

## The Effect of the Hot Springs at the Umm Qeis Archaeological Site and Museum

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Abstract: Several recent studies have pointed out that northern parts of Jordan are exposed to high levels of the effect of the hot spring, which is widely known to have severe impacts on health, vegetation and structures. North Jordan has a wealth of ancient heritage including six out of the ten Decapolis Cities. Air pollution that comes out from the hot springs is alleged to deteriorate and erode buildings, structures, statues and monuments through acid deposition. Therefore, this research was conducted to assess air quality at Gadara, the capital of the ancient Decapolis and suggest mitigation measures that have to be adopted in order to save the ancient heritage against further deterioration. Measurements revealed that most criteria air pollutants including sulfur dioxide, nitrogen dioxide and carbon monoxide attain corresponding national ambient air quality standards. Atmospheric concentrations of NO are strongly linked to the amount of  $O_3$ . Simultaneous exposure to  $SO_2$  and  $NO_2$  demonstrated that a catalytic reaction takes place which increases the rate of sulphate production after 30 h exposure.

Key words: Decapolis, Gadara, air pollution, sulfur dioxide, nitrogen oxides, carbon monoxide, ground ozone.

## 1. Introduction

All the progressive countries worldwide are driving more efforts toward the enhancement of the conservation of the cultural heritage now, for the sake of figuring out the presence of high level of air pollution in its atmosphere. In the study of Umm Qeis "Gadara", it has been observed that the site within its surroundings has been identified as the present of the most dangerous gases in the air and their impacts on the cultural heritage in Um Qeis. And evaluate the results in order to find out the right level of air pollution that should be taken into consideration in the policies amid in the general management and conservation of the site against the air pollution threats.

## 2. Materials

The modern town of Umm Qeis is the site of

ancient Greco-Roman town of Gadara—one of the cities of the Decapolis (Fig. 1).

The Greeks were the first to marvel at breathtaking view and established their acropolis, later Roman Byzantine and ottomans would follow, leaving their own marks on this site.

The intensive successive occupation during the rich past of the city has deposited gigantic cultural layers in the site. On the other hand, the city has witnessed a natural crisis in which destructive earthquakes destroyed many buildings during the Umayyad period from 661 AD till 799 AD. After that, the city was abandoned and by dawn of the Islamic era Gadara, had become just another village. Later, it was reoccupied during the Ottoman period and recovered its significance as a major county.

### 2.1 The Natural and Geographical Background

Gadara situated 110 km north of Amman (Fig. 2). The strategic location of Gadara was an important

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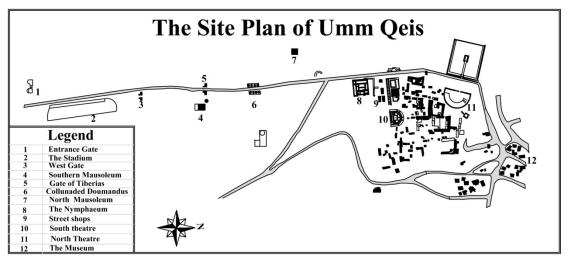


Fig. 1 A site plan for Umm Qeis "Gadara".

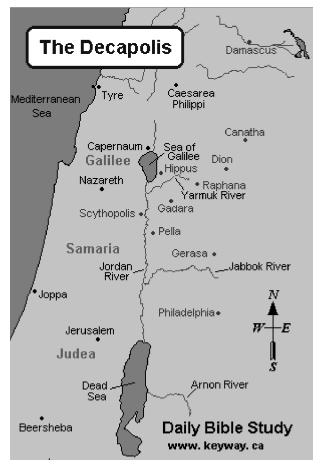


Fig. 2 Map of the Decapolis showing location of Gadara.

factor in its settlement, Umm Qeis covers the east side of a triangular plateau, the Yarmouk river is visible to the north, the south offers the forested hills of Ajloun, the Irbid plateau to the east and the fertile Jordan valley to the west. These rich surrounding made it an excellent location for inhibitors, it also offers a serene view of the fertile northern Jordan Valley.

