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Inorganic and Organic Environmental Geochemical Issues of the Gaza Strip-Palestine

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Berichte aus der Umweltwissenschaft

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Inorganic and Organic Environmental Geochemical Issues of the Gaza Strip-Palestine

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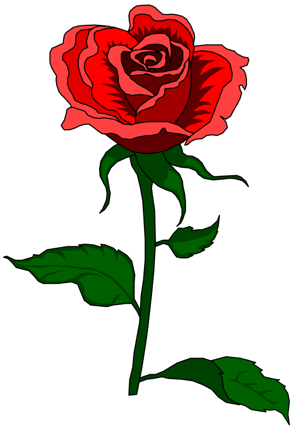
’’ رب أوزعني أن أشكر نعمتك التي أنعمت علي وعلى والدي وأن أعمل
صالحاً ترضاه وأدخلني برحمتك في عبادك الصالحين‘‘

“O my Lord! So order me that I may be grateful for Thy favours, which Thou has bestowed on me and on my parents, and that I may work the righteousness that will please Thee: and admit me, by Thy Grace, to the ranks of Thy Righteous Servants”

To my parents, Raeda, Yara and beloved Hasan



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SUMMARY

The multi-faceted nature of the environmental issues in the Gaza Strip, Palestine requires an interdisciplinary, integrated approach to management strategies. The Palestinian Ministry of Environmental Affairs (MEnA) has set research priorities based on an understanding of the complexity of the Gaza environment through many years of study. The top priority has been and will remain the human health risks and hazards due to the deterioration of the water, air, and soil. Environmental deterioration is not a new problem. It is rather an accumulation of natural, political, economic, and social conditions. These conditions add a layer of complexity to ameliorating the environmental problems. Although this research mainly focuses on the scientific side, the researchers recognize that addressing political, economic, and social factors is essential for any proposed solution to the deteriorated environment.

While this study focuses on Gaza, some of the research extended to areas beyond Gaza. Environmental problem generally extend beyond small geographic areas and do not respect political boundaries. Thus, it is important to understand the regional environmental situation so as to establish regional cooperative efforts that are based on scientific awareness.

This study was conducted in parallel with a research project (Gaza Project) that is funded by the German Ministry of Education and Scientific Research. Through this project, we collected and tested the required samples and consulted with the local experts. This study has combined two branches of science that are rarely combined dissertation projects; the organic and the inorganic geochemistry. For this reason, knowledge not only in organic and inorganic geochemistry but also in many other relevant subjects was necessary. Examples of these subjects include, but not limited to, water quality, water quality management, soil science and geology, microorganisms and biology, and statistics and its applications. Moreover, it was also important to follow some of available literature, specialized lectures, local and international conferences, and weekly meetings at the institute where this study was conducted.

Each chapter in this study reflects a focused scientific approach that essentially allows it to stand by itself as independent study. The chapters contain some repetitions especially in describing sampling methods and the study area (Gaza Strip). These repetitions result because each chapter constitutes an article that has been published or is in the process of being published in a specialized international scientific journal. All these articles are put together to form one complete study.

The sequencing of the chapters is not based on chronological order, but on the priorities of the national Palestinian environmental strategy. Hence, water and public health come first followed by wastewater, solid waste, land use, agricultural practices and their impacts. The first chapter focuses on the geochemistry of groundwater while the second studies examples of pollutants and their impacts on the public health. The third and fourth chapters tackle wastewater issues, including reuse potential, and the impact on soil and groundwater. Wadi Gaza, which is a hub for wastewater and solid waste disposal, is the fifth chapter. The sixth chapter looks at geochemical properties of the soil in Gaza, while the final two chapters focus on the effect of agricultural practices on the soil, including pesticide concentrations and transport in soil and groundwater, and trace metals concentrations. The following is a brief description of each chapter.

Chapter One: Groundwater. In a course of a 3-year monitoring program, the results show that the trace elements in the groundwater of the Gaza Strip do not generally pose any health or environmental hazard. In spite of that, only 10 % of the municipal wells meet the World Health Organization (WHO) standards. Cl^-, NO_3^- and F^- concentrations are 2-5 times higher than the WHO standards in 90 % of the wells tested with average concentrations of 750, 75 and 1.6 mg/l, respectively. Several private wells should not be used for drinking purposes as the average levels of Zn, Cd, Pb, Fe and As were 58, 30, 270, 468 and 10 µg/l, respectively. A severe water dilemma will appear in the near future from both quality and quantity aspects.

Chapter Two: Fluoride: an example of groundwater pollution and the impact on human health. Fluoride is selected to represent groundwater pollution and the impact on human health. Monitoring of fluoride levels in 73 groundwater wells and 20 topsoil samples for the last three years revealed a general trend of increasing levels from north to south of the Gaza Strip. However, X-ray diffraction (XRD) showed that none of the four major fluoride minerals were detected in soil samples. The PHREEQC model showed that fluorite (CaF_2) was the main donating mineral of fluoride ions to groundwater. A high positive correlation was found between fluoride concentrations in groundwater and occurrence of dental fluorosis. Among 353 school children of the five geographic areas of the Gaza Strip, 60% had signs of dental fluorosis in permanent dentitions. The highest occurrence, 94%, was in Khan Yunis, followed by 82% in Rafah, 68% in the middle area, 29% in Gaza and the lowest occurrence of 9% was in the northern area. These percentages were directly proportional to the average concentrations of fluoride in groundwater of each area: 2.6, 0.9, 1.7, 1.2, and 0.7 ppm, respectively. The occurrence of the disease was due to intake of high amounts of fluorides in drinking water, tea and fish.

Chapter Three: Wastewater in the Gaza Strip. About 40% (50,000 m^3/day) of the wastewater generated in Gaza is currently discharged into the sea; a minor part infiltrates into the soil and contaminates the groundwater. Up to now there has been very little production of sludge as all existing wastewater treatment plants are deficient and operating with old technologies. The main objective of this chapter is to describe the concentrations of trace metals and some major parameters of domestic and industrial wastewater and sludge for the first time. Moreover, the chapter tries to highlight the various options that aim to reuse the treated wastewater and sludge in the Gaza Strip in a manner that will ensure agriculturally sustainable development. The results revealed that domestic wastewater effluent contains considerable amounts of trace metals and the partially functional treatment plants of Gaza are able to remove 40-70% of most metals during the treatment process. Trace metals in 31 industrial wastewater effluents are within the ranges of international standards and the existing treatment plants are capable of absorbing the industrial effluents with no significant impact on treatment bioprocesses.

Although there are no treatment facilities for sludge within the treatment plants, the results indicated that sludge in general does not contain trace metals. Only zinc showed 2000 mg/kg in more than 85% of sludge samples. AOX was 550 mg Cl/kg for the same sludge samples. Both Zn and AOX exceed the standards of all industrial countries for sludge to be used in land application.

Chapter Four: Impact of wastewater on soil and groundwater. The aim of the study was to determine the interaction between the natural geochemistry and anthropogenic activities through developing trace element profiles in an area of the Gaza Strip with a high potential for pollution. Five boreholes were dug in the area of the Gaza wastewater treatment plant. Several analytical techniques were used to study the geology, and mineralogy of the soil, and the geochemistry of wastewater, sludge, soil, and groundwater. Among 26 elements analyzed, only a few trace metals showed environmental importance: As, Cd, Cr, Hg, Zn, and to a lesser extent Pb.

The results of the geochemical investigations confirmed that the upper 40 cm of soil were affected by wastewater and sludge. The trace metal accumulations were characterized by a large spatial variability, with some 'hot spots' of Cu and Zn reaching topsoil concentrations of up to 240 and 2005 mg/kg, respectively. In spite of that, the results of the groundwater testing revealed that no trace metals were detected at concentrations that exceeded the WHO (World Health Organization) standards. Moreover, it was shown that both anthropogenic activities as well as seawater intrusion caused the high levels of nitrate and salinity. The study describes the infrastructure needed for further research focusing on the natural infiltration potential and artificial recharge of groundwater, and the impact of agricultural activities. The study results can be used as baseline measures, since this was the first time these parameters have been quantified in soil and groundwater.

Chapter Five: Wadi Gaza. Water and sediment samples were collected from 18 sampling stations in Wadi Gaza for two successive years in order to: (1) establish baselines for the geochemistry of surface water and sediments; (2) assess the impact of seasonal variation on distribution of trace metals and major ions; and (3) identify possible natural and anthropogenic sources of pollution. The trace metal concentrations in the sediments of the lake (downstream) were higher than those of the eastern eight stations (upstream) where the water was shallower. The discharge of wastewater from an olive oil mill was evident in the Ca, Na, Mg, K and P concentrations in sediments of one of the sampling stations.

Water in shallower areas showed greater temporal variation than deeper areas. Several elements (P, Fe, Mn and As) showed the greatest temporal variability. For example, in the winter rainy season these elements decreased 2-10 times compared to their values in summer. Additionally, Ca, Na, Cl, PO_4, and NO_3 decreased 3, 3, 5, 2, 4 times, respectively. Some of the trace metals were more abundant in these waters compared to the domestic wastewaters of the study area. The averages of Cd and Co were 6 and 43 μg/l, respectively and they were 50 times higher than the domestic wastewater results.

Chapter Six: Soil geochemistry. The aims of this study were to establish the current types and concentrations of trace metals and major elements in agricultural soils of the Gaza Strip, and to identify the main anthropogenic inputs affecting trace metals. An extensive soil survey was conducted in agricultural and non-agricultural areas. One hundred sixty sites were selected representing a broad range of soil types and locations. The results revealed that soils fall within the range of the uncontaminated to slightly contaminated category. Up to 90% of the tested soils had trace metal concentrations representing the international background values. Ten percent showed slight contamination mainly by Zn, Cu, As and Pb due to anthropogenic inputs, and their mean concentrations were 180, 45, 13 and 190 mg/kg, respectively. The trace metal concentrations vary with the highest concentrations detected in the southern regions (clay soil and low precipitation) and the lowest in the northern areas (sandy soil and high precipitation). The soil geochemistry is dependent on soil type and location and to a lesser extent on crop pattern and fertilizer and fungicide application. Anthropogenic inputs lead to the enrichment of Zn, Pb, Cu and Cd in the agricultural soils. Pollution of several sites was found to be most severe for Zn, Pb, Cu and Cd and to a somewhat lesser extent for As, whereas anthropogenic input of Hg, Ni and Co seem to be less important. The application of Cd-containing phosphate fertilizers coupled with Cu-containing fungicides may be important sources of Cd and Cu in several soils. High Zn levels (1000 ppm) in several soils may be caused by sewage sludge that has an average Zn content of 2000 ppm. Saline-sodic soils were found in the central and southern regions where the soils are characterized by high contents of Na and salty groundwater. Elevated Cl, Na, Zn and Pb concentrations in some areas need further investigation for their ecological and health implications.

Chapter Seven: Fate of pesticides in the Gaza Strip. Agricultural activities in the Gaza Strip have associated with excessive and uncontrolled use of dozens of pesticides. Accordingly, groundwater and soil are potentially contaminated causing severe threat to the crowded population. The present study describes in a 3-year monitoring program types and level of contamination by various pesticides used in Gaza. Two analytical instruments (GC/MS and HPLC/MS) were applied to achieve this objective.

More than 92% of targeted pesticides in groundwater were much lower than their allowable limit of the World Health Organization. However, the municipal groundwater wells showed better quality as they are located in the residential areas than the private wells in the agricultural regions. Atrazine, atrazine-desisopropyl, propazine, simazine were detected in water samples with average concentrations of 3.5, 1.2, 1.5 and 2.3 µg/l, respectively. A linear correlation was found between the chloride concentrations in groundwater and atrazine for the same geographic areas. Generally speaking, shallow aquifers of low annual precipitation in the southern areas of Gaza showed detectable concentrations of pesticides. In soil, pesticides presence was found to depend on type of soils. Clay soils for instance, showed 3-4 times more than sandy soils for the same pesticide species.

A linear regression analysis found a correlation coefficient of $r = 0.87$ between the strawberry greenhouses and the occurrence of propazine, sebutylazine, terbutylazine, 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD in soil. The averages of propazine, sebutylazine and terbutylazine were 19, 13 and 39 µg/kg, respectively. One soil sample showed contents of 4,4'-DDE and 4,4'-DDT up to 1104 and 793 µg/kg , respectively.

Chapter Eight: Trace metals in pesticides: Two different techniques were used to determine different elements in pesticides; a semi-quantitative EMMA-XRF technique followed by ICP/OES was used to test the concentrations of Al, As, Ba, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sc, Se, Sr Ti and Zn in the most used 53 different species of solid pesticides collected from many markets of the Gaza Strip. The results revealed that the pesticides contain considerable amounts of trace metals and they do not comply with the expected-theoretical structure of each species; moreover, they do not reflect the actual constituents mentioned in the trade labels. Interviews with market owners and field surveys confirmed that pesticides were not pure and they have been mixed in local markets with minor inorganic species without a scientific basis; or they have been smuggled to Gaza with different impurities. The results propose that pesticides should be considered as a source of some trace metals (Cu, Mn, and Zn) and other elements (Br, Sr and Ti) that may affect their mass balances in soil and groundwater as well as plant uptake. Models of trace metal transport in soil and groundwater of the Gaza Strip should include pesticides as an additional source of certain trace metals.

In summary, this series of studies describes some important aspects of soil and water in the Gaza Strip. It forms the basis for additional specialized research related to the interaction of the environment and human health in the region.

