

POLLUTANT DISTRIBUTION IN A SHALLOW AQUIFER IN THE EASTERN PROVINCE OF SAUDI ARABIA

Muhammad Sadiq* and I. Alam**

*Water Resources and Environment Division, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

**Deputy Mayor for Municipal Services, Jeddah Municipality, Saudi Arabia

ABSTRACT

Duplicate shallow aquifer groundwater samples were collected from 100 monitoring wells in the Eastern Province of Saudi Arabia. Concentrations of cadmium, copper, chromium, iron, nickel, lead, vanadium, and zinc were determined in these samples. Auxiliary data such as concentrations of calcium, magnesium, potassium, sodium, chloride, sulfate, alkalinity, salinity, total dissolved salts, and pH were also collected in this study. Analysis of variance showed significantly ($p < 0.05$) wide variations in the concentrations of the above parameters. The contour maps of metal concentrations indicated that these variations were related to important landmarks in the study area. The results of correlation analyses suggest that geographical as well as chemical factors may influence metal distribution in the groundwater samples. The analytical data were normalized and attempts were made to separate geographical and chemical variations of pollutants in the study area.

KEYWORDS

Groundwater, metals, salinity, contamination, aquifers, alkalinity, metal distribution.

INTRODUCTION

The Industrial City of Jubail petrochemical complex spreads over an area of about 170 km² on the southern Saudi coast of the Arabian Gulf (O'Brien et al. 1992), out of which an area of about 40 km² was specially prepared by landfilling, with either virgin sand or dredged marine material, for the construction of primary and secondary industrial facilities over alkha terrain. The Industrial City of Jubail is still expanding and diversifying its facilities.

All industrial facilities produce wastes that could become environmentally hazardous if managed improperly, and the Industrial City of Jubail is no exception. Accidental spillage of industrial wastes and subsequent seepage may contaminate soil and groundwater. The Industrial City of Jubail stores its hazardous wastes in specially constructed lined landfill sites. A rupture of the landfill liner thus may let hazardous waste leachate escape and

contaminate soil and groundwater. In summary, there are several possibilities of soil and groundwater contamination in the Industrial City of Jubail.

Soon after the establishment of Industrial City of Jubail, the shallow groundwater table in the area started to increase gradually. Presently, shallow aquifers in are a few meters below the surface. The Royal Commission for Jubail and Yanbu is endeavoring to contain groundwater levels in the City (O'Brien et al. 1992).

The shallow groundwater aquifers in Industrial City of Jubail are saline (O'Brien et al. 1992). Because of high salinity, these aquifers are of limited economic or social significance. As stated above, the shallow groundwater aquifers in Industrial City of Jubail may be threatened by the leakage and later seepage of industrial wastes into the soil (NCFC: 1993). These shallow aquifers appear to be inter-connected and ultimately connected to the Arabian Gulf (Dames and Moore, 1976) and their contamination thus may affect the marine ecosystem of the Gulf. Accordingly, in spite of the limited economic and social utility of the saline aquifers at present, there is an environmental urgency to protect these shallow groundwater aquifers from pollution. This paper is to discuss current distribution of selected pollutants in the shallow groundwater aquifers of the Industrial City of Jubail and attributes the distribution to both geographical and industrial features.

MATERIALS AND METHODS

On the basis of available information (RCJY, 1988), the shallow aquifers in the Industrial City of Jubail were divided into hypersaline, saline, and non-saline groundwater. Sampling locations were selected to represent these salinity conditions. Groundwater samples were also collected from the vicinity of obviously potential pollution point sources in the study area. A geographical location map of 100 sampling locations, along with major landform features, are shown in Figure 1.

Groundwater samples were collected by following the guidelines of the USEPA (Scalf et al., 1980). The stagnant water in the sampling well was pumped out and after a 30 minute settling period, the groundwater in the wells was gently drawn up using plastic tubing. The groundwater was allowed to flow for two minutes, the plastic container was rinsed three times with the same groundwater, and then a four liter water sample was collected. Duplicate samples, collected apart by five minutes only, were taken from each well. The samples were placed on ice and transported to the laboratory for analyses. In the laboratory, the groundwater samples were filtered through 0.45 micron pore size filter papers. The filtered water samples were used for chemical analyses.