The fact that a landscape component in Umm Qeis region has changed over time, which tend only to increase its significance as a historical setting. However, the modern human life conducted within the site and his surroundings (the hot springs) (Fig. 3) were disturbing the cultural landscape and caused the destruction of some buildings as a result of the wrong environmental policies at all levels in the last decades.

#### 2.2 The Natural and Cultural Context in Umm Qeis

The region of Umm Qeis as a whole can be divided into two main parts: the ancient city of Umm Qeis including the Greco-Roman, Byzantine until the Ottoman occupation level and the other part is the modern village of Umm Qeis and the rural landscape including farms and green spaces within the region.

First of all, the critical analysis will be made for the ancient city. The Greco-Roman remains are with great importance in the city, from the fact that the remaining parts of this period are so interesting and show the main features of an integrated Roman city in terms of city planning, monuments and artistic works, as well as its distinctive type of basalt stone.



Fig. 3 Closer view of the hot spring (Al-Hemma).

The Byzantine part of the city is dominant from the octagonal church at the side of the Cardo Street which is astonishing in its style and the dark basalt stone. What does it mean by presenting the significant and distinctive parts of the city are the emphasis of their original potential values from the historic point of view.

The Ottoman village is the most interesting part of the city. Umm Qeis, on the road from Damascus to Tiberias and hence, to the Palestinian seaports, overlooked Lake Tiberias and the Golan Heights, attracted the people during the Ottoman period to construct the village.

The main roads of Cardo and Documanos suffer from the poor management and treatment of the problem that exists by which most of the columns are fallen and the drums are scattered along those two main streets in the city. Actually, these drums were used for constructing small dwellings during the early Islamic periods settled in the region, especially, the Ottoman period. It makes use of the Roman and Byzantine remains to build their own houses and the existing Ottoman village, which shows the black basalt stone taken from the original remains of the previous periods that occupied the site. This topic should be examined and managed along with the main and secondary paths within the historic site of Umm Qeis in order to ease the movement of visitors.

### 2.3 Umm Qeis in Antiquity

Umm Qeis charm still lingers today. A large portion of the western roman theater has survived history's upheavals. Vaulted passageway supports its rows of seats, built of hard basalt stones, a row of elaborately carved seats for dignitaries stand near the orchestra, and in the century, was a large headless white marble statue of Tyche. Goddess of fortune and of the city, now displayed, at local museum.

Across from the theater is the main colonnaded street (Cardo) which was in all likelihood the town's commercial center. Also, near the black basalt theater is the terrace and along the east-west colonnaded street (decumanus), ruins of the Nymphaeum, a bath complex and a well-preserved roman mausoleum can be seen. After a few hundred meters, one can barely make out remains of what was once a hippodrome.

## 3. Method

#### 3.1 Water Analysis (Determination of Sulphate)

Sulphate is widely distributed in nature and may be present in natural water in concentrations ranging from a few to several thousand milligrams/liter. Sulphate is a divalent polyanion, having the formula of  $SO_4^{2^-}$ . It is a common contaminant, occurring widely in wastewaters, wastes and potable waters. Sulphates are of considerable concern because they are indirectly responsible for two serious problems which often associated with the handling and treatment of wastewater. Odor and sewer corrosion problem result from the reduction of sulphates to hydrogen sulphide under anaerobic conditions.

Sulphates can be determined by:

- 1. Gravimetric method with ignition of residue;
- 2. Gravimetric method with drying of residue;
- 3. Turbidimetric method.

In this exercise, the standard solution could be used in environmental analysis and be used as the Turbidmetric method for sulphate determination.

As it was assumed, that the presence of chlorine and sulphur components is coming from the hot springs, a water sample from one of the hot springs was analyzed at the Royal Scientific Society—Environmental Research Center—in Jordan. The results are given in Table 1.