ZUSAMMENFASSUNG

Die Vielfalt der Umweltemissionen im Gazastreifen, Palästina, erfordert einen interdisziplinären, ganzheitlichen Ansatz für Managementstrategien. Das Palästinensische Umweltministerium (MEnA) legt den Forschungsschwerpunkt seit vielen Jahren auf ein Verständnis der Komplexität der Umwelt in Gaza. Das Hauptaugenmerk lag und liegt weiterhin auf der Abschätzung des Risikos und der Gefahr für die menschliche Gesundheit durch die Schädigung von Wasser, Luft und Boden. Die Zerstörung der Umwelt ist kein neues Problem. Es ist vielmehr die Ansammlung natürlicher, politischer, wirtschaftlicher und sozialer Gegebenheiten. Dies veranschaulicht die Komplexität und führt so zu einer Verdeutlichung der Umweltprobleme. Obwohl sich diese Arbeit hauptsächlich mit der wissenschaftlichen Seite befasst, ist es den Forschern klar, dass zur Lösung der Umweltprobleme auch die politischen, wirtschaftlichen und sozialen Faktoren angesprochen werden müssen.

Obwohl sich diese Studie mit der Umweltsituation des Gaza Streifens befasst, können einige erzielte Forschungsergebnisse über das Gebiet hinaus übertragen werden. Da die Umweltprobleme sich generell nicht nur über kleine geographische Einheiten erstrecken und nicht an politischen Grenzen enden, ist es deshalb wichtig, die örtliche Umweltsituation zu verstehen um regionale Kooperationen aus dem wissenschaftlichen Bewusstsein heraus aufzubauen.

Diese Studie wurde im Rahmen des Forschungsprojektes "Monitoring of Groundwater and soil pollution levels in Gaza Strip", das vom Bundesministerium für Bildung und Forschung (BMBF) gefördert wird, durchgeführt. In Zusammenarbeit mit den örtlichen Experten in Gaza konnten im diesem Rahmen alle benötigten Beprobungen und Feldmessungen durchgeführt werden.

In dieser Arbeit werden mit organischer und anorganischer Geochemie zwei Wissenschaftszweige zusammengefasst, die im Rahmen von Dissertationen nur selten gemeinsam bearbeitet werden. Aus diesem Grund war nicht nur Wissen auf diesen sondern auch auf damit verbundenen Gebieten nötig. So wurden Kenntnisse aus der Bodenkunde, Geologie, Biologie, der Trinkwasserbehandlung und Statistik miteinbezogen.

Jedes Kapitel dieser Arbeit spiegelt einen eigenständigen wissenschaftlichen Ansatz wider. Da jedes Kapitel einen Artikel repräsentiert, der in einem internationalen Journal publiziert wurde oder den entsprechenden Prozess gerade durchläuft, waren Wiederholungen der Beschreibung von Probenahmen, Untersuchungsgebieten und Methodik sowie der Formatierungen der Kapitel unvermeidlich. Die Arbeit fasst alle diese Artikel zu einer Übersicht zusammen.

Die Reihenfolge der Kapitel richtet sich nicht nach der chronologischen Abfolge ihres Erscheinens sondern nach den Prioritäten der Umweltprobleme im Untersuchungsgebiet, die wie auch von der palästinensischen Umweltplanung mit Wasser und öffentlicher Gesundheit beginnen und von Abwasser, Abfall, Landnutzung und Landwirtschaft und deren negativen Auswirkungen, gefolgt werden.

Im ersten Kapitel wurde die Geochemie des Grundwassers erläutert. Im zweiten werden Beispiele von Verunreinigungen und deren Wirkungen auf die Gesundheit aufgezeigt. Abwasserprobleme und die Beeinflussung von Boden und Grundwasser sowie Möglichkeiten

der Wiederverwendung des Abwassers wurden im dritten und im vierten Abschnitt untersucht.

Wadi Gaza als zentraler Ort für Abwasser und Mülldeponie ist Gegenstand des fünften Kapitels, während der sechste Beitrag die Geochemie des Bodens in Gaza untersucht. Schließlich werden in den letzten zwei Abschnitten die Einflusse der Landwirtschaft auf den Boden beleuchtet. Gehalte und Transportvorgänge von Pestiziden und Schwermetallen im Boden und Grundwasser wurden untersucht.

Eine kurze Beschreibung der einzelnen Kapitel kann nachfolgend entnommen werden:

Kapitel Eins: Das Grundwasser: Obwohl 10 % der kommunalen Brunnen Spurenelementgehalte, die die Standards der World Health Organisation (WHO) erreichen, zeigen die erzielten Ergebnisse im Verlauf des dreijährigen Monitoring Programms, dass die Spurenelemente im Grundwasser des Gaza Streifens generell keine gesundheitliche oder umweltrelevante Gefährdung darstellen. Die Konzentrationen von Cl^-, NO_3^- und F^- sind mit jeweils durchschnittlichen Werten von 750, 75 und 1,6 mg/l in 90% der getesteten Brunnen zwei- bis fünffach höher als die WHO Standards.

In einigen privaten Brunnen wurden Durchschnittgehalte für Zn, Cd, Pb, Fe und As von jeweils 58, 30, 270, 468 und 10 µg/l gemessen, was für eine Benutzung zum Zweck einer Trinkwasserförderung nicht zu empfehlen wäre. Die Untersuchungen zeigen, dass in der nahen Zukunft eine drastische Verschlechterung der Trinkwassersituation, was Qualität und Quantität betrifft, erwartet werden kann.

Kapitel Zwei: Fluorid: Die Untersuchungen von Fluorid sind ein Beispiel, wie Grundwasserbelastungen direkte Auswirkungen auf die menschliche Gesundheit verursachen können. Die Überwachung der Fluorid-Gehalte in 73 Brunnen und 20 Bodenproben zwischen 2001 und 2003 lässt einen klaren Trend erkennen: Die F-Werte steigen in dem Untersuchungsgebiet vom Norden nach Süden auf das dreifache.

Untersuchungen mit dem Röntgendiffraktometer (XRD) zeigen allerdings, dass keines der vier häufigsten Fluorid Minerale in den Bodenproben vorkommt. Modellierungen mit PHREEQC haben ergeben, dass Fluorit (CaF_2) die größte Quelle für Fluorid-Ionen im Grundwasser darstellt. Weiterhin wurde eine hohe positive Korrelation zwischen Fluorid-Gehalten im Grundwasser und dem Auftreten von Erkrankungen der Zähne bei Schulkindern durch Fluor beobachtet.

Die Untersuchungen von 353 Schulkindern aus 5 verschiedenen Gebieten des Gaza Streifens zeigen, dass 60% der Untersuchten Anzeichen von Zahnschäden durch Fluor aufweisen. Davon wurde der Maximalwert von 94% in Khan Yunis im Süden des Gaza Streifen, 82% in Rafah, 68% im mittleren Gebiet, 29% in Gaza und der geringste Prozentsatz von 9% im nördlichsten Gebiet ermittelt. Diese Zahlen stehen direkt proportional zu den durchschnittlichen Fluorid-Konzentrationen der jeweiligen Grundwässer der verschiedenen Gebiete von 2.6, 0.9, 1.7, 1.2 und 0.7 ppm. Dabei wird die Vermutung verstärkt, dass das Auftreten der Krankheit durch die Aufnahme von großen Mengen Fluorid neben dem Trinkwasser, auch aus Tee und Fisch resultierte.

Kapitel Drei: Abwasser im Gaza Streifen: Bisher werden ca. 40% (50,000 m^3/Tag) der Abwässer des Gaza Streifens in das Meer ungeklärt eingeleitet. Ein kleiner Teil sickert in den Boden und stellt eine Bedrohung für das Grundwasser dar. Auf Grund mangelhaft ausgerüstete Kläranlagen sowie fehlende Technologien wird nur eine geringe Menge an Klärschlamm produziert. In diesem Kapitel wird erstmalig für den Gaza Streifen die Bestimmung der Spurenmetall-Konzentrationen sowie andere wichtigste Parameter in kommunalem und industriellem Abwasser und Klärschlamm durchgeführt. Weiterhin werden die verschiedenen Möglichkeiten der Wiederverwendung des Abwassers und des Schlammes im Rahmen einer landwirtschaftlich nachhaltigen Entwicklung im Gaza Streifen erkundet. Die Ergebnisse zeigen, dass kommunales Abwasser beträchtliche Konzentrationen von Schwermetallen aufweist. 40-70% der meisten dieser Metalle können jedoch während des Klärprozesses in den Kläranlagen entfernt werden. Die Ergebnisse der Untersuchungen zeigen, dass die Schwermetallkonzentrationen von 31 industriellen Abwässern sich innerhalb der Grenzen der internationalen Standards bewegen. Die existierenden Kläranlagen sind in der Lage diese Abwässer zu absorbieren, ohne dass sich Auswirkungen auf die biologischen Klärprozesse zeigen.

Generell weist der anfallende Klärschlamm nur geringe Schwermetallgehalte auf. Eine Ausnahme wurde für Zink bestimmt, das erhöhte Konzentrationen aufweist. Mehr als 85% der Schlammproben zeigen für Zink Durchschnittkonzentrationen um 2000 mg/kg. Auch die AOX-Werte lagen erhöht im Klärschlamm vor. Mit >2000 mg/kg für Zn und 550 mgCl/kg für AOX wurden die Standards aller Industrieländer für landwirtschaftlich nutzbaren Klärschlamm überschritten.

Kapitel Vier: Der Einfluss von Abwasser auf Boden und Grundwasser: Durch die Untersuchung von Spurenelement-Profilen einer der umweltrelevantesten Gegenden des Gaza-Streifens war das Ziel dieser Arbeit die Ermittlung der Wechselwirkungen zwischen der natürlichen Geochemie und dem anthropogenen Einfluss im Boden. Es wurden fünf Bohrungen in der Umgebung der Kläranlage von Gaza niedergebracht. Neben Untersuchungen der Geologie, Mineralogie und Geochemie der Bodenprofile wurde die Geochemie des Abwassers, des Klärschlamms und des Grundwassers durch verschiedene analytische Methoden bestimmt. Die Arbeit stellt in Gaza die ersten Grundlagen, um weitere Untersuchungen durchführen zu können, vor.

Von 26 analysierten Elementen wurden nur einige Schwermetalle als umweltrelevant eingestuft. Vor allem As, Cd, Cr, Hg, Zn und zu einem geringeren Anteil auch Pb sind für die Umwelt in Gaza von Bedeutung. Die Ergebnisse der geochemischen Untersuchungen bestätigen, dass die oberen 40 cm des Bodens durch Abwasser und Klärschlamm beeinträchtigt wurden. Die Schwermetallvorkommen in den Böden sind durch eine große räumliche Variabilität mit einigen lokalen Anreicherungen von Cu, Zn gekennzeichnet, die jeweils Konzentrationen von 240, 2005 mg/kg erreichten. Trotz dieser Anreicherungen in den Bodenprofilen, zeigen die Grundwasseranalysen, dass im Grundwasser keines dieser Elemente Konzentrationen erreicht, die die Standards der WHO (World Health Organisation) überschreitet. Weiterhin konnte gezeigt werden, dass die hohen Nitratwerte und die hohe Salinität anthropogen verursacht sind und dem Eindringen von Meerwasser in den Aquifer resultieren.

Kapitel Fünf: Wadi Gaza: An insgesamt 18 Beprobungsstellen im Wadi Gaza sind innerhalb von zwei aufeinander folgenden Jahren Wasser- und Sedimentproben entnommen und untersucht worden. Dabei sollten folgende Forschungsaufgaben durchgeführt werden: a) die geochemischen Hintergrundbedingungen des Oberflächenwassers und des Sediments ermitteln; b) den Einfluss saisonaler Schwankungen auf die Verteilung von Schwermetallen und Hauptionen abschätzen; und c) potenzielle Quellen natürlicher und anthropogener Verunreinigungen identifizieren.

Die Ergebnisse haben gezeigt, dass die Schwermetallkonzentrationen im Sediment des Sees (abstromig) höher als diejenigen der östlichen acht Beprobungsstellen (oberstromig) lagen und die durch flacheres Wasser gekennzeichnet waren. Sedimentproben einer

Beprobungsstelle belegten den Abfluss von Olivenölmühlen-Abwasser anhand ihrer Ca, Na, Mg, K und P Konzentrationen.
Im Flachwasser wurden größere saisonale Schwankungen der Konzentrationen als im Tiefwasser des Sees festgestellt. Einige Elemente wie P, Fe, Mn und As zeigten die größte zeitliche Variabilität. Für diese Elemente nahmen z.B. die Werte innerhalb der niederschlagsreichen Wintersaison um das 2- bis 10-fache gegenüber Werten im Sommer ab. Ferner nahmen Ca, Na, Cl, PO_4 and NO_3 um das 3-, 3-, 5-, 2- bzw. 4-fache ab. Einige Spurenmetalle kamen in den Wässern des Wadis häufiger vor als in häuslichen Abwässern des Untersuchungsgebietes. Die Durchschnittswerte von Cd and Co lagen bei 6 bzw. 43 µg/l und waren 50-mal höher als Messwerte häuslicher Abwässer.

