة لموضوعات حيوية و تهم الدارسين و الباحثين في مختلف حقول علوم الأرض والبيئة. ويجري تحكيم كل ما تنشره المجلة من قبل محكمّين من ذوي الاختصاص والخبرة. يشتمل العدد الأول على خمسة مقالات أبحاث أصيلة تعالج جوانب متعددة في علوم الأرض والبيئة.

أتقدم بالشكر العميق لأعضاء هيئة التحرير وأعضاء الهيئة الاستشارية الدولية للمجلة الذين قدموا النصح والمشورة لإصدار هذا العدد من المجلة. كما أتقدم بالشكر والعرفان للزملاء الذين قاموا بتحكيم الأبحاث على الوقت و الجهد الذي بذلوه في مراجعة وتحكيم هذه الأبحاث الامر الذي أدى الى تحسينها وتطويرها. وكذلك أتقدم بالشكر لكافة الزملاء للذين تقدموا بأبحاثهم للمجلة، سواء ما تم قبوله منها أو من لم يقبل، حيث أن أبحاثهم هي العنصر الأساسي في إصدار هذه المجلة.

وختاما، و بالنيابة عن هيئة التحرير و بالأصالة عن نفسي، نرجو أن نكون وفقنا على تقديم كل ما هو مفيد لكافة الباحثين والعاملين في ميادين علوم الأرض والبيئة المختلفة من خلال هذه المجلة، آملين من الباحثين والقراء الكرام عدم التردد في المساعدة وإرسال مساهماتهم واقتراحاتهم واستفساراتهم للارتقاء بهذه الدورية العلمية المتخصصة لما فيه مصلحة الجميع . والله ولي التوفيق.

أ. د. عبد الرحيم أحمد حمدان
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ISSN 1995-6681

المجلة الأردنية لعلوم الأرض والبيئة

مجلة علمية عالمية محكمة

المجلة الأردنية لعلوم الأرض والبيئة : مجلة علمية عالمية محكمة أسستها اللجنة العليا للبحث العلمي، وزارة التعليم العالي والبحث العلمي، الأردن، وتصدر عن عمادة البحث العلمي والدراسات العليا، الجامعة الهاشمية، الزرقاء، الأردن.

ترسل البحوث إلى العنوان التالي:

رئيس تحرير المجلة الأردنية لعلوم الأرض والبيئة
عمادة البحث العلمي والدراسات العليا
الجامعة الهاشمية
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