The analysis of the water sample from the hot spring reveals a presence of  $SO_4^{2-}$  and  $CI^-$  in the sample. Therefore, it is suggested that chlorine and sulphur present in the surrounding environment and in the indoor environment of Umm Qeis museum, comes from the hot springs.

## 3.2 Turbidimetric Method

Sulphate ion is precipitated as  $BaSO_4$  in an acid medium, reacting with  $BaCl_2$ . The solution turns turbid due to white  $BaSO_4$  precipitate. The turbidity is measured by a nephelometer. Alternatively, the light absorbance of the BaSO<sub>4</sub> suspension is measured at 420 nm by a spectrophotometer providing a light path of 2.5 cm to 10 cm. A filter photometer equipped with a violet filter may also be used to measure the light transmittance at 420 nm. Concentration of  $SO_4^{2-}$  in the sample is determined from a standard calibration curve.

Turbidimetric method is applicable when the  $SO_4^{2-}$  concentrations is between 5 mg/L and 50 mg/L. For concentrations above 50 mg/L, dilute the sample and analyze.

Presence of a large amount of suspended matter or color in the sample would interfere in the test. Filter the sample to remove suspended matter.

#### 3.3 Standard Solutions

Are those of known concentration that are widely used in chemical analysis? Basically, a standard solution is one against a solution of unknown concentration which can be compared to determine the concentration of the latter.

## 3.4 Procedure

(1) Dilute part of the paste extract into a 100 mL volumetric flask to get  $(SO_4) < 1$  me/L;

(2) Place the solution into 250 mL Erlenmeyer flask;

(3) Pipette 100 mL aliquots of standard solutions into 250 mL Erlenmeyer flasks;

(4) Add 5 mL of conditioning solution to each flask;

(5) Introduce a clean stirring bar into the blank flask (0 me/L);

(6) Place the flask on a magnetic stirrer preset at a constant speed;

 Table 1
 Result of analysis of a water sample collected from Alshonah As-shamaliyah hot spring.

Parameter	Results (mg/L)	Test method no. & date*
NO <sub>3</sub>	< 0.1	4110-B, 2/7/2014
$SO_4$	96.5	4110-B, 2/7/2014
Cl	141	4500-Cl, D, 2/7/2014

\* Standard methods for the examination of water and wastewater.

(7) While stirring, add at once 0.2 g of  $BaCl_2 \cdot 2H_2O$  crystals with a measuring spoon;

(8) Stir for exactly 60 s and then, remove the flask;

(9) Read absorbance at 340 nm after 1-3 min.

Repeat the same procedure for the other standards and unknown samples. If the relation between standard concentrations and absorbance is linear, regress one on the other, and get an estimate of  $(SO_4^{2-})$ in the unknown samples.

$$mg SO_4^{2^-}/L$$

$$= \frac{mg so_4^{2^-} read from the calibration curve \times 1000}{mL sample}$$
(1)

# 3.5 Experimental Protocol and Measurements (Hot Springs Sampling and Water Analysis)

Spring water samples were collected from hot springs in North Jordan Valley and were analyzed for sulfur at HU Water Laboratories in the Faculty of Natural Resources and Environment.

## 3.6 Air Quality Monitoring

Gaseous air pollutants will be monitored at the proposed sampling location within Jadara—the ancient city. Monitoring station is designed to provide continuous measurement of carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub> = NO<sub>2</sub> and NO), sulfur dioxide (SO<sub>2</sub>) and ground level ozone (O<sub>3</sub>).

3.6.1 UV photometric O<sub>3</sub> analyzer

Operations based on the principle that ozone  $(O_3)$  molecules absorb UV light at a wavelength of 254 nm. The absorption is directly related to concentration by beer-lambert law, the sample is drawn through sample bulkhead and is spilt into two gas streams, one gas stream flows through on ozone scrubber to become the reference gas (Io). The reference gas then flows to the reference solenoid valve. The sample gas (I) flows directly to sample solenoid valve. The solenoid valve alternates the reference and sample gas streams between cells (A) and (B) every 10 seconds.