Kapitel Sechs: Boden Geochemie: Die Ziele dieser Untersuchung waren die rezenten Gehalte von Schwermetallen und Hauptelementen in landwirtschaftlich genutzten Böden des Gaza Streifens zu bestimmen, sowie die hauptsächlichen anthropogenen Einträge zu identifizieren, welche die Schwermetallgehalte beeinflussen. Eine ausgedehnte Erfassung von Böden in landwirtschaftlich und nicht-landwirtschaftlich genutzten Gebieten wurde durchgeführt. Insgesamt 160 Flächen wurden ausgewählt, die einen weiten Bereich von Bodenarten und Lokalitäten repräsentieren. Die Ergebnisse zeigten, dass die untersuchten Böden in die Kategorie nicht bis schwach kontaminiert fallen. Bis zu 90% der untersuchten Böden wiesen Schwermetallgehalte im Bereich internationaler Hintergrundgehalte auf. 10% zeigten eine schwache Kontamination hauptsächlich durch Zn, Cu, As and Pb aufgrund anthropogenen Eintrags, bei mittleren Konzentrationen von 180, 45, 13 bzw. 190 mg/kg. Die Schwermetalle variieren zwischen hohen Gehalten in den südlichen Regionen (Lehmböden und geringer Niederschlag) und geringen Gehalten in den nördlichen Gebieten (sandige Böden und hoher Niederschlag). Die geochemischen Bedingungen des Bodens sind abhängig von der Bodenart und der Lokalität sowie zu einem geringeren Ausmaß von der angebauten Fruchtart und der Anwendung von Dünger und Fungizid. Anthropogene Einträge führen zu einer Anreicherung von Zn, Pb, Cu und Cd in landwirtschaftlich genutzten Böden. Die Verunreinigung verschiedener untersuchter Flächen stellte sich als am schwersten für Zn, Pb, Cu und Cd heraus sowie in einem etwas geringeren Ausmaß für As, während der anthropogene Eintrag von Hg, Ni und Co weniger bedeutend zu sein scheint. Die Ausbringung Cd-haltiger Phosphatdünger in Kombination mit Cu-haltigen Fungiziden sind möglicherweise bedeutende Quellen für Cd und Cu in einigen Böden. Hohe Zn-Gehalte (1000 ppm) in verschiedenen Böden werden möglicherweise durch Klärschlamm verursacht, der einen mittleren Zn-Gehalt von 2000 ppm aufweist. Sodasalinare Böden wurden in den zentralen und südlichen Regionen gefunden, in denen die Böden durch hohe Na-Gehalte und salzhaltiges Grundwasser charakterisiert sind. Erhöhte Cl-, Na-, Zn- und Pb-Gehalte in einigen Gebieten bedürfen weiterer Untersuchungen bezüglich ihrer ökologischen und gesundheitlichen Folgen.

Kapitel Sieben: Erfassung von Pestiziden im Grundwasser und im Boden des Gaza Streifens: Landwirtschaftliche Nutzung ist im Gaza Streifen mit einer exzessiven und unkontrollierten Anwendung duzender Pestizide einhergegangen. Dementsprechend sind Grundwasser und Boden potenziell kontaminiert und stellen eine mögliche Bedrohung für die dicht siedelnde Bevölkerung dar. Die hier vorgestellte Untersuchung beschreibt in einem dreijährigen Erhebungs-Programm die Arten und das Ausmaß der Kontamination durch verschiedene Pestizide, die im Gaza Streifen verwendet werden. Um dieses Ziel zu erreichen, wurden zwei Messgeräte eingesetzt (GC/MS und HPLC/MS).
Mehr als 92% der erfassten Pestizide im Grundwasser lagen weit unterhalb ihres zulässigen Grenzwertes der Weltgesundheitsorganisation. Insgesamt zeigten die in Wohngebieten

gelegenen städtischen Grundwasserbrunnen eine bessere Qualität als die in landwirtschaftlich genutzten Regionen gelegenen privaten Brunnen. Atrazin, Atrazin-Desisopropylen, Propazin und Simazin wurden in Grundwasserproben mit Konzentrationen von 3,5, 1,2, 1,5 bzw. 2,3 µg/l nachgewiesen. Zwischen den Chlorid- und Atrazin- Konzentrationen in Grundwasserproben desselben geographischen Gebiets wurde eine lineare Korrelation beobachtet. Im Allgemeinen zeigten flache Grundwasserleiter mit einem geringen Jahresniederschlag in den südlichen Gebieten des Gaza Streifens nachweisbare Konzentrationen von Pestiziden. Das Vorkommen von Pestiziden im Boden stellte sich als abhängig von der Bodenart heraus. Lehmböden zeigten z.B. für dieselbe Pestizidspezies 3-4 mal so hohe Werte wie sandige Böden.

Durch eine lineare Regressionsanalyse wurde zwischen Erdbeergewächshäusern und dem Auftreten von Propazin, Sebutylazin, Terbutylazin, 4,4'DDT, 4,4'DDE und 4,4'DDD im Boden ein Korrelationskoeffizient von r = 0,87 nachgewiesen. Mittlere Propazin-, Sebutylazin- and Terbutylazin- Konzentrationen lagen bei 19, 13 bzw. 39 µg/kg. Eine Bodenprobe zeigte 4,4'DDE- und 4,4'DDT- Gehalte bis zu 1104 bzw. 793 µg/kg.

Kapitel Acht: Schwermetalle in Pestiziden: Zur Bestimmung verschiedener Elemente in Pestiziden wurden zwei verschiedene Methoden angewendet; eine semiquantitative EMMA-XRF Methode gefolgt durch ICP/OES wurde verwendet, um die Konzentrationen von Al, As, Ba, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sc, Se, Sr, Ti und Zn in den 53 meist benutzten festen Pestiziden zu bestimmen, die von Märkten im Gaza Streifen zusammengetragen wurden. Die Ergebnisse belegten, dass die untersuchten Pestizide bemerkenswerte Mengen an Schwermetallen enthalten, und dass jede Spezies nicht der theoretisch zu erwartenden chemischen Struktur entspricht; darüber hinaus zeigen sie nicht die tatsächlichen Inhaltsstoffe, die in der Warenbeschriftung angegeben sind. Befragungen von Marktbetreibern und Felduntersuchungen bestätigten, dass Pestizide unrein waren und dass sie auf lokalen Märkten ohne eine wissenschaftliche Grundlage mit geringen Anteilen anorganischer Spezies vermengt wurden; oder sie sind mit verschiedenen Unreinheiten in den Gaza Streifen geschmuggelt worden. Die Ergebnisse lassen vermuten, dass Pestizide als eine Quelle bestimmter Schwermetalle (Cu, Mn und Zn) und anderer Elemente (Br, Sr and Ti) angenommen werden sollten, die sowohl ihre Massenbilanz im Boden und Grundwasser, als auch die Aufnahme durch Pflanzen beeinflussen kann. Verschiedene Szenarios und Modellierungen des Schwermetalltransports im Boden und Grundwasser des Gaza Streifens sollten Pestizide als zusätzliche Quelle bestimmter Schwermetalle berücksichtigen.

Diese Arbeit offenbart einige der aktuellsten wissenschaftlichen Forschungen im Zusammenhang mit dem Gaza Streifen. Sie bildet die Basis für weitergehende Forschungen auf dem Gebiet der Umwelt und Gesundheit in der Region.

الخلاصة

تتداخل القضايا البيئية في قطاع غزة (فلسطين) إلى حد يصعب فيه التعاطي مع أيها دون الأخرى، ومن خلال إدراك الواقع البيئي وتعقيداته وعلى مدار سنوات طويلة، أمكن وضع أولويات بحثية، انسجمت مع الاستراتيجية الوطنية الفلسطينية للبيئة ولخطة العمل المنبثقة عنها، ويأتي على رأس هذه القضايا المخاطر الصحية التي يتعرض لها الإنسان جراء تردي البيئة التي يعيش فيها، مثل الماء والهواء والمياه العادمة والنفايات الصلبة إلخ، وكلها أمثلة لهذه المخاطر. والمشكلات البيئية في قطاع غزة ليست وليدة اللحظة، بل فاقمتها الظروف السياسية والإقتصادية والإجتماعية والطبيعية أيضا. وهذه الظروف أعطت أبعادا إضافية لا يمكن بمعزل عنها وضع الأطر الزمنية والخطط العملية لمجابهة الواقع البيئي المتردي. إن هذه الدراسة وإن اشتملت على موضوعات علمية بحتة أُعطيت لها المساحة الأكبر، فإنها لا تقلل على الإطلاق من أهمية الظروف السياسية والإقتصادية والإجتماعية التي لم تناقش هنا لأسباب علمية منهجية. ومع ذلك فهناك العديد من الإشارات الهامة في الكثير من المواضع التي يحتاجها السياق.

وحيث أن البيئة بعناصرها المتداخلة لا تنحصر في مكان صغير مثل غزة، بل إنها تتأثر بمحيطها الأقليمي علاوة على أنها تؤثر فيه ولو بنسبة أقل، لذا تأتي هذه الدراسة لتبرز بعضا من الإشكالات البيئية التي تمتد خارج المكان وتتطلب جهودا متكاملة وعلى صعد شتى، لرسم صورة بيئية أكثر فهما، يمكن بموجبها العمل المشترك على أسس علمية واعية.

إن هذه المساحة التي تعج بالقضايا السياسية على مدار الساعة، تحتوي في ذات الوقت على موضوعات بيئية ساخنة جدا، وما تلوث أكثر من 90 % من المياه الجوفية بالأملاح والنترات والفلور وغيرها الكثير، علاوة على ندرة مصادر المياه أصلا، والتلوث الحاصل جراء المياه العادمة والنفايات الصلبة إلاّ أمثلة بسيطة على عظم المشكلة.

إن هذه الدراسة جاءت بالتوازي مع أحد المشاريع البحثية الهامة بالجامعة (مشروع غزة) والذي تموله وزارة التعليم والبحث العلمي الألمانية، ومن خلال المشروع أمكن تأمين العينات البيئية اللازمة، والتشاور مع المختصين في غزة والإفادة منهم.

لعله يجدر التنويه إلى أن الدراسة جمعت بين فرعين يندر وجودهما في أطروحات درجة الدكتوراة، وهما الجيوكيمياء العضوية وغير العضوية، ولذا فقد تطلبت الدراسة الإلمام ليس فقط بالكيمياء العضوية وغير العضوية، بل بالعديد من دروب المعرفة ذات العلاقة، جودة المياه وإدارتها، الجيولوجيا وعلوم التربة، البيولوجيا العامة والأحياء الدقيقة، الإحصاء وتطبيقاته، وهذه بعض الأمثلة، علاوة على الإفادة المباشرة من بعض المقررات الدراسية، والأدبيات المتاحة بالمكتبة الجامعية، والمحاضرات التخصصية، والمؤتمرات المحلية والعالمية، واللقاءات العلمية الأسبوعية في المعهد حيث أجريت فيه الدراسة.

ولذا فإن كل فصل في الدراسة يعكس توجها علميا أساسيا ومحوريا، فضلا عن الأساسيات العلمية الأخرى التي تجعل من كل فصل دراسة قائمة بذاتها. والدراسة لا تخلو من بعض التكرار وخصوصا في طرق القياس المخبرية أو مكان الدراسة (قطاع غزة)، وهذا مرده أن كل فصل يمثل دراسة تم نشرها أو في طريقها للنشر في مجلة علمية عالمية متخصصة، ووضعت كل دراسة في فصل لتلتأم بجمعها الدراسة الكلية.

ولقد تم ترتيب فصول الدراسة ليس على أساس زمني أو وفق نشرها في المجلات، وإنما بناء على أهميتها التي حددتها الأستراتيجية الوطنية الفلسطينية للبيئة، فالمياه والصحة العامة تحتل المرتبة الأولى، تليها المياه العادمة، ثم النفايات الصلبة، واستخدام الأراضي، والنشاط الزراعي وآثاره، إلخ. ولذا تم ترتيب الدراسة بحيث يكون الفصل الأول للمياه الجوفية، ثم أمثلة على آثار تلوثها على الصحة العامة، تلى ذلك المياه العادمة وإمكانية الإفادة منها، وآثارها على التربة والمياه الجوفية، ثم وادي غزة الذي تصرف إليه النفايات السائلة والصلبة، والخصائص الجيوكيميائية للتربة في غزة، وكيف يؤثر النشاط الزراعي فيها،

وأخيرا المبيدات الزراعية ومصيرها في التربة والمياه الجوفية، ثم مدى أحتوائها على المعادن الثقيلة. وفيما يلي عرض سريع لكل فصل مع بعض التوصيات العامة.

الفصل الأول: المياه الجوفية: عبر قاعدة للبيانات اشتملت على تحليل المياه الجوفية لأكثر من تسعين بئرا، ولمدة ثلاث سنوات متتالية، أمكن التعرف على تركيز مختلف العناصر سواء تلك التي يمكن تحليلها في غزة أو تلك التي يصعب تحليلها، نظرا لقلة التجهيزات المخبرية اللازمة. وقد أظهرت النتائج أن المياه الجوفية تحتوي على نسب ضئيلة من المعادن الثقيلة وهي ضمن معايير منظمة الصحة العالمية، في حين كانت نتائج كل من الزنك والكادميوم والرصاص والحديد لبعض الآبار الخاصة التي تستخدم في الزراعة تزيد على تلك المعيير، الأمر الذي يتطلب مزيدا من المراقبة وتحديدا لوظائف هذه الآبار. ومن نافلة القول التأكيد على أن أكثر 90 % من الآبار الجوفية تحتوي نسبا من الكلور والفلور والنترات تزيد على 2-5 أضعاف عن المسموح به صحيا. وفي ضوء ذلك يلزم اتخاذ خطوات عملية عاجلة وعلى كل المستويات للحد من تدهور جودة المياه وإلا فإن المنطقة مقبلة على أزمة حقيقية خلال السنوات القليلة القادمة.