Concentrations of total dissolved salts in the samples were determined gravimetrically. On the basis of salt concentrations, the samples were sorted into low salinity (total dissolved solids <10,000 mg/l), medium salinity (total dissolved solids between 10,000 and 50,000 mg/l), and hypersaline (total dissolved solids > 50,000 mg/l) groundwater. The low salinity groundwater samples were analyzed for all metals directly using an inductively coupled argon plasma optical emission spectrometer (ICAP). Concentrations of cadmium, cobalt, copper, iron, manganese, molybdenum, nickel, lead, vanadium, and zinc in the medium and hypersaline groundwater samples were complexed with pyrrolidine carbo dithioic acid (PCDA) and extracted in chloroform (ASTM, 1990). Aluminum in the samples was determined using a spectrophotometric technique that uses the ethylene diamine tetra-acetic

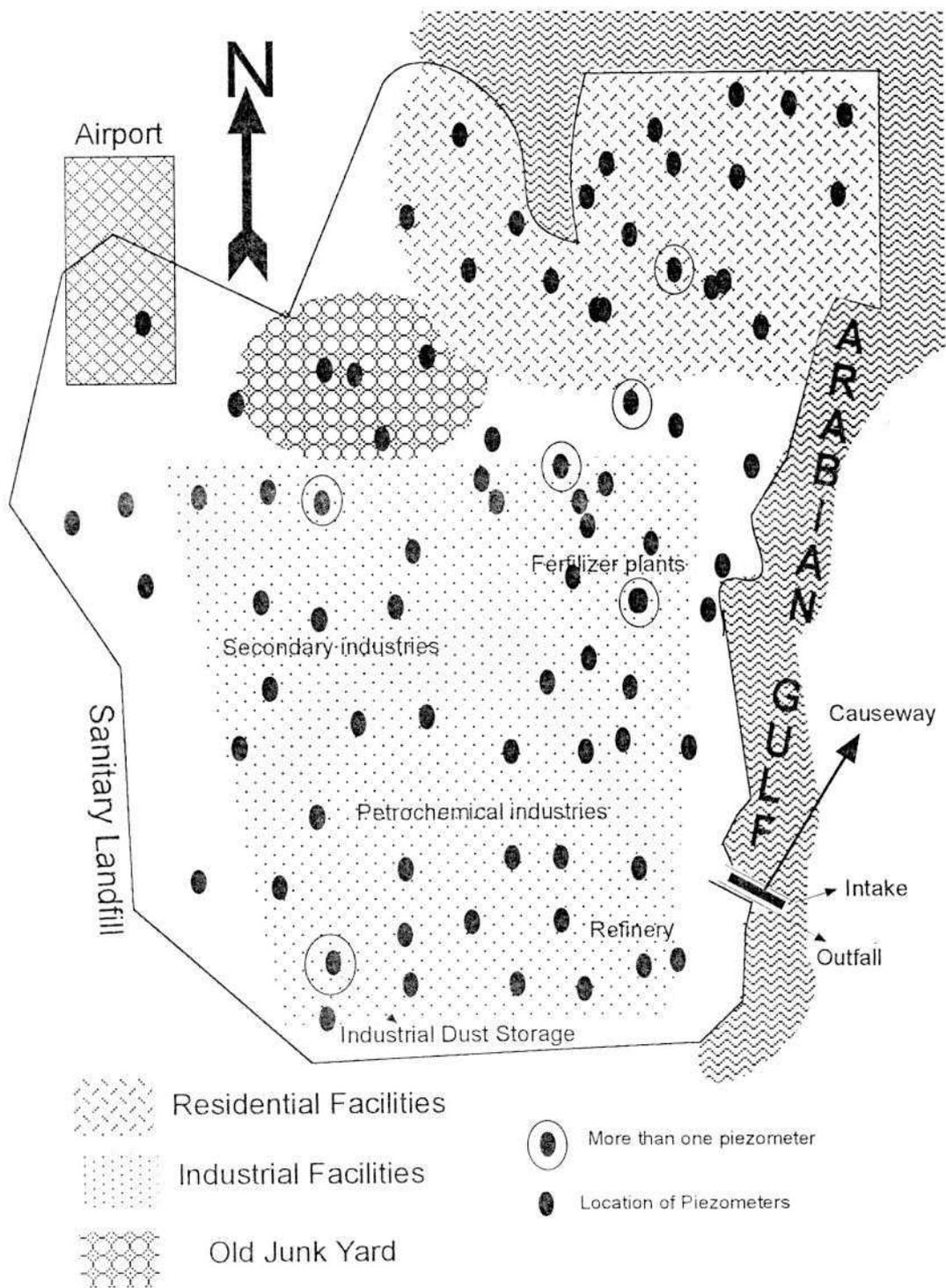


Fig. 1. A map of the groundwater sampling locations and important landmarks in the study area.

acid - EDTA procedure (Grasshoff et al. 1983). Total dissolved chromium (both Cr(VI) and Cr(III)) in all the samples was co-precipitated with Fe(III) hydroxide prior to analysis using the ICAP (Grasshoff et al., 1983). Concentrations of calcium, strontium, magnesium, potassium, titanium, and sodium were determined directly using an ICAP. Arsenic concentrations in the groundwater samples were determined using a hydride generation technique. The pH of each groundwater sample was determined in the field using a combination glass electrode. Concentrations of chloride, alkalinity, and sulfate in the groundwater samples were determined using procedures recommended by USEPA (1979).