3.6.2 Chemiluminescence NO-NO<sub>2</sub>-NO<sub>X</sub> Analyzer

Operations based on the principle that nitric oxide

(NO) and ozone (O<sub>3</sub>) reacts to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission result when electronically excited NO<sub>2</sub> molecules decay to lower energy states specifically. Nitrogen dioxide (NO<sub>2</sub>) must first be transformed into NO before it can be measured using the Chemiluminescent reaction. NO<sub>2</sub> is converted to NO by a molybdenum NO<sub>2</sub>-to-NO converted heated to about 325 °C (the optional stainless steel converter is heated to 625 °C). The ambient air sample is drawn into the analyzer through the sample bulkhead. The sample flows through a capillary and then, to the mode solenoid valve. The solenoid valve routs the sample either straight to the reaction chamber (NO mode) or through the NO<sub>2</sub>-to-NO converter and then, to the reaction chamber (NO<sub>x</sub> mode). A flow sensor to the reaction chamber measures the sample flow. Dry air enters the analyzer through the dry air bulkhead, passes through a flow switch, through a silent discharge ozonator. The ozonator generates the ozone needed for the chemiluminescence reaction. At the reaction chamber, the ozone reacts with the NO in the sample to produce excited NO2 molecules. A Photo Multiplier Tube (PMT) housed in a thermoelectric cooler detects the luminescence generated during this reaction. From the reaction chamber, the exhaust travels through the ozone (O<sub>3</sub>) converter to the pump, and is released through the vent.

3.6.3 Pulsed Fluorescence SO<sub>2</sub> Analyzer

 $SO_2$  is measured by pulsed fluorescence  $SO_2$ analyzer that operates on the principle that  $SO_2$ molecule absorb ultraviolet (UV) light and become excited at one wavelength, then decay to a lower energy state emitting UV light at a difference wavelength. The sample is drawn into the analyzer through the sample bulkhead. The sample flows through a hydrocarbon "kicker", which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO<sub>2</sub> molecules pass through hydrocarbon "kicker" unaffected. The sample then flows into the fluorescence chamber, where pulsating UV light excites the SO<sub>2</sub> molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths which excite SO<sub>2</sub> molecules. As the excited SO<sub>2</sub> molecules decay to lower energy states, they emit UV light that is proportional to the SO<sub>2</sub> concentration. The band pass filter allows only the wavelengths emitted by excited SO<sub>2</sub> molecules to reach the photomultiplier tube (PMT). The PMT detects the UV light emission from the decaying SO<sub>2</sub> molecules. The photo detector, located at the back of fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light as the sample leaves the optical chamber. It passes through a flow sensor, a capillary and the "shell" side of hydrocarbon kicker. The sample then flows to the pump and is exhausted out the exhaust bulk head of the analyzer.

#### 3.7 Calibration of the Instruments

The calibration of the analyzers will be periodically made to ensure confidence in collected data (Table 2). Analyzers are calibrated by two points by using ozone generator: the first one is zero air point (blank sample) and the second one is span point, which is a pre-prepared known concentration. In order to assure high reliability, the weekly checking was made. Zero air point check, air-conditioned check, external battery check and vacuum pump check were made twice per week. Span point and filters checks were made monthly.

#### 3.8 Mitigation Plan

During the past decade, there has been a growing concern about the changes in urban air quality [1]. Ozone is a very reactive gas. Troposphene ozone causes negative health effects in humans and can deteriorate valuable materials [2-4]. It is 100 times or more faster than the catalytic action of iron and manganese with  $O_2$  [5].

Ozone is produced in the stratosphere at a height of 20-30 km by the action of UV radiation on oxygen. The UV concerned here is of much shorter wavelength than ever penetrates to the surface of the earth [6].

A complementary issue is the effect on building materials, particularly, their deterioration and maintenance arising from pollution. Presently, those concerns relate specifically to the rise of pollution from vehicles [1].