الفصل الثاني: أمثلة لملوثات المياه الجوفية وآثارها: يعرض هذا الفصل لمثال هام وواضح له أبعاد صحية خطيرة، وهو الفلور، في حين أن الوقت لم يسعفنا لكي نضم نتائج البحث العلمي الموسع حول النترات، والتي لا زال العمل جاريا فيها حول وجودها في المياه الجوفيه، والمياه العادمة، والحمأة، والتربة، والأسمدة والمخصبات، وكذلك قياس نظائر النيتروجين في المياه الجوفية لتحديد مصدر إرتفاع النترات في المياه الجوفية بشكل دقيق، وقد تأخرت نتائج الدراسة لأسباب فنية بحتة تتعلق بعمل الأجهزة اللازمة.
لقد أظهرت الدراسة الأولى أن الفلور ترتفع نسبته في العديد من مناطق قطاع غزة عن ما قررته منظمة الصحة العالمية (1.5 mg/l)، الأمر الذي أوجد مرضا يعرف بتبقع الأسنان وهشاشتها. ونتائج الدراسة المعملية أظهرت اتفاقا في تركيز الفلور في المياه الجوفية والتربة، الأمر الذي يرجح أن يكون مصدر الفلور في المياه طبيعيا، ولمعرفة أي أملاح الفلور يزود المياه الجوفية بأيونات الفلور عبر التحاليل المخبرية وبرامج الكمبيوتر الخاصة، أمكن القول أن فلوريد الكالسيوم (CaF_2) هو المغذي الأكبر. إن ارتفاع نسبة الفلور في مياه الشرب لبعض المناطق علاوة على وجوده عاليا في الشاي والغذاء، أوجد أطفالا أكثر عرضة للإصابة بتبقع الأسنان وخصوصا في منطقة خانيونس التي يزيد فيها الفلور عن ثلاثة أضعاف المعيار المسموح به. ولذا فإن هذا المرض يصل إلى حد الوباء ويجب التعاطي معه وفق المقررات العلمية التي أرستها العديد من الجهات المعنية عالميا وعلى رأسها منظمة الصحة العالمية.

الفصل الثالث: واقع المياه العادمة وإمكانية الإفادة منها: تعاني المنطقة من شحة وندرة في المياه، الأمر الذي يجعل من إمكانية الإفادة من المياه العادمة المعالجة أمرا حيويا وملحا، هذا إذا علمنا أن أكثر من مائة ألف مترا مكعبا يتم تصريفها إما للبحر أو إلى الوديان والأماكن المفتوحة، ولدراسة هذا الخيار وإقراره للأهمية، أُجريت الدراسة على محطتي غزة وبيت لاهيا، وذلك لتبيان نوعية هذه المياه الداخلة والخارجة (المعالجة) وغطت الجانب الكيميائي بالتفصيل، مع إدراكها لأهمية الجانب البيولوجي (البكتيري والفيروسي). كما وغطت الدراسة وبشكل مستفيض المواصفات الكيميائة للحمأة (Sludge). وخلصت الدراسة إلى أن محطات المعالجة المتواضعة في أدائها، قادرة على استيعاب ومعالجة المياه العادمة التي تصل إليها، كما أنها قادرة على معالجة المياه العادمة الصناعية التي تصل إليها (حتى وقت الدراسة)، بحيث أن المياه المعالجة الخارجة من المحطتين تتشابه إلى حد

كبير وتنسجم والمعايير العالمية، ولذا توصي الدراسة بالإفادة من هذه المياه المعالجة، واعتبارها مصدرا هاما للمياه يجب عدم التفريط فيه، واستخدامها في قطاع الزراعة وخصوصا الأشجار، أو نقلها إلى وادي غزة ضمن خطة تهدف إلى النهوض بهذا القطاع البيئي الحيوي الهام، ضمن دراسات علمية واعية.

إلا أن مانعا هاما يحد من إمكانية الإفادة من الحمأة في الزراعة ألا وهو إرتفاع نسبة كل من الزنك (>2000 mg/l) والهالوجينات العضوية والمذابة (Adsorbable Organic Halogens) إلى أكثر من (500 mg Cl/kg) وهذه النسب تزيد عن معايير الدول الصناعية.

الفصل الرابع: آثارالمياه العادمة على التربة والمياه الجوفية: تمت دراسة آثار المياه العادمة والحمأة على التربة والمياه الجوفية في منطقة محطة المجاري المركزية في غزة. وقد تم حفر العديد من الآبار سواء داخل أحواض المعالجة أو حولها، وتم جمع عينات التربة من الأعماق المختلفة وصولا للمياه الجوفة التي تم جمعا، وحاولت الدراسة إيجاد الرابط بين السطح والحوض الجوفي. وخلصت الدراسة إلى أن الطبقة السطحية (40 cm) من التربة هي التي تتأثر مباشرة بما يعلوها من مياه عادمة أو حمأة، وبعد ذلك تبدو التربة أبعد ما يكون عن التأثر، كما أظهرت الدراسة الإرتباط الوثيق بين أنواع التربة ومدى أحتوائها على العناصر، فالقطاعات الطينية أكثر أحتواء من الرملية، والأولى تشكل طبقة غير منفذة تقريبا الأمر الذي يفسر التركيز القليل للعناصر مباشرة تحت القطاعات الطينية. وباستثناء النترات التي مصدر بعضها من المياه العادمة، فإن مجمل العناصر الثقيلة والأيوات الشائعة نسبتها تماثل نظيرتها في المياه الجوفية للعديد من الآبار المحيطة، وتوصي الدراسة من جديد بإمكانية الإفادة من المياه المعالجة في الزراعة خصوصا للأشجار التي يزيد عمق جذورها عن النصف متر.

الفصل الخامس: وادي غزة: لقد حظي وادي غزة بجهد مميز خلال السنوات القليلة الماضية، عبر العديد من المشاريع الجادة التي تهدف إلى النهوض بهذا المرفق الحيوي الوحيد من نوعه في قطاع غزة، وقد ركزت المشاريع على دراسة التنوع الحيوي والتحديات الراهنة، والتعرض الدائم للمخلفات الصلبة والسائلة والسياسات اللازمة لجعل الوادي محمية طبيعية واعدة، لكن هذا الفصل يقدم للمرة الأولى معلومات عن الخصائص الجيوكيميائية لمياه وادي غزة والرواسب الرملية والطينية (Sediments)، والعلاقة الكيميائية التبادلية بينها، علاوة على تأثير الإختلاف الفصلي (الصيف والشتاء) في هذه الخصائص. كما وتوضع الدراسة بعض التوصيات الهامة اللازمة لتحسين المياه في الوادي والرواسب.

الفصل السادس: الخصائص الجيوكيميائية للتربة في غزة: رغم صغر مساحة قطاع غزة فإن هناك تنوعا واضحا في أنواع التربة فيه، وقد رصدت الدراسة هذه الأنواع وتوزيعها، وركزت على تأثير النشاط البشري على الخصائص الجيوكيميائية للتربة. إن العينات التي جمعت تمثل كافة المناطق في القطاع، وتمثل كذلك التربة تحت تأثير زراعات مختلفة، البيوت البلاستيكية، الخضروات الصيفية والشتوية، والأشجار المثمرة. كما لم تغفل الدراسة تأثير المياه العادمة والحمأة والنفايات الصلبة على التربة، إضافة لموقع التربة وقربها من طرق المواصلات السريعة وتأثرها بها. وقد أفادت الدراسة من تحليل العناصر الثقيلة لأهم الأسمدة والمخصبات الزراعية وتأثيرها في التربة.

الفصل السابع: المبيدات الزراعية ومصيرها في التربة والمياه الجوفية: يعاني قطاع غزة مثله مثل باقي المنطقة العربية، يعاني نقصا حادا في المعلومات المتعلقة بوجود المبيدات الزراعية في البيئة، مصادرها، تصنيعها، استخدامها، وآثارها. وذلك لعدة أسباب

أهمها، غياب أنظمة الرقابة والتفتيش، وقلة الوعي لدى الباعة والمزارعين، ونقص التجهيزات المخبرية والخبرات البشرية، كذلك الطرق المعقدة والمكلفة والتي تستغرق وقتا طويلا للقيام بالتحاليل اللازمة. لذا تجيء هذه الدراسة الأولى من نوعها في المنطقة، لتجمع أكثر من ثلاث مائة عينة بيئية وعبر ثلاث سنوات تم تجهيز هذه العينات وتحليلها، ومن ثم محاولة الإجابة على السؤال الهام: أين تذهب المبيدات الزراعية التي تستخدم في غزة عبر وجودها في التربة والمياه الجوفية؟ لقد اقترن النشاط الزراعي في قطاع غزة باستخدام العديد من المبيدات الزراعية الأمر الذي هدد كلا من التربة والمياه وجعلهما عرضة للتلوث. وقد تمت مراقبة كل آبار البلديات وبعض الآبار الخاصة وعلى مدار ثلاثة أعوام علاوة على العديد من عينات التربة التي تغطي مختلف مناطق القطاع. وأظهرت النتائج أن المبيدات في أكثر من 92% من الآبار تحت المستوى الذي قررته منظمة الصحة العالمية. إلا أن النسبة الباقية أظهرت أرقاما مرتفعة لبعض المبيدات. وهذه الأرقام تجاوزت بكثير ما هو مسموح به عالميا في مياه الشرب. كما أظهرت الدراسة تلازما واضحا بين ملوحة المياه وتركيز Atrazine. وعموما فإن آبار البلديات أفضل من الآبار الزراعية الخاصة، علما بأن بعض آبار البلديات التي استخدمت لعقود ماضية كآبار زراعية أظهرت تلوثا ببعض المبيدات. وأما عينات التربة فإن العديد من المبيدات الممنوعة دوليا قد وجدت بنسب عالية مثل DDT ومشتقاته.

الفصل الثامن: مدى أحتواء المبيدات الزراعية على المعادن الثقيلة: تلتفت الأنظار عادة إلى الكيمياء العضوية عندما تذكر المبيدات الزراعية، لكن الكيمياء غير العضوية للمبيدات لا تحظى بالإهتمام المشابه، وفي ذلك كل الحق، هذا إذا افترضنا وجود رقابة دائمة على تصنيع واستيراد وتسويق المبيدات، الأمر الذي مآله التطابق التام بين التركيب الكيميائي النظري للمبيد الزراعي وتركيبه الذي تكشفه الفحوصات المخبرية، إنه من خلال إدراك واقع المبيدات الزراعية في غزة، نخلص إلى القول بأنها في سوادها الأعظم مستوردة أو مهربة، والقليل منها مصنع محليا. وإن غياب أنظمة المراقبة والتفتيش علاوة على الجهل بأسلوب التعامل مع المبيدات وطرق حفظها وتخزينها وتركيبها وبيعها أظهر أن معظم المبيدات الزراعية في الأسواق لا يتفق تركيبها الكيميائي الموضح عليها (إن وجد) مع النتائج العملية للتحاليل المخبرية، وترجح الدراسة أن تكون الأسباب علاوة على ما سبق، هي خلط المبيدات الزراعية دون أسس علمية ولكن لمعايير مادية بحتة، وكذلك تخزينها في عبوات تؤثر وتتأثر بالمبيدات.

ختاما، فقد طرحت الدراسة مواضيع علمية للمرة الأولى في قطاع غزة، وهي تشكل أساسا للعديد من الأبحاث التخصصية المتعمقة مستقبلا، وخصوصا تلك التي تعنى بالمستقبل البيئي للمنطقة وصحة الإنسان.

BACKGROUND FOR GROUWNDWATER, WASTEWATER, SOIL, WADI GAZA AND PESTICIDES IN THE ENVIRONMENT OF THE GAZA STRIP

FOREWORD

The issue of environmental protection is one of the top priorities to governments and individuals of all countries. The problems of environmental pollution are of global concern due to drastic effects they have on human health, on air, water and soil, on ecological systems and on all kinds of life on the planet earth. Nowadays, pollution is considered the first priority among the environmental problems facing the contemporary world.

The environment in Palestine suffers from considerable strains. The severe effects of occupation and the shortage and pollution of resources, coupled with high population growth and insufficient job opportunities have created many environmental hazards. Shortage of water and deterioration of water quality constitute a limiting factor in the economic development of Palestine. Occupation’s security pretexts and frequent closures of Palestinian territories caused disruption of economic and municipal activities and aggravated the existing pollution in every city, town or village in Palestine.

The Gaza Strip as one of the most densely populated areas in the world with limited and deteriorated resources has already started to suffer the outcomes of environmental quality deterioration. The situation in the Gaza Strip is below the desired standard which is attributed to the prolonged occupation and the absence of environmental legislation and the public awareness. Therefore, there should be collective and serious efforts on the local, regional and international levels to improve and protect the environment by prevention and monitoring the environmental themes with emphasis on the environmental hot spots.

The earth witnesses today an unprecedented increase in environmental problems. The enormous overall population growth and consequent industrial, agricultural, energy generation and communication boom of activities have led to the disturbance of environmental equilibrium dynamics.

The following section summarizes the PhD work according to the guidelines and instructions of the Faculty for accumulative thesis. The section shows major units of the work starting from the main objectives, methodology, results, conclusions and recommendations. It was so hard to bring different topics in one section, so the following section treats these topics on scientific bases with logical framework keeping details, figures, tables in the main chapters of the study. The structure of this section integrates water issues in one unit, then wastewater and sludge, soil, Wadi Gaza and pesticides. The sequence is based on the fact that more population causes more stress and pressure on the available-limited natural resources in terms of exploitation and contamination.

Groundwater is the only source of water in Gaza and several factors are causing the deterioration of water quality. The study tries to find these factors and the role of each factor.

The generated wastewater is affecting most of environmental elements in Gaza, contamination of sea and seashore, soil, wadies, and groundwater.