RESULTS AND DISCUSSION

Concentrations of the above mentioned parameters in the collected groundwater samples are summarized in Table 1. The wide variations ($p < 0.05$) in the ranges of analytical data in Table 1 suggest that composition of groundwater samples is affected by some external sources. Analysis of variance of the analytical data also showed that sampling locations significantly ($p < 0.05$) influenced the elemental composition of groundwater samples.

Table 2. A summary of chemical composition of groundwater samples collected from the industrial complex.

Parameter	Observations	Mean	Standard Deviation	Minimum	Maximum
Aluminum (mg/l)	100	14.09	18.17	0.02	92.50
Arsenic (ug/l)	100	2.19	2.06	0.05	11.14
Cadmium (ug/l)	100	1.11	1.30	0.04	8.42
Cobalt (ug/l)	81	1.14	2.22	0.02	15.93
Chromium (ug/l)	20	14.07	7.64	5.99	37.35
Copper (ug/l)	100	6.16	5.20	1.82	51.73
Iron (ug/l)	100	90.36	160.72	6.44	912.10
Lead (ug/l)	100	88.21	212.46	0.08	1570.20
Manganese (ug/l)	100	0.09	0.17	0.03	1.27
Molybdenum (ug/l)	100	59.34	86.99	0.18	552.16
Nickel (ug/l)	100	5.05	3.59	0.25	20.03
Strontium (mg/l)	100	23.39	19.60	0.16	89.60
Titanium (ug/l)	100	0.23	0.56	0.01	4.75
Vanadium (ug/l)	94	7.46	11.60	0.04	55.69
Zinc (ug/l)	100	70.57	73.39	4.25	323.80
Calcium (mg/l)	100	1119	938	21	3846
Magnesium (mg/l)	100	2324	2537	7	8958
Potassium (mg/l)	100	688	761	3	2626
Sodium (mg/l)	100	20730	23402	30	81650
Alkalinity (mg/l)	100	88	49	10	281
Chloride (mg/l)	100	37583	42740	55	173720
Sulfate (mg/l)	100	2416	2122	16	10120
pH	100	7.64	0.43	6.57	8.48