It is worth noting that NO emission from vehicles have doubled during the period 1950-1985, whilst over the same period, recession rates for calcareous stone have dropped by a factor of 10 [1]. In fact, the reason why there is no UV of wavelength shorter than 300 nm at ground level is that the ozone in the stratosphere effectively absorbs it [6].

The destruction of the ozone shield would have serious consequences for life on earth, and there is current argument on the one hand, supersonic aircraft, and on the other hand, fluorocarbon aerosol propellants [6].

 Table 2
 Instrument accuracy, parameter measured, lower detectable limit and output frequency for every instrument used in this study.

Instrument type	Measured parameters	Accuracy	Lower detectable limit	Output frequency
UV photometric O <sub>3</sub> analyzer	Ground level ozone (O <sub>3</sub> ppb)	$\pm 1 \text{ ppb}$	1 ppb	Every 5 minutes
Chemiluminnescence NO-NO2-NOx analyzer	Nitrogen oxides (NO <sub>x</sub> ppb)	$\pm 0.04 \text{ ppb}$	0.4 ppb	Every 5 minutes
Pulsed fluorescence SO <sub>2</sub> analyzer	Sulfur dioxide (SO <sub>2</sub> ppb)	$\pm 1$ ppb	1 ppb	Every 5 minutes
Temperature sensor	Temperature (°C)	$\pm 0.3$ °C	0.3 °C	Every 5 minutes
Humidity sensor	Relative humidity (%)	$\pm 3\%$	3%	Every 5 minutes
Wind speed sensor	Wind speed (m/s)	$\pm 0.3 \text{ m/s}$	0.3 m/s	Every 5 minutes

Airborne pollutants affect buildings in two ways of decay and soiling. Soiling is the discoloration of a building whilst decay result in the destruction of the building fabric [1]. It has been found that indoor concentrations of ozone are generally lower than outdoor concentrations [4, 7]. Typical concentrations in museum rooms are 1-10 ppb for museum rooms, the recommended concentration of ozone is set to 0 ppb [6, 8]. Most of their indoor ozone seemed to originate outdoor as indoor and outdoor concentrations correlated closely over time [4, 9].

Indoor  $O_3$  levels also correlate positively with outdoor temperatures. In addition, the I/O ratio is affected by homogenous and heterogeneous chemical reactions. That is to say ozone is removed by reactions in the gas phase and by deposition and reaction on the room surfaces. Consequently, a high rate of reaction of  $O_3$ on indoor materials will reduce the I/O ratio [10].

The ozone surface reaction could be a pure decomposition of ozone or an oxidation of the surface material. On organic materials with unsaturated carbon bonds, a surface oxidation reaction could increase the reaction rate. Aldehydes and some other VOCs have been detected as reaction products of ozone deposition on polymeric organic materials [4, 11, 12].

Ozone has a specific and complete action on unsaturated organic compounds, that is to say it will break every double bond on a carbon chain with which it comes into contact. This destroys the material. In this way, transverse cracks appear on rubber bands which then snap when stretched. However, the attack by ozone does not end with rubber bands which can get many other materials. It is a powerful oxidant, that is to say destroyer of almost all organic material. The effect of ozone on certain material such as cellulose may be due to its partial conversion to hydrogen peroxide by reaction with water [6].

Ozone also increases the rate of oxidation of silver and iron and of sulphidation of silver and copper. Hopefully, one may suppose that the visitors may in this case help conservation, since every inhalation is likely to destroy all the ozone in the breath [6].

It seems that ozone undergoes unimolecular decomposition on surface. The surface would, form moderate to high humidity, be covered with an increasing number of mono layers of water molecules [13].

The work studied by Sehested et al. [14] showed that  $O_3$  is most probably diffusing to the surface where it would solvate to some extent before further decompositions. The decomposition reaction is differently initiated in alkaline and acidic solutions.