1. Groundwater Quality

Objectives

1. To achieve an understanding of the quality of the groundwater as it currently exists and to determine if any of the parameters tested pose a threat to human health in the Gaza Strip.
2. To determine the average levels of fluoride in groundwater and top soils of the Gaza Strip.
3. To determine the levels of fluoride in the prepared tea and tea leaves used in Gaza.
4. To identify the major fluoride minerals in soil that may supply groundwater with fluoride ions.
5. To determine the dental fluorosis index (DFI) for school children of both sexes in the age range 5-16 years, and then the community fluorosis index (CFI) followed by the number of teeth with caries.

General Methodology (Sampling and Analysis)

Groundwater (and surface water) samples were collected in laboratory certified clean bottles and labeled as to the well location, date and time of sample collection, analyses to be performed, and field preservation performed, if any. Preservation of samples in the field was done to avoid revisiting the wells if mistakes occurred while adding the chemicals to the samples.

One-liter samples were collected and placed in a sampling ice-box and transferred to the laboratory. The sample was divided into two subsamples: the first (500 ml) was filtered in an acid-washed filter holder and through 0.45 µm pore size membrane filters, the first few milliliters were used for rinsing, then they were discarded, and the filtrate was transferred to clean acid-washed polyetheylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v), and stored at 4 ^{o}C until analyses by ICP/MS (Perkin Elmer-Sciex, Elan 6000). The total content of Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr and Zn was determined next to the cations of Ca, K, Mg and Na. The other part of the water was filtered with no additives and stored at 4 ^{o}C for anion analyses by Ion Chromatography (IC). Several parameters were measured in the water samples during the fieldwork: temperature, turbidity, electric conductivity and pH; other parameters were measured in the laboratory.

As excessive fluoride concentrations are known to be problematic in this area, fluorides were measured also, using Ion Selective Electrode (ISE) according to the American standard methods (APHA, 1995).

Fluorides in tea and soil were determined in composite soil samples. Samples were collected using a stainless steel dredge; approximately 0.5 kg was put in polyethylene cups and stored at 4 ^{o}C during its transport to laboratories where the soil was dried in an oven at 50 ^{o}C until it reached a constant weight. Then the samples were shipped to Germany in plastic sampling bags. The samples were sieved through a 20-µm sieve and ground to a very soft powder by using a sand mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 50 mg of sample was placed in a nickel crucible, then 2 g of 1:1 Na_2CO_3-K_2CO_3 (anhydrous dried at 110 ^{o}C overnight) was added to the sample in the crucible. The crucibles were placed in a muffle furnace at 800 ^{o}C for 15 min.

After cooling, 15 ml of 1 M citric acid was added to the crucible and the mixture was allowed to digest until CO_2 evolution was no longer detected (3-4 h, or preferably overnight). Then 25 ml of sodium citrate buffer (1M) was added to the contents of the crucible. Finally, the mixture was transferred to a 100-ml polypropylene volumetric flask where it was diluted to the mark by deionized H_2O.

The semi-quantitative X-ray diffraction technique (XR Diffractometer-SIEMENS) was used to identify the major fluoride minerals in soil samples; the four major fluoride minerals were investigated (topaz: $Al_2(F,OH)_2SiO_4$; fluorite: CaF_2; fluoroapatite: $Ca_{10}(PO_4)_6F_2$; cryolite: Na_3AlF_6). Moreover, PHREEQC (a small program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations) was applied to achieve the same purpose by using groundwater data of five wells in the area of Khan Yunis where the fluoride level is high.

Main Results

The best aquifer -in terms of fresh water- was located in Beit Lahia at the north western corner of the Gaza Strip; the lowest EC value was 520 µS/cm and the highest was about 1000 µS/cm. The most deteriorated and salty water was in the regions of Khan Yunis and Rafah.
Approximately 85% of the wells sampled showed nitrate levels above the WHO standard (50 mg/l). The lowest value of chloride in the north area was 40 mg/l while the highest value in the eastern parts of Rafah area was 3000 mg/l.
The results showed that the trend of the fluoride in the groundwater of the Gaza Strip was similar to Cl, with some exceptions in the middle area. Most of the wells in Gaza have levels less than the WHO standard (1998) of sulfate (250 mg/l), while phosphates were not detected. Approximately 65 of the wells tested (>50% of the wells sampled) had sodium levels higher than the WHO standard (200 mg/l). The value of K was less than 5 mg/l. The average of Ca was 93 mg/l and the Mg/Ca ratio showed almost all points with about a 1:1 ratio.
The high fluoride contents in the groundwater (1.8 to 4 mg/l) were the main reason of the dental fluorosis disease for school children of the Gaza Strip. Soil samples showed the same trend of fluoride contents as the water samples. The fluoride contents in tea was 2.7 - 4.7 ppm. The average number of cups drank per person per day is indicated, the highest, 3.19 cups, being in Rafah and the lowest, 2.50 cups, in Khan Yunis. Overall, the DFI increased going from north to south as the lowest value being in the northern area of Jabalia, 2.85, and the highest value, 4.39, in eastern villages of Khan Yunis. The CFI for the Gaza Strip as a whole was calculated as 2.42. Results of PHREEQC model found that the main donating fluoride mineral is fluorite (CaF_2).
The Fe, Zn, Mn, Cd, Cr, Co, Al, Hg and Ni concentrations were lower than the WHO standards.

Discussion

The results of fluoride study will be discussed in this section. The sources of fluorides in the groundwater of Gaza Strip are believed to be natural bedrock that supplies the fluoride ions to the water. The results of soil samples showed good correlation with the groundwater results, as the same general increase of fluoride is shown from north to south. For the soil samples and the wells nearby, the correlation coefficient r of soil/water fluoride was 0.93. None of the four fluoride minerals screened by the XRD were found in the tested soil samples. The semi-quantitative analysis and the limit of detection of the XRD showed that there were no distinguished peaks for the four major fluoride minerals tested. In spite of that the computer model suggested fluorite (CaF_2) as a donating fluoride mineral to groundwater.
DFI showed a slight increasing trend going from north to south. Linear regression analysis found a correlation ($r = 0.72$) between the level of fluorides in drinking water and the DFI. It must be noted here that dental fluorosis was formed during the tooth development period and

years before the water was analyzed, suggesting that water resources have recently been altered.
The CFI for Gaza as a whole was calculated to be 2.42. According to Dean (1942) if the CFI rises above 0.6, it begins to constitute a public health problem warranting increasing consideration.
An epidemiological study of Rugg-Gunn *et al*., (1997) suggested that the prevalence of dental fluorosis was high among children suffering from malnutrition. Some correlation between drinking water type fluorosis and the population's socio-economic condition and nutritional status is indicated. Fluorosis prevalence increases through the agricultural towns of Khan Yunis to urban regions.

General Conclusions

1. Water in both municipal and private wells is polluted by one parameter or another; however, the municipal groundwater wells are less polluted. The results showed that 80% of the groundwater wells are not suitable for drinking purposes because of the high contents of nitrates, chlorides and fluorides and some heavy metals which exceed 2-7 times the WHO standards. Some wells have a permissible limit of nitrates but high amounts of chloride or fluoride and vice verse.

2. The governmental classification of the Gaza Strip into five regions correlates with the quality of the groundwater of each region.

3. The average results of trace elements in the groundwater indicated that they do not generally pose any health or environmental hazard in the Gaza Strip. In spite of that several private wells showed concentrations of Zn, Pb, As and Cd of more than the WHO standards. These wells should not be used for drinking purposes. These wells are exposed to the contaminants of the leachate of solid waste, wastewater and manure.

4. The well depth does not affect its water quality, while the location does. The ion ratios indicated that the high levels of chloride and other ions do not appear to be due to seawater intrusion into the aquifer only, but other water sources, including through flow from Israel, and natural chemical changes due to soil/water interactions may cause the majority of the ion variability in the aquifer.

5. The results of the study and the archive of groundwater geochemistry additional to the ion ratios revealed that the reasons of the anomalous-elevated levels of Cl and other ions are the anthropogenic factors, the lateral groundwater flow and the natural chemical changes and to a lesser extent the seawater intrusion.

6. The levels of fluorides found in groundwater and topsoil showed a general increasing trend from northern to southern areas of the Gaza Strip. Dental fluorosis occurred in many areas especially in Khan Yunis (south and south-east) where the average level of fluoride for all tested wells was 2.6 mg F/l.

7. The sources of fluorides in groundwater are believed to be natural bedrock that supplies fluoride ions to the groundwater; however the XRD results showed that none of the major fluoride minerals tested in soil samples were detected, the computer model-PHREEQC revealed that fluorite (CaF_2) was the donating mineral of fluoride ions to the groundwater.

General Recommendations

1. Several studies should be conducted mainly on the health risk assessment and water toxicology.

2. To improve our understanding of water quality in the aquifer an integrated monitoring program should be conducted. The municipal wells should be sampled 2-4 times a year for the analysis of anions, cations, heavy metals and pesticides. The data of the groundwater quality should be centralized in a data bank or a water archive.

3. The risk of deterioration of water quality is an urgent theme. The objective of the Palestinian water institutions should be how to safeguard the water resources system from pollution.

4. The situation in which fluorides play an important factor in public health must be addressed on an urgent basis to avoid an environmental health catastrophe. One of the recommendations we suggest is integrating the water supply for Gaza as a whole.

2. Wastewater and Sludge

Objectives

1. To introduce the concentration of trace metals and some major parameters in domestic, industrial wastewater and sludge for the first time.
2. To highlight the various options that aim to reuse the treated wastewater and sludge in the Gaza Strip in a manner that will ensure agriculturally sustainable development.

General Methodology (Sampling and Analysis)

Grab samples of wastewater were combined in a container to form a composite sample. Finally, one liter of the mixture was taken in an acid-washed bottle and transferred to the laboratory, where it was filtered in an acid-washed filter holder and through 0.45 µm pore size Sartorius membrane filters; the first few milliliters were used for rinsing, then discarded, and the filtrate was transferred to clean acid-washed polyethylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v) to pH <2 and stored at 4 ^{o}C until analyses by the inductive coupled plasma mass spectrometer (ICP/MS - Perkin Elmer-Sciex, Elan 6000) were performed. Several parameters were measured during the fieldwork: temperature, electric conductivity, and pH; other parameters (Settleable solids SS, total suspended solids TSS, total dissolved solids TDS, chemical oxygen demand COD, and biochemical oxygen demand BOD_5) were measured a few hours later according to the American standard methods (APHA, 1995). All other parameters were analyzed as described for groundwater samples.
Analysis of sludge samples was the same as soil and sediment mentioned below.

Main Results

The averages of calculated total organic carbon TOC for sludge are 17-22 % for Beit Lahai and Gaza, respectively, while the results of nitrogen for the two plants showed averages that are less than 2% (the American standards); nitrogen in Beit Lahia WWTP was 1.35% while it was 1.6 in Gaza WWTP. This range puts the sludge of Gaza in an acceptable ranking for land application.

The average of phosphorus in the sludge of Gaza plant was 0.7% while it was only 0.4% in the sludge of the Beit Lahia plant.

Fe, Cr, Co and As have similar concentrations and no significant changes occurred during the 3 years of monitoring; however the results for As and Zn were 2-3 times higher in the years 2001 and 2002, respectively. Nickel was 2-3 times higher in Beit Lahia WWTP while Mn and Pb were 2 times higher in the sludge of Gaza WWTP; the reason is expected to be the fluctuation of industrial activities and the irregular production load of these elements in the industrial wastewater. The high concentrations of Na in the sludge of Gaza (2-3 times) may be connected to the same ratio of Na in groundwater and wastewater for the two areas.

It was found that concentration of Adsorbable organic halogens (AOX) is in the range of 200-600 mg Cl/kg, while the German and EU standard is 500 mg Cl/kg.

Discussion

The results indicated that the concentrations of major anions (Cl, F, NO_3 and SO_4) and major cations (Na, Ca, Mg and K) in wastewater were similar to their values in the groundwater of the area of each treatment plant.

This raises the question about the main sources of Zn in sludge. Based on the field surveys, the Zn sources are expected to be domestic and commercial in origin. Domestic sources of Zn are corrosion and leaching of plumbing, water-proofing products, anti-pest products, wood preservatives, deodorants and cosmetics, medicines and ointments, paints and pigments, printing inks and coloring agents. The commercial sources are galvanization processes, brass and bronze alloy production, tires, batteries, paints, plastics, rubber, fungicides, paper, textiles, taxidermy, building materials, special cements, and also cosmetics and pharmaceuticals.

It is proposed that the main source of AOX in sludge was the 26 paper industries distributed in Gaza and the northern area. These industries were using old technologies and they represented the largest consumer of chlorine and the greatest source of toxic organochlorine discharges directly into waterways.

General Conclusions

1. The existing wastewater treatment plants in Gaza show a similar performance and the heavy metal contents of the effluent are less than that of the standards of neighboring countries, and the treated wastewater could be used in agriculture with respect to heavy metals.

2. The industries in Gaza are light and they have no treatment facilities. Some individual industries produce high amounts of heavy metals in their effluents but the wastewater treatment plants have the capability to absorb the industrial effluents with no significant impact on the treatment bioprocesses.

3. The existing plants produce small amounts of sludge with low contents of all tested heavy metals except Zn, which exceeds the standards of all industrial countries. This is additional to the AOX which is found to be more than 500mg Cl/kg in some sludge samples of Gaza treatment plant while more than 85% of the samples have less than 500mg Cl/kg.

General Recommendations

1. In addition to total metal concentrations the determination of specific chemical forms of heavy metals and their mode of binding in soil is very important in order to estimate their mobility, bioavailability and related ecotoxicity. Education, information, and training of farmers also play an important role in promoting sensible reuse practices.

2. Gaza Strip is a good example for similar studies in all neighboring countries which have similar conditions of metrology and climate, environment and natural resources, population growth, water scarcity, wastewater management problems and finally socio-economic situations. The findings and conclusions of wastewater reuse and sludge application could be imitated in these similar areas not only in the region but also in many developing countries.