Figure 1 shows several landmarks which might affect groundwater composition in the study area. The north-eastern part of the study area (residential area) is heavily irrigated with the treated wastewater from the municipal and industrial sources within the Industrial City of Jubail. In addition to the residential area, there is a greenbelt along the coast of the Arabian Gulf which is also irrigated with the treated industrial wastewater. Seepage of irrigation water to shallow aquifers can alter groundwater composition. A small airport facility is situated on the northwestern side of the study area. Another important feature is the sanitary landfill area on the southwestern side of the industrial city. All hazardous wastes generated at the industrial city are stored here in specially constructed landfill sites. The landfill site is well maintained. However, any leakage from the landfill area could contaminate groundwater in its vicinity. Industrial dust from the bag-house of a steel manufacturing complex is stored in the open in the factory's compound as shown in Figure 1. This dust is typically rich in metals, such as chromium, molybdenum, nickel, titanium, etc., some of which might have been leached to the groundwater over time. All industrial facilities are concentrated in the southeastern part of the industrial city. Recently, it has been reported that process water from a fertilizer plant has leaked to groundwater (NCFC, 1993). Unfortunately, no record was available to the authors regarding the occurrence of such incidents in the past. It must be assumed, given the nature of the industrial facilities present, that other similar incidents might have contaminated groundwater, or might in the future.

A contour mapping technique was used to investigate the location (geographical) effects on the distribution of metal concentrations in groundwater samples. The contour technique considers the actual concentration data and location of each well. Location of each well was graphically determined. Sampling location position and respective metal concentration were entered in a computer. Using "Surfer" software, contour maps of metal distribution in the groundwater samples were developed. As an example, the distribution of iron in the groundwater samples is shown in Figure 2. Two higher iron concentration areas are recognizable in this figure. The most extensive high iron region is located in the residential area. It has been shown that corrosion of reinforced bars in the foundations of buildings in the residential area has been very severe. The corrosion product appears to be responsible for elevated levels of iron in groundwater samples from this area. The other area of high iron concentrations is located around the industrial dust storage and Al Hadeed steel plant. Leachate from the dust and emissions from Al Hadeed may be responsible for high iron concentrations in this area.

A contour map of copper concentrations in the groundwater samples is shown in Figure 3. Like the iron distribution, the highest copper concentrations were found in the residential area. Corrosion of utility pipes may be responsible for the elevated levels of copper in the groundwater samples from the residential area. Copper concentrations in the middle of the Industrial City were also relatively high. Many primary industries (Petmark, Refinery 2, Al Hadeed) and secondary industries are located in this area. Contributions of these industrial facilities to copper concentrations in groundwater samples could not be ascertained. Contour distribution maps of other elements were prepared similarly. It was found that in many cases, contamination of groundwater appears to be related to the main features of the study area as discussed above.