Lowered measured deposition velocities of  $O_3$  in conservation runs on the concrete sample may be related to changed surface properties probably affecting the bonding strength and surface coverage of adsorbed water.

Sulphur dioxide and nitrogen oxides are gaseous components which react directly with the stone surface by forming acids in the presence of water and oxidizing agents. These acids react with the stone to form salt which either crystallizes out within the stonework resulting in physical damage or they are washed away resulting in a loss of material [1].

#### 4. Results and Discussion

Atmospheric concentrations of NO are strongly linked to the amount of  $O_3$ —another major oxidant within the system. The balance between the two is also affected by the presence of free radicals. The principle reaction at night time is the formation of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, accompanied by a reduction in O<sub>3</sub>. N<sub>2</sub>O<sub>5</sub> is a moderately strong oxidizing agent and readily removed by water vapor to form the acid HNO<sub>3</sub> [1]. Thus, a reduction in the erosion rates would be anticipated with the reduction in sculpture dioxide [15].

Johnson et al. [16] looked at the co-deposition of HCL, SO<sub>2</sub>, NO and O<sub>3</sub> gas in conjunction with coal and diesel coated sample using mass change and water soluble reaction products as the measure of

deterioration. They conclude that HCL acts addictively with all combination of the gases and again observe the marked increase in the amount of deterioration when  $SO_2$ , NO and  $O_3$  are combined.

Elfving et al. [17] used IR at gas concentration of 1 ppm to establish the effect of both NO<sub>2</sub> and O<sub>3</sub> in the process of sulphation. For SO<sub>2</sub> alone, there is an immediate formation of sulphite at the surface of the calcite under humid conditions. NO sulphite is formed in dry conditions. The surface sulphite gradually deteriorates under humid condition. On preconditioned sulphite surfaces formed on calcite,  $NO_2$  is less efficient than  $O_3$  in oxidizing the sulphite NO<sub>2</sub>. Moisture requires present whilst the O<sub>3</sub> operates in both moist and dry conditions albeit at slower rates for the latter condition.

Exposing calcite to  $SO_2$  and  $O_3$  simultaneously demonstrated that sulphate is the preferred reaction product. Simultaneous exposure to  $SO_2$  and  $NO_2$ demonstrated that a catalytic reaction takes place which increases the rate of sulphate production after 30 h exposure. The author's conclusions from this experimentation are:

Ozone reacts rapidly with surface sulphite to form sulphate both at dry and humid conditions;

Simultaneous exposure of calcite to  $O_3$  and  $SO_2$  at dry conditions does not result in any sulphite nor sulphate formation at the surface;

Simultaneous exposure of calcite to  $O_3$  and  $SO_2$  at humid conditions results in rapid sulphate formation [17].

This suggests that the reaction occurs at the surface of the calcite and not in the gaseous phases and the increased production of sulphate is by an activated complex, involving the surface water film,  $NO_2$ ,  $SO_4$ and  $O_2$ .

## 5. Conclusions

This study was undertaken in order to assess air quality at northern Jordan which includes seven ancient cities formed the historic Decapolis trade center. Measurements took place at Gadara, the capital of the Decapolis. Criteria air pollutants that were measured include carbon monoxide, sulfur dioxide, oxides nitrogen and ground ozone. Basic meteorological parameters were also measured. Findings indicate that most detected air pollutants where below their maximum corresponding national limits that are set by Jordanian ministry of environment. However, ground ozone was exhibited several incidences where it has exceeded maximum limits set by WHO. High ozone values go in line with previously published modeling results which predict high values of ground ozone at north Jordan. There is a great concern that ozone may expedite erosion and deterioration rates of rocks at Gadara, therefore, a mitigation plan has to be strictly adopted in order to protect the treasures of Gadara as well as other historic sites at north Jordan. Findings also indicate that westerly and northwesterly wind dominated wind site during this measurement campaign, which implies that the monitoring site and the city of ancient Gadara, are impacted by air pollutants that are originated somewhere to the west or northwest of Gadara.

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