3. By the reuse of treated wastewater, Gaza can not only reduce the pollution load of the Mediterranean Sea by wastewater contaminants but also consider wastewater as a precious source of water which could be used in agriculture.

3. Soil Profile and Topsoil

Objectives

1. To establish the topsoil geochemistry in the Gaza Strip.
2. To identify the major anthropogenic inputs affecting soil geochemistry.
3. To introduce all relevant information from the Gaza central wastewater treatment plant on hydrogeology, geochemistry, and geology.
4. To study the geochemical characteristics of an on site column of wastewater, sludge, soil, and groundwater in the area of the Gaza central wastewater treatment plant.

General Methodology (Sampling and Analysis)

Soil samples were properly labeled and placed in waterproof plastic bags before being placed in wooden boxes. Approximately 0.5 kg of soil was put in polyethylene cups and stored at 4 ^{o}C during transport to laboratories where soil was dried in an oven at 50 ^{o}C until constant weight. Then they were shipped to Germany in plastic sampling bags.
Samples were freeze-dried until complete dryness and sieved through a 2-µm sieve and ground to a powder by using a ring mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 0.5 to 1.0 g of each homogenized sample was dissolved in 10.5 ml of concentrated HCl (37% p.a.) and 3.5 ml of concentrated HNO_3 (65% p.a.) in 50 ml retorts. The samples were degassed (12 h) then heated to 160 °C on a sand bath until a complete extraction had taken place (3 h). After cooling, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for analysis.

Elements were analyzed by different instruments; a flame atomic absorption (AAS vario 6-Analytik Jena) for determination of Ca, Cu, K, Li, Mg, and Na; an ICP/OES (VARIAN, VISTA-MPX) for determination of As, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, and Zn; and an energy-dispersive miniprobe multielement analyzer (EMMA-XRF) (Cheburkin and Shotyk, 1996) for determination of Br, Rb, Se, Th, U, Y and Zr. Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of freeze-dried samples (50-100 mg) and Hg pre-concentration on a single gold trap by means of an AMA 254 solid phase Hg-Analyzer (LECO).

Total carbon and sulfur were determined directly in dried samples by using a carbon-sulfur determinator (LECO CS-225); and finally carbonates were measured directly by a carbonate bomb (Müller and Gastner, 1971). The total organic carbon (TOC) was calculated by the subtraction of inorganic carbon from total carbon. The distribution of total P represented as (PO_4) was measured according to APHA (1995).

Adsorbable organic halogen (AOX) was determined by a Euroglas organic halogen analyzer-The Netherlands according to the DIN 38414 S18 Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Sludge and Sediment (Group S) Determination of AOX (DIN, 1989).

In order to determine soil mineralogy, a semi-quantitative X-ray Diffraction technique (XR Diffractometer, SIEMENS) (Moore and Reynolds, 1989) was used.

Main Results

The upper 40-50 cm represent a mixture of sludge and fine sand and its color starts from dark black in the surface layer up to very light dark downward. A well-distinguished soil appears from 20 cm depth and more. The four examples of X-ray diffractograms show that the soil mineralogy is mainly composed, in order of abundance, of quartz, calcite, kaolinite, and some feldspars.

Among a total of 27 elements analyzed, only a few trace elements showed environmental relevance in Gaza: As, Cd, Cr, Hg and to a lesser extent Pb. The trace metal accumulations in the soils affected by sludge were characterized by a large spatial variability, with some ‘hot spots’ of Cu and Zn with concentrations of up to 1220, 1500 mg/kg, respectively.

The results of Ni, As, Se, Rb, Y and Zr were below the detection limit of the analytical procedure. The AOX in the soils of Gaza was very low and it ranged between the detection limit (0.5) and 20 mgCl/kg. A few sites showed high AOX values of 250 mgCl/kg due to their location near the sludge disposal areas and solid waste dumping sites.

Total P concentration in the top soil varies between about 0.4 and 1.2 gP/kg, and total C was between 0.5-3%. The lowest percentage of S in the soils of the Gaza Strip was 0.016% while the highest was 0.07%. $CaCO_3$ was 1.6-19%, while Ca was between 0.7 and 5.4%. Several of the residual soils in Gaza are relatively low in Mg (0.03%). Sodium contents in soils were 110-825 mg/kg. The lowest and the highest K averages were 330 and 4500 mg/kg, respectively.

Fe in the soils of Gaza ranging between 0.2 and 2% and Mn levels were between 37 to 542 mg/kg. The median of Cu in soils of the Gaza Strip was 10 mg/kg. The lowest Zn (2 mg/kg) was found in the local reference samples, with the highest (1800 mg/kg) being found in the soils exposed directly to domestic sludge. More than 75% of the soil samples showed Cd results below the detection limit (10 µg/kg).

Nickel was low with an average of 28 mg/kg and one guava farm showed a high level of Pb (145 mg/kg) while the rest of the soils showed an average of 30 mg/kg. An anomalous result for Cr (472 mg/kg) was found in the area of Beit Hanoun. The averages of Co, As for all soils was 6 mg/kg and e average of As was 2.2 mg/kg, while the site near the solid waste dumping site reached 19 mg/kg. Finally, the average of Hg in the soils of Gaza was 10 µg/kg with many samples being below the detection limit of the analytical method.

Discussion

The wastewater treatment plant was able to remove >92%, >88%, >60% of BOD_5, COD, and both total P and total N, respectively. This indicates that the majority of the metals have been transferred from the wastewater to the sewage sludge where Zn, Pb, Cu, and Cr in the sludge were 2100, 125, 240, and 75 mg/kg, respectively. The new results agree with the findings of Shomar *et al*., (2004), however, 20% may be lost in the treated effluent, depending on the solubility, and this may be as high as 40-60% for the most soluble metal, Ni (Scancar *et al*., 2000). The average of Zn removal in the treatment process was 55%; this ratio finds its way to the sludge and this may explain the high contents of Zn in the sludge (>2100 mg/kg).

The most affected zone by wastewater and sludge is the upper 40-50 cm of the soil profile and the metal content decreased with depth. Element mobility sequence was Ni>Ca>Cu>>Fe where the concentrations in the upper 5 cm were 40 mg/kg, 10%, 240 mg/kg, and 1.5% and in the lower 40 cm were 2, 0.5, 5, and 0.3, respectively. This result agrees with that of Legret (1993) and Cornu (2001). Nickel is the most soluble metal in sludge, and thus the most mobile (Henry and Harrison, 1992).

It was found that the soil metal content was affected by soil structure. The total contents of studied elements indicate that the concentrations of Zn, Mn, Cu, Fe, and partly As and Pb correlate with the clay content in the individual soil profile.
The results revealed that the occurrence of trace metals in the different soils of the Gaza Strip was dependent not only on the soil type but also on the location of the soil, the vegetation cover, the climatic conditions and the agricultural activities.

General Conclusions

1. A very good agreement was observed between soil physical characteristics and the vertical distribution of metals. The trend of most elements was: clay>sandclay>loose sandstone>sandstone>fine sand. The trend showed that the clay layer of 6-9 m depth had high contents of Al, Ca, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Y, Zn, and Zr, and to a lesser extent of Cd, Co, and Hg.

2. Except for the upper half-meter of the soil profile which is directly affected by waster and sludge, the lateral distribution of elements was dependent on the physical characteristics of the soil and not on the depth.

3. The treated wastewater is a promising water resource for agriculture, and regular monitoring systems on soil, crops and groundwater should be adopted. Sludges, on the other hand, have high Zn (>2000 mg/kg) and AOX (>500mg Cl/kg) concentrations, which exceed the standards of all industrialized countries for land application.

4. Although the groundwater samples were collected from the aquifer below the wastewater treatment plant, no anomalous concentrations were found with respect to metals. However, several studies showed that elevated salinity, nitrate, chloride, and sulfate are believed to be a result of both anthropogenic and natural sources.

5. The soil types, crop patterns, and specific location factors largely control the distribution of trace metals (Pb, Cu, Zn, Cd and Mn) in soils. Linear regression analysis found a correlation

coefficient of r =0.85 between Zn and Cd concentrations in soils and the presence of highways nearby.

6. The irrigation water, the applied fertilizers and fungicides, and the sludge and wastewater nearby have played a major role and contributed significantly the enrichment of several soils with Zn, Pb, Cu and Fe. Affected soils by sludge, solid wastes and wastewater showed similar contents of trace metals.

7. With respect to the global comparison, it may be noted that the values for the trace metals in the different soils of the Gaza Strip were well within the worldwide soil average values. These levels were still low and probably harmless to the soil ecosystem. However, the distribution pattern for Zn, Cd, and Cu in several soils clearly indicated that their contamination due to anthropogenic factors were on the rise and may become alarming if mitigation measures are not taken.

General Recommendations

1. Soil information system in the Gaza Strip should be established for classification, identification of the hot spots and sensitive areas, protection of soils against pollution and degradation.

2. For soil related issues great consideration should be given: soil rating; environmental protection; urban planning; agricultural needs; education, research and publicity; and accessibility to scientific information.

3. Considering some suggested strategies for soil such as: soil quality promotion; soil conservation; building a comprehensive soil information system in a well defined national and international networks; climatic aspects; geochemical studies; monitoring changes in land use; urbanization; increasing and preserving the areas of high productivity; social and educational programs; and strengthening and upgrading the institutional capacity building.

4. Wadi Gaza

Objectives

1. To establish a baseline study of water and sediment quality of the Wadi Gaza.
2. To identify the extent to which the relevant water and sediment quality parameters vary seasonally.

General Methodology (Sampling and Analysis)

Generally, water of Wadi Gaza was analyzed as the same as groundwater samples while sediment samples were similar to soil samples.

Main Results

The heavy metal concentrations in the sediments of the lake (downstream) were higher than those of the eastern eight stations (upstream) where the water was shallower. The discharge of olive oil mill wastewater was recorded in the Ca, Na, Mg, K and P concentrations in sediments of one of the sampling stations.

Water in shallower areas showed greater temporal variation than deeper areas. Several elements (P, Fe, Mn and As) showed the greatest temporal variability. For example, in the winter rainy season these elements decreased 2-10 times compared to their values in summer. Moreover, Ca, Na, Cl, PO_4, and NO_3 decreased 3, 3, 5, 2, 4 times, respectively. Some of the trace metals were more abundant in these waters compared to the domestic wastewaters of the study area. The averages of Cd and Co were 6 and 43 µg/l, respectively and they were 50 times higher than the domestic wastewater results.

Discussion

The wastes of the olive oil mill in the Wadi reduced the pH of surface water in summer and increased the Na, Mg, Ca and P concentrations. Water of Wadi Gaza was oxygenated (DO = 9.6 mgO_2/l) and the Fe and Mn were in the oxidized soluble forms.

The impact of seasonal variation was recorded for As and Cd and they showed opposite behavior, while Pb, Co, and Cu were not significantly affected.

Phosphorus in sediment followed an opposite trend to P in water; P in sediment was high in winter and low in summer.

During the summer sampling, some medical wastes were found in the area, as a result of the disposal activities by local clinics. The recent observations agreed with the findings of Zoarob (1997) who identified Wadi Gaza as a disposal site of medical wastes. This is probably the main source of Hg in the area. Mercury values were not affected by seasonal variation.

The summer season had many impacts on water and sediment and the sediment-water exchange of P was much dependent on the season. In the summer the sediment released P whereas in the winter, a P accumulation took place. In the summer season this phosphorus was used as a main source of nutrients needed for water plants covering the Wadi. Higher temperatures could lead to anoxic conditions in sediment resulting in Fe and P release. In winter the sediments are oxygen-rich, and Fe is in the Fe(III) form, which forms an insoluble bond with phosphate. Under anaerobic conditions of summer (to be more specific, at redox potentials below 150 mV), the Fe(III) was reduced to Fe(II). Since Fe(II)-phosphates are 100 times more soluble than Fe(III)-phosphates, this gave rise to a P release from Fe-P bondings.

General Conclusions

1. The results obtained served to increase our knowledge of the geochemistry of water and sediment of the Wadi Gaza. In spite of this, the study has highlighted the need for further research, by increasing sampling density and regularity to better characterize the geochemical conditions of the Wadi.

2. Excluding Station 7, no major contamination of Fe, Zn, Cu, Mn, As, Pb, Cr, Cd, and Co was found in water at most of the stations. Sediments in only two stations had high Hg, Cd, Fe and Zn compared to background values of Turekian and Wedepohl (1961). Heavy metal contents in sediment samples were low in the eastern stations and higher in the lake.

3. The various anthropogenic inputs may lead to the enrichment of many metals in the sediments of Wadi Gaza. Pollution of several sites was found to be considerably high for Hg, Cd, Fe and Zn and to a somewhat lesser extent for As, Pb, Ni, Cu and Co, whereas anthropogenic input of Ga, Se and Th seems to be less important.

4. The chemical composition of water and sediments exhibited seasonal variation. The human inputs affect the concentrations of the tested parameters in summer; while the precipitation inputs in winter diluted pollutants to minimum levels.

General Recommendations

1. Wadi Gaza is the only wetland in the Gaza Strip and its unique habitat and species warrant careful management. The opportunity exists to apply measures which can bring both ecological and socio-economic benefits. Measures to clean up and restore the wetland would bring ecological, landscape and visual improvements. This may improve the health and the environmental conditions for local people, bring new opportunities in education, recreation, tourism and research, as well as maintain a range of cultural, social and historical heritage values.