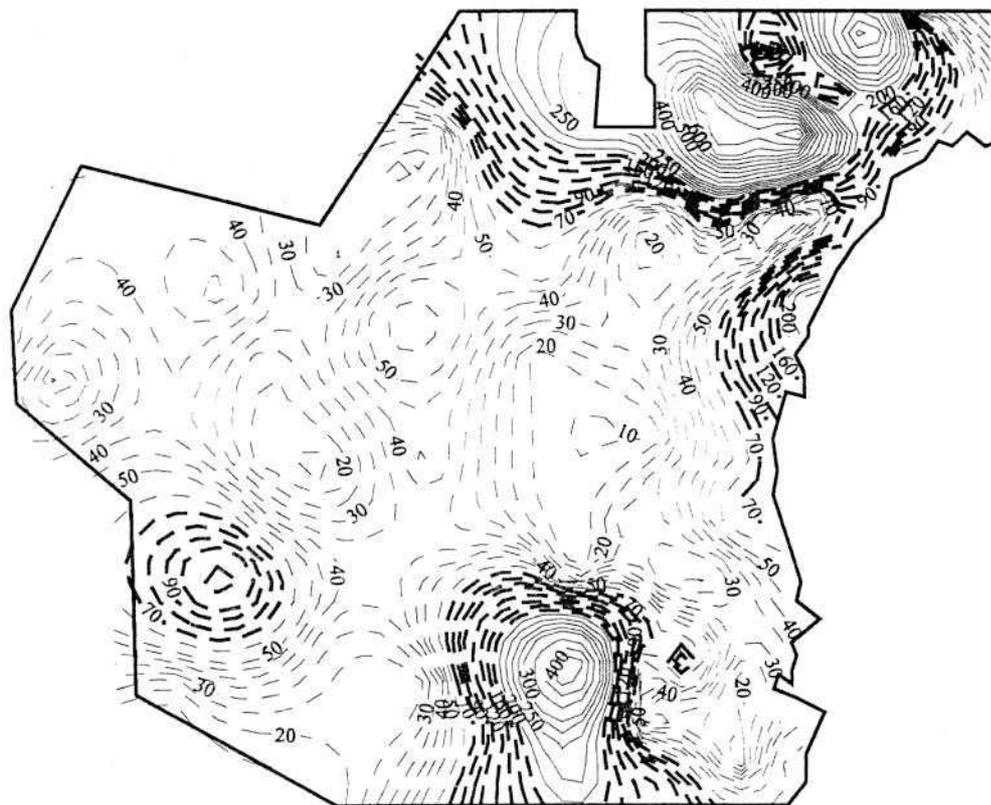


Fig. 2. A contour map of iron concentrations ($\mu\text{g/l}$) in the groundwater samples.

Contour mapping showed elevated concentrations of aluminum, cadmium, lead, and molybdenum in the groundwater samples from the northwestern area of the industrial city. There was a junkyard containing metallic objects, such as cars, steel bars, etc., in this area which was overlaid by filling material during site preparation for the industrial complex. The nature and exact location of the objects in the junkyard could not be determined. Corrosion of the buried metallic structures and subsequent dissolution of corrosion products in groundwater may be responsible for the elevated concentrations of the above metals in this area. Groundwater in this area was hypersaline (very high chloride concentrations). Complex formation with chloride may be another factor that contributes to elevate metal concentrations in this area.

Elevated concentrations of zinc were found to the north of the seawater cooling canal intake and stretches along the coast. This area is an established greenbelt region which is irrigated with treated industrial wastewater containing 0.01 to 0.2 mg/l of zinc. Another source of contamination of groundwater may be leakage of process water from a fertilizer plant in this area as recently reported (NCFC, 1993). Chemical composition of the process water from the fertilizer plant was not available. Concentrations above background of copper, nickel, lead, and zinc were found in the groundwater samples collected from the vicinity of the sanitary landfill area.