2. The main pressures should be reduced in short, medium and long term measures. These pressures include overgrazing, pollution from the untreated wastewater, discharge of oils and pesticides, cutting and burning of natural vegetation, building roads, agricultural encroachment, hunting and poaching. By reduction of these pressures, the ecosystem functions and productivity will be restored. Examples of short term measures would be to open the mouth of the Wadi to the Mediterranean Sea and to stop the use of oil and pesticides for combating mosquitoes. Examples of medium and long term measures would be to stop the discharge of raw wastewater to the Wadi and to cooperate with the upstream regions in management of the Wadi water resources. Because the Wadi is subject to many jurisdictions, local, governmental, and nongovernmental institutions should all play a role in protecting and conserving the Wadi. The efforts should aim to support the conservation of the wetland by implementing activities such as: (a) cleaning campaigns, (b) removal of construction debris, (c) development of recreational areas, (d) building of bridges of culverts, hiking trails, observation towers, and water retention structures and (e) planting of trees in the site.

5. Pesticides in Groundwater and Topsoil

Objectives

1. To identify and quantify the concentration of pesticides in the groundwater and the topsoil of the Gaza Strip.
2. To introduce a general method for determination of heavy metals in solid pesticides; and to reveal the heavy metal contents and some elements in 53 pesticides which are intensively being used in Gaza.
3. To prove that even pesticides originally with no heavy metals in their chemical structure have impurities of such metals that have been added by local markets.

General Methodology (Sampling and Analysis)

Water was collected in 1-liter glass bottle and treated with 5 ml phosphoric acid (85%, analytical grade) followed by 100 µl internal standard solution (5 µg/ml) of 2,4-dichlorophenoxyacetic acid (Ring $^{13}C_6$) in methanol. The bottles were thoroughly shaken and placed in an ice cooling box and later extracted using a solid phase extraction (SPE-cartridge type: Oasis HLB, 200 mg, 6 ccm, 30 µm grain size) technique as described by Stan (1995).

The SPE was rinsed with 3 ml ethyl acetate (analytical grade) followed by 3 ml Milli-Q water. The water sample was extracted through the SPE with fixed filtration flow rate of 10 ml/min. At the end of the extraction step, the SPE was washed with 5 ml Milli-Q water and some air was sucked through the cartridge for several seconds. The SPE cartridges were wrapped in aluminum foils in order to protect them from contamination and were kept frozen until they have been sent to Germany for analysis.

For the final preparation of water samples, the solid phase extractors were cleaned by 6 ml methanol/ tert-butyl- methyl ether (TBME), 20:80 (v:v). Then 100 µl of internal standard mix 33 (5 µg/ml) was added. The final volume was reduced to 0.5 ml by a gentle stream of N_2 where it was transferred into measuring vials. 100 µl diazomethane solution were added and the vials were degassed and kept at 4 ^{o}C.

Soil samples were freeze-dried for 48 h until complete dryness and sieved through a 2-mm sieve. Approximately 10 to 20 g was placed in a Soxhelt extraction-cartridge and extracted over night (12 h) with 75 ml n-hexane/ethylacetate (100:2 v/v). To the extract, 100 µl of the internal standard for the GC/MS (Ehrenstorfer internal standard mix 33, (5µ/ml) was added followed by 1 g anhydrous Na_2SO_4. The samples were evaporated to about 6 ml through a rotary evaporator, then to 1 ml by a gentle stream of N_2. About 0.8 g home made silica gel/$AgNO_3$ (100:5 wt:wt) was poured into the SPE followed by few drops absolute methanol for activation. The SPE cartridges were conditioned by 6 ml n-hexane/ethylacetate. The extract was cleaned by 6 ml n-hexane/ethylacetate where they were received in glass tubes and reduced by a gentle stream of N_2 to 0.5 ml, so an enrichment factor of 20 was reached.
A gas chromatograph mass spectrometer (GC/MS) and a high performance liquid chromatograph mass spectrometer (HPLC/MS) were used for determination of organochlorine pesticides in extracted water and soil samples.

Pesticides, fertilizers and fungicides were freeze-dried and ground to powder. Determination of trace elements in major pesticides, fertilizers and fungicides was measured using EMMA-XRF for K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb. As the results of the EMMA-XRF are semi-quantitative and showed a signal to go for detailed quantitative determination, full digestion procedure and ICP instrument was used. The samples were handled with great care, under a hood, and about 0.5 to 1.0 grams of the homogenized sample were dissolved with 10 ml of concentrated nitric acid (Merck 65% p.a.) in 50 ml retorts. The samples were allowed to degas (24 h), and then they were heated on a sand bath to 50 ^{o}C for 30 minutes then to 160 °C for 3 hours. After cooling, the solutions were diluted with Milli-Q water in 50 ml volumetric flasks, then filtered through 0.45 µm pore size membrane filters and transferred in 100 ml polyethylene bottles for analysis. Elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sc, Sr and Zn) were analyzed by ICP/OES (VISTA-MPX, VARIAN). The detection limit of the ICP/OES was estimated 10% less than the lowest standard used for calibration.

Main Results

Despite the fact that more than 52 different pesticides were applied across agricultural farmlands in Gaza, only few pesticides were detected in the soils of Gaza and many were found in the groundwater.

The LC/MS and GC/MS results showed that 92% of target pesticides in the groundwater were less than the instrumental detection limit.

Also, the results of the analysis indicated low levels of pesticides in 13 of the 94 wells tested. Of the 13 wells, 5 were agricultural wells, and the remaining were municipal wells. The wells are mostly in the areas of Khan Yunis and Rafah.

Bromacil was 0.5 µg/l in Safa 1 and Atrazine-desisopropyl was 0.1 µg/l in Safa 2 (R/25a). Most results of the GC/MS of other target pesticides were generally less than the detection limit. Several private wells in Rafah area showed traces of endrin, heptachlorepoxide, DDT, DDE, and DDD.

Atrazine was detected in 47% of groundwater samples, while atrazine-desisopropyl, propazine, simazine were detected in 40%, 24%, and 13% of water samples, respectively. All showed results above the instrumental detection limit. Two water samples showed 5 µg/l of triadimenol, the wells are private and located in the area of Gaza wastewater treatment plant.

Several soil samples of strawberry greenhouses in Beit Lahia showed detectable values of propazine, sebutylazine, terbutylazine, 4,4’-DDT, 4,4’-DDE, and 4,4’-DDD. The averages of propazine, sebutylazine and terbutylazine were 19, 13 and 39 µg/kg, respectively. A linear regression r = 0.87 was obtained between the occurrence of detected pesticides and soils of strawberry greenhouses.

The results showed that one soil sample had high contents of 4,4'-DDE and 4,4'-DDT which were 1104 and 793 µg/kg , respectively. This sample was collected from the northern area of Beit Lahia in a vegetable farm.

The calculated value of each element in the analyzed pesticides is much higher than the measured value. Al, for example, in fosetyl-aluminum was 4 times higher than the measured value and it was 3 times higher in the second sample of the same pesticide; Zn was 11, 6, 1 and 12 in propineb, mancozeb, metiram, and zineb respectively; Mn was 4 and 9 times higher than the measured value in mancozeb and maneb respectively; Br 3 times higher in the two samples of bromacil; while it is 6895 and 9480 times higher in the two samples of bromadiolone; and finally Cu was 2 times higher in both copper oxychloride and copper sulfate.

Discussion

The levels of pesticides found in 92% of the tested wells were below the WHO allowable drinking water standards. Approximately half of the wells, in which pesticides were detected, were below the detection limit for the pesticide in question, and therefore should be used with caution, since at these low levels, the results may not be repeatable; wells P/10 and P/10a are examples of these wells. Some private wells showed a sum of detected pesticides more than the EC standards (1998) and the German legislation (Trinkwasserverordnung, 2001).

The higher detection of pesticides in the groundwater of the southern areas may be due to the presence of large number of greenhouses, which possibly use large quantities of pesticides. The area in the north near well E/45 is also heavily agricultural, with strawberries being a main crop.

The differences in the results of the 3 consecutive years for the same well was insignificant while there was a significant variation in pesticide concentrations for the well depth and location. The deeper the water table, the less likely that pesticides reach groundwater. Most of groundwater wells that showed detectable pesticides have 25-50 m depth. A deep aquifer of municipal wells provides more opportunities and time than does a shallow aquifer of private wells for pesticide adsorption, degradation and other processes to occur. The recharge of rainwater and agricultural activities can carry pesticides down to the aquifer.

There was a correlation between the occurrence of some pesticides in groundwater such as atrazine and water salinity ($r = 0.64$) and this conclusion agrees with Gascon *et al.*, 1998. Most of agricultural wells of the southern area have average Cl concentrations of 1200 mg/l and the highest values of atrazine range between 6-20 µg/l. Wells D20 and E11b in the northern area showed anomalous results as they are old and were used for decades as private wells before they became municipal.
The field surveys revealed that the potential sources of pesticide contamination of private wells include sites used for pesticide storage mainly in the well building, mixing, loading, disposal, or application. Most of private wells are located inside the farm and surrounded by intensive agriculture.

It is found that farmers of Gaza use atrazine more than any other pesticide because it is highly effective and less expensive compared to other herbicide options currently available. One of the reasons why all atrazine containing products are classified as restricted use pesticides is that atrazine is relatively mobile and can move with water or sediment, through runoff or leaching (USNRCS, 2004).

General Conclusions

1. Several pesticides were detected in the groundwater of Gaza and the minority has concentrations exceeded their respective WHO maximum contaminant levels or health advisory levels for drinking water.

2. Private groundwater wells showed higher contents of pesticides than the municipal wells. The levels of pesticides found in the municipal wells were at levels well below the water quality guidelines, and many were at levels close to the detection limit for the method and should therefore be used with caution.

3. Several factors affecting the occurrence of pesticides in the groundwater of Gaza; soil type, aquifer characteristics and meteorological conditions, well location, well depth and groundwater quality.

4. Tested pesticides have considerable amounts of heavy metals and there is no agreement between measured and calculated values; the calculated values are much higher.

5. The same pesticides have different names in the same shop and in different shops, as well as different amounts of the same heavy metals.

6. Many tested pesticides have no heavy metals in their chemical structure in the pure form but they have them in the marketed forms in Gaza.

7. The field surveys revealed that the contamination of pesticides by heavy metals may occur due to bad procedures of storage and preservation; mixing of some pesticides in the market itself without scientific rules; and finally the absence of legislations and governmental inspection programs.

8. Pesticides should be considered as a source of some heavy metals in soil and groundwater of the Gaza Strip and they should be included in mass balance and geochemical cycle of some heavy metals.

General Recommendations

1. Special care should be given to the pesticide markets, storage, preservation and labeling to regulate the banned and restricted pesticides.

2. The results propose that pesticides should be considered as a source of certain trace metals (Cu, Mn, and Zn) and other elements (Br, Sr and Ti) that may affect their mass balances in soil and groundwater as well as plant uptake; and different scenarios and calculation models of heavy metal transport in soil and groundwater of the Gaza Strip should include pesticides as an additional source of certain heavy metals.

3. As the environment of Gaza is extremely susceptible to contamination, regular monitoring programs of pesticides in soil, groundwater and crops should be conducted. As well as epidemiological studies are needed with detailed exposure assessment for individual pesticides, taking measures to reduce risk into consideration.

4. As pesticides are often misused by the non-professional, inexperienced farmers, awareness campaigns and training courses for all relevant people and in all levels should be implemented.

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Chap. 6

Chap. 7

CHAPTER ONE

Deterioration of Groundwater Quality in the Gaza Strip: Alarm for Actions (*)

ABSTRACT

A large database is available of dissolved-fraction groundwater concentrations for Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr and Zn in the course of a 3-year monitoring program in the Gaza Strip. The results show that the trace elements of the groundwater of the Gaza Strip do not generally pose any health or environmental hazard. In spite of that, only 10 % of the municipal wells meet the WHO standards. Cl^-, NO_3^- and F^- concentrations exceeded 2-5 times the WHO standards in 90 % of the wells tested with average concentrations of 750, 75 and 1.6 mg/l, respectively. Several private wells should not be used for drinking purposes as the average of Zn, Cd, Pb, Fe and As was 58, 30, 270, 468 and 10 µg/l, respectively. A severe water dilemma will appear in the near future from both quality and quantity aspects.

Key words: Anions, Gaza Strip, Groundwater, Heavy metals.

(*) *The study was submitted to an International Journal.*

INTRODUCTION

The environment in Palestine suffers considerable strain. The shortage and pollution of resources, coupled with a high population growth and insufficient job opportunities have created many environmental problems (MEnA, 2000). Shortage of water and deterioration of water quality constitute limiting factors in the economic development of Palestine (MEnA, 2001). Palestine is experiencing a severe water crisis caused mainly by the lack of control over the Palestinian water resources.

At present the average per capita water consumption by the Palestinian population is approximately 55 l/c/d, or 55% of the WHO minimum standard of 100 l/c/d. This means that the communal water supply for the Palestinian population is substantially inadequate by international standards. The average per capita water availability in Palestine, which is 105 m^3d, is the lowest in the world (Abu Zahra, 2001).

Wise management, development, protection, and allocation of water resources should be based on sound data regarding the location, quantity, quality, and use of water and how these characteristics are changing over time. The quantity and quality of available water varies over space and time, and is influenced by multifaceted natural and man-made factors including climate, hydrogeology, management practices, pollution, etc. The foundation for water - resources decision - making, sound data must be continuous over space and time (PEPA, 1994).