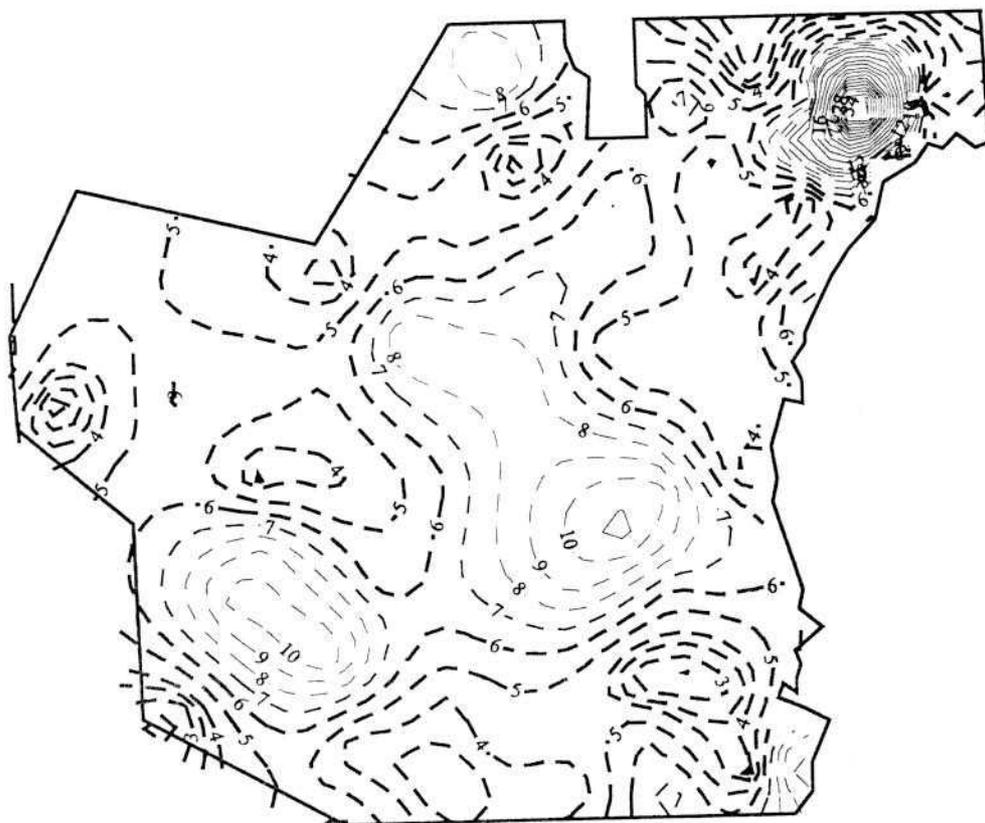


Fig. 3. A contour map of copper concentrations ($\mu\text{g/l}$) in the groundwater samples.

Groundwater samples collected from the vicinity of the steel factory contained concentrations of chromium, iron, titanium, nickel, vanadium, and zinc higher than the background. Industrial dust from the bag house of the steel factory has been stored in the open in the steel factory compound and appears to be a contributing cause. Chemical composition of one dust sample was as follows:

Chromium	400 mg/kg
Lead	200 mg/kg
Nickel	3000 mg/kg
Titanium	200 mg/kg
Vanadium	500 mg/kg
Zinc	1000 mg/kg

Leaching of the above metals from the dust pile could be responsible for higher chromium, iron, titanium, nickel, vanadium, and zinc in the groundwater in this area.

Groundwater samples from the residential area contained elevated concentrations of iron, lead, nickel, molybdenum, vanadium, and zinc. Several factors may contribute to increase metal contamination in this area. Some of those factors have already been discussed. Vegetation in the residential area is irrigated with the treated industrial wastewater. The average chemical composition of 10 irrigation water samples (Alam and Sadiq, 1993) is summarized below:

Iron	0.2-0.7 mg/l
Lead	0.1-0.3 mg/l
Copper	<0.1 mg/l
Zinc	0.01-0.22 mg/l

Irrigation may be contributing to relatively higher concentrations of iron, lead, and zinc in the residential area. It has also been reported that reinforcing bars in the foundations in the residential area are severely suffering from corrosion (personnel communication). Dispersion and dissolution of the corrosion product may also be partially responsible for the elevated concentrations of the above metals.

In addition to the above trace metals, concentrations of major cations (sodium, calcium, potassium, magnesium, and strontium) and anions (chloride, sulfate, and bicarbonates) were also determined in the groundwater samples. The above ions are naturally occurring elements in the Saudi groundwater. A comparison between the distribution patterns of major elements with those of the trace metals will help in further explaining the chemistry of trace metals in the Jubail shallow aquifers.

Inter-elemental associations were investigated by using correlation techniques. Strong affinities between metals (aluminum, cadmium, and lead) and anions, such as chloride and sulfate, were found. As an example, interactions between aluminum and chloride are shown in Figure 4. In addition to contamination from point sources, complexes of the above metals with anions may be another reason for the elevated concentrations of aluminum, lead, and cadmium found in the groundwater samples from the contaminated areas (Lindsay, 1979; Sadiq 1992).

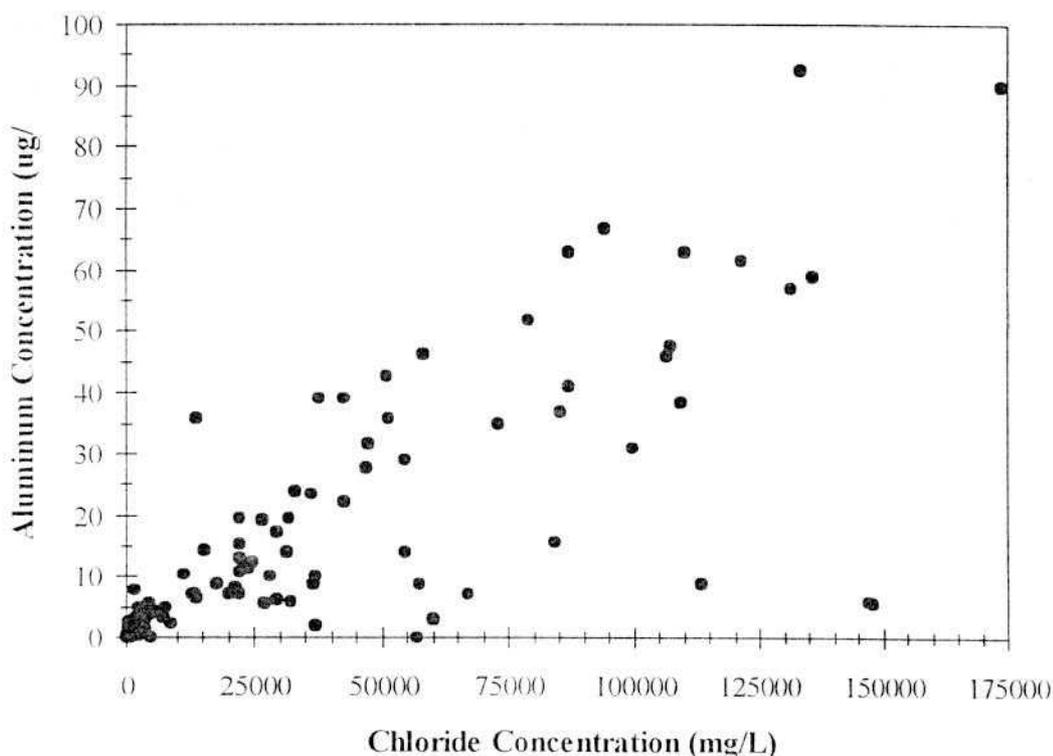


Fig. 4. Association between aluminum and chloride concentrations in the groundwater samples.

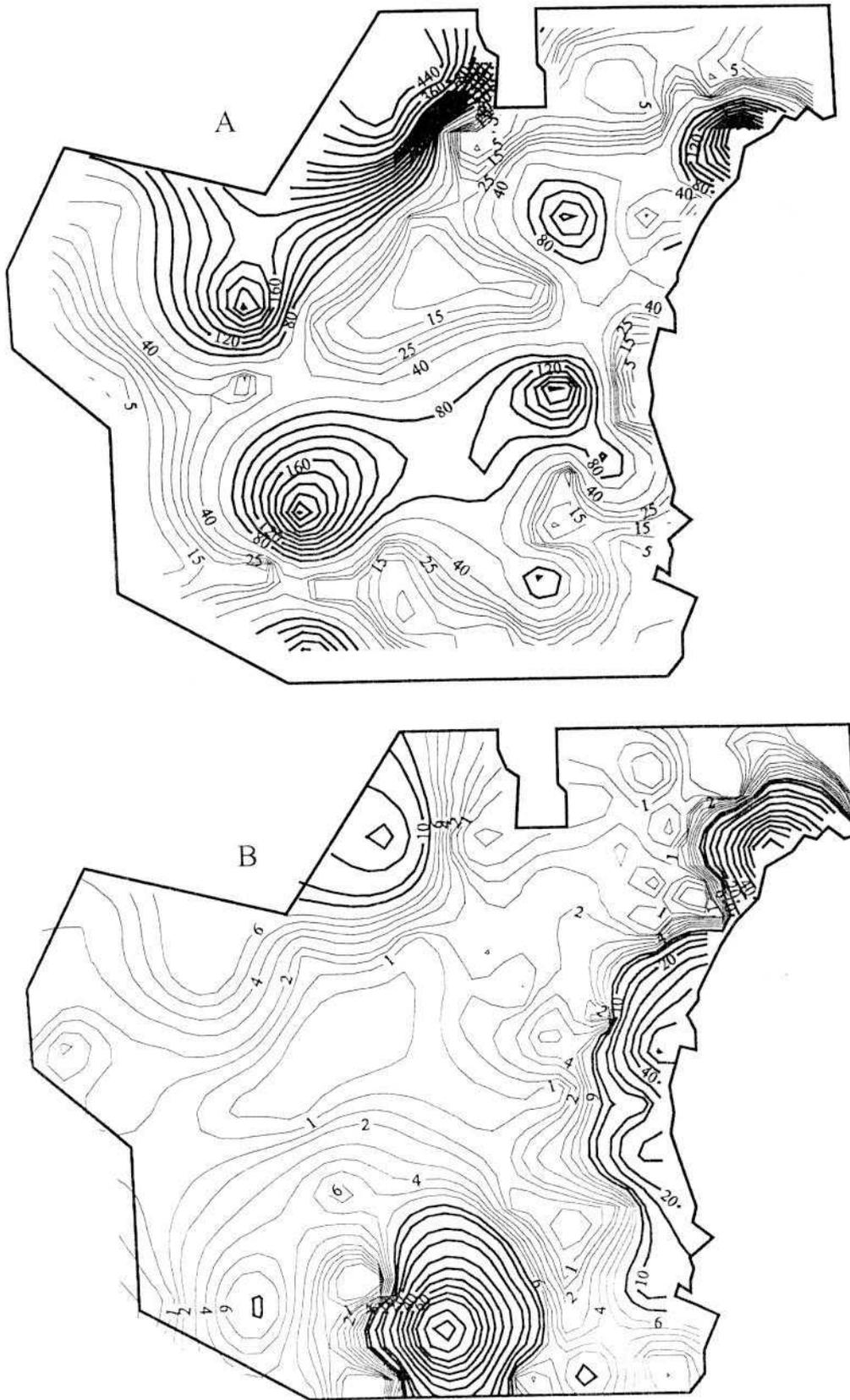


Fig. 5. Contour maps of lead concentrations (Fig. A, in $\mu\text{g/l}$) and lead/chloride values (Fig. B) in groundwater samples.

The foregoing paragraph indicates that geographical as well as chemical factors may influence metal distribution in the groundwater samples. To investigate the geographical effects, the analytical data were normalized for chemical variability. Chloride and sodium are conservative elements, i.e., are not affected by pollution point sources in the study area. Therefore, chloride concentrations were used for data normalization. If there is no contamination from a point source in the study area, trace metal/chloride ratios should vary in a narrow range, whereas extreme variations in the metal/chloride may suggest groundwater contamination from a pollution point source.

Ratios of metal/chloride were computed and used, instead of actual concentrations, to evaluate the influence of geographic features. Concentrations of lead and values of lead/chloride ratios are plotted in Figure 5. When normalized for chloride association, the distribution changed significantly (Figure 5B). The highest lead contamination was found in the vicinity of the industrial dust storage. Another area of lead contamination was found along the coast of the Arabian Gulf. This area has a green belt and is heavily irrigated with the treated industrial wastewater which contains 0.1 to 0.3 mg/l of lead. The seepage of irrigation water to shallow groundwater in this area may be responsible for the elevated lead concentrations in groundwater samples from this area. Contour maps of aluminum concentrations and values of aluminum/chloride are shown in Figure 6. Similar to the lead concentrations, contour maps of aluminum also indicate different patterns of aluminum concentrations and values of aluminum/chloride.

Contour maps of other element/chloride ratio were developed similarly. It was found that major cation/chloride, salinity/chloride, and total dissolved salts/chloride ratios vary in a relatively narrow ranges. Contour mapping of the major elements ratio data did not show a particular geographical trend. Contrary to the major elements, values of trace metal/chloride ratio vary over a wide range and suggest point pollution sources. For example, the groundwater samples from the industrial dust area indicated higher variability between chloride and chromium, copper, iron, nickel, lead, and zinc concentrations. Another geographical area where metal/chloride ratio were found to be large was in the vicinity of an oil refinery. This group of elements consists of cadmium, copper, molybdenum, nickel, titanium, and vanadium. The exact reasons for the elevated ratio data are not known. Groundwater samples collected from the vicinity of a fertilizer plant and green belt area contained relatively higher ratios of aluminum, copper, lead, zinc, and nickel to chloride.

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