Natural and anthropogenic contamination of groundwater by heavy metals has become a crucial water quality problem in many parts of the world. Municipal and industrial wastes of the Gaza Strip represent a real threat to groundwater; they can contaminate groundwater where infiltering precipitation can carry leached pollutants from dumping sites (Shomar, 1999). The water quality in Gaza is affected by many different water sources including inflow of groundwater through the 1948 borders, soil/water interaction in the unsaturated zone due to recharge and return flows, mobilization of deep brines, sea water intrusion or upconing and disposal of domestic and industrial wastes into the aquifer. The seawater intrusion and the upconing of brines in some areas may be due to a water imbalance in the aquifer, since the rate of water extraction exceeds the rate of groundwater replenishment. Previous reports on the water quality in Gaza have extensively discussed the high levels of chloride and nitrate in the drinking water, but they did not address their impact on the human health. Fortunately, recent studies on the health-effects of nitrate in drinking water indicate that the effects are less severe than assumed before, and that nitrate may even play a protecting role against gastro-intestinal infections (L”Hirondel and L”Hironedel, 2002). The high concentrations of nitrates in the groundwater appear to be due to fertilizers and sewage contamination from within Gaza. Data indicate that levels of nitrate east of Gaza, byond the 1948 borders, are lower than those in Gaza (CAMP, 2001).

Municipal wells are being used for drinking and domestic purposes while private wells are being used for irrigation. More than 90% of the population in the Gaza Strip is connected to the municipal drinking water network while the other 10% of the rural areas are dependent on the private wells.

In the Gaza Strip, the geology, hydrology, the groundwater flow and aquifer recharge have been investigated (Shomar et al., 2004b). Little or no information is, however, available with regard to the content of the trace constituents, hydrocarbons, pesticides, and microbes in the groundwater of the Gaza Strip. Trace elements are contributed to the groundwater from a variety of natural and anthropogenic sources. Once elements are taken up by the groundwater, their distribution is continually reset by complex geochemical processes (e.g. equilibrium and non-equilibrium water/solid interactions, advection, dispersion, absorption, precipitation, coprecipitation, chelation, colloidal interaction) and biological processes (Newcobm and Rimstidt, 2002; Al-Awadi et al., 2003).

During the preparation phase of this study, it became apparent that the chloride and nitrate contamination of the groundwater in Gaza is not the only threat to the groundwater and therefore the drinking water. Many of the agricultural wells have large surface openings (greater than 1m) where oil products, fertilizers, or any other items stored in the well housing may enter the aquifer by carelessness or accidental spilling of materials into the well. In general the largest threat to the aquifer from these wells appear to be petroleum based products or pesticides, since both of these products tend to be stored in the well building.

The objective of this paper was to achieve an understanding of the quality of the groundwater as it currently exists and to determine if any of the parameters tested pose a threat to human health in the Gaza Strip. Specific analysis of contaminant such as finger printing of heavy metals in this scale is being conducted for the first time.

MATERIALS AND METHODS

Study Area

The Gaza Strip, as one of the most densely populated areas in the world (2638/km^2; PCBS, 2000), with limited and deteriorated resources, has already started to suffer the outcomes of environmental quality deterioration. The study area is a part of the coastal zone in the transitional area between the temperate Mediterranean climate to the east and north and the arid desert climate of the Negav and Sinai deserts to the east and south (Fig. 1). As a result, the Gaza Strip has a characteristically semi-arid climate. The hydrogeology of the coastal aquifer consists of one sedimentary basin, the post-Eocene marine clay (Saqiya), which fills the bottom of the aquifer.

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. Ample supplies of high quality water are essential for economic growth, quality of life, environmental sustainability, and - when considered in the extreme - for survival.

Water quality in Gaza is tested by different agencies for different reasons. The Ministry of Health tests all of the municipal wells twice a year for the major ions, nitrates, and coliforms to insure that the drinking water is safe for public consumption. The Ministry of Agriculture tests more than 340 wells twice a year for chlorides and nitrates and some additional ions to assess the quality of the irrigation water in Gaza. In addition, the United Nations Welfare Relief Agency (UNWRA) tests their drinking water wells in the Refugee Camps on a regular basis.

In the Gaza Strip, qualified laboratories for trace element analysis in the groundwater and soil are virtually absent and the existing ones are private and very expensive. Because of these reasons trace element monitoring programs in the groundwater and soil are absent and have received relatively less attention when compared to major anions (Cl, F, NO_3 and SO_4) and cations (Ca, Na, K and Mg).

Criteria of Sampling and Analysis

The groundwater sampling campaigns were performed according to many justifications fitted to Gaza. Previous data, meteorological conditions, natural and anthropogenic factors, agricultural practices, well ownership, different and interfered factors affecting groundwater quality, etc. are examples of these justifications. To provide an overall level of information on the water quality and the health risks, all available municipal wells were sampled. Additionally, 20 agricultural wells were monitored for the same purpose. Under the above mentioned factors and for better understanding, the Gaza Strip was classified into 5 regions according to the governmental system, north, Gaza, middle, Khan Yunis and Rafah. This classification may help people and decision makers in each region to take actions when required.

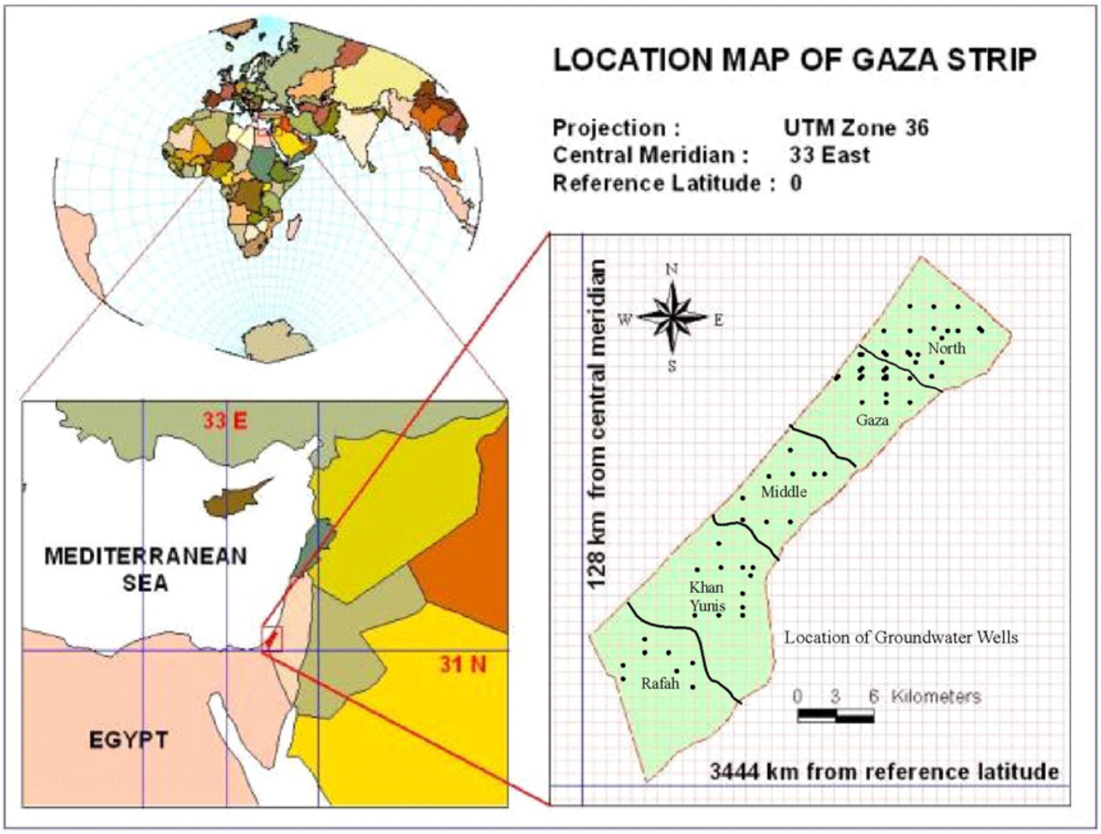

Figure (1) The study area, classification of the Gaza Strip and the location of the groundwater wells.

Based on the complexity and the political conflict in the region, the sampling started in the areas far away from political conflicts especially in the north area, Gaza area and middle area, and then extended to the south where the situation was very difficult. However, some of the agricultural wells in the south required several visits to obtain samples because the wells were not running and the owners were not present. The sampling program went smoothly, and all but 15 of the wells that were initially selected were not sampled because of political conflicts in the region.

Due to the difficulty and expense of characterizing the groundwater system, the priority was given to the municipal wells used for drinking and domestic purposes and several private wells used for irrigation. The private wells were selected to represent the five geographic areas of the Gaza Strip.

The sampling campaigns were conducted in three different seasons. The first coincided with the end of the annual summer dry season (October and November 2001). The second was conducted at the end of the annual winter rainy season (April and May 2002), while the third program took place during the winter rainy season and rain fell in considerable amounts during the sampling period (January and February 2003).

Chlorides were measured in all wells as it is the well-known parameter for salinity and freshness, not only for specialists but also for the public, especially in the last few years as people started to use home-filters or buy mineral water.

Nitrates are known as a reason of methaemoglobinaemia. It is documented in the files of children hospitals of the Gaza Strip that there is a strong correlation between the high levels of nitrate in drinking water and the distribution of methaemoglobinaemia. On the other hand, this correlation may be indirect; high levels of nitrate are commonly associated with fecal pollution, and the true cause of methaemoglobinaemia seems to be the intestinal infections; l”Hirondel and l”Hirondel (op.cit.p.44) state: “to conclude, the hypothesis that well-water methaemoglobinaemia is caused by nitrate in the feed being reduced to nitrite in the digestive tract seems unreasonable”. They also report on the (unethical) experiments of Cornblath and Hartman, who gave small infants artificial well water with 1000 mg NO_3^-/l and observed no clinical methaemoglobinaemia.

Fluorides are known as a reason of dental fluorosis; and Shomar et al., (2004d) confirmed the correlation of the disease among the school children and the high levels of fluoride in the groundwater.

Heavy metals were measured for the first time in the scale of a three-years monitoring program to find the wells with high levels of metals and the proposed sources of such metals in the groundwater.

In order to assure that the sample collected was from the groundwater and not water standing in the well, it was originally proposed that the well should be pumped for a minimum of one to two hours prior to the collection of the sample. However, this was not always possible. The second sampling program occurred at the end of the winter rainy season, and many agricultural well owners were not using their wells extensively. However, if it is assumed that the average agricultural well has a 10-meter depth of standing water in a 12-inch diameter pipe, the standing well volume is approximately 1m^3. Therefore one hour of pumping at a rate between 45 and 70 m^3/hr is sufficient to purge at least three standing well volumes; this principle is a USEPA rule of thumb for well purging.

Groundwater Samples

Prior to the field work a one month intensive course was given to the field staff in Germany to provide them with an understanding of the field techniques to be used, the preparation of sampling containers, the calibration and the usage of the portable kits, the sample's additives, the labeling, the preservation procedures and finally the preparation for shipments to Germany.

All samples were collected in laboratory certified clean bottles and labeled as to the well location, date and time of sample collection, analyses to be performed, and field preservation performed, if any. Preservation of samples in the field was done to avoid revisiting the wells if mistakes occurred while adding the chemicals to the samples.

Figure 1 shows the distribution of the selected groundwater wells in the study area. Samples were collected from 90 groundwater wells; all were municipal and used for drinking purposes. They represented all geographic areas: 23 north, 24 Gaza, 9 middle, 9 Khan Yunis and 4 Rafah. Twenty private wells were selected but some do not have an ID but the location is known. Table 1 shows the well ID and to which region it belongs. (For the exact locations of groundwater wells see the attached map in the appendices).

Table (1) Monitored municipal groundwater wells in each area of the Gaza Strip.

Region	Well ID	Region	Well ID	Region	Well ID
North (Jabalia)	E/156	Gaza	R/162L	Middle Area	D/72
	E/4		R/162 L1		G/49
	E/1		R/162E		S/71
	Q/40B		R/162B		S/42
	E/90		R/162C		J/32
	D/74		R/162D		J/146
	E/61		R/162H		S/69
	E/142		R/162Hnew		K/21
	D/20		E/154		K/20
	D/60		E/157	Khan Yunis	D/72
	E/11B		D/68		G/49
	E/11C		D/69		S/71
	E/138		D/70		S/42
North (Beit Hanoun)	C/128		R/162G		J/32
	C/20		D/71		J/146
	C/76		D/72		S/69
	C/127		R/254		K/21
	C/79		R/265		K/20
North (Beit Lahia)	A/185		R/271	Rafah	P/15
	E/6		Sh.Ej.5		P/24
	D67		R/74		P/145
	Attatra		R/25B		P/153
	A180		R/25A		
			R/25D		

One-liter samples were collected and placed in a sampling ice-box and transferred to the laboratory. The sample was divided into two subsamples: the first (500 ml) was filtered in an acid-washed filter holder and through 0.45 µm pore size membrane filters, the first few milliliters were used for rinsing, then they were discarded, and the filtrate was transferred to clean acid-washed polyetheylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v), and stored at 4 ^{o}C until analyses by ICP/MS (Perkin Elmer-Sciex, Elan 6000). The total content of Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sr and Zn was determined next to the cations of Ca, K, Mg and Na. The other part of the water was filtered with no additives and stored at 4 ^{o}C for anion analyses by Ion Chromatography (IC). Several parameters were measured in the water samples during the fieldwork: temperature, turbidity, electric conductivity and pH; other parameters were measured in the laboratory.

Quality Control

For quality control, analytical blanks and two samples with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents. For the groundwater analysis, Standard Reference Materials 1643c and 1643d were used for the determination of trace elements (NIST, 1991 and 1994). As an independent check of the major parameters, they were also measured in two laboratories with different methods (Table 2). The results of the analyses were also reviewed in terms of the milli-equivalent balance, which compares the ionic charges of the major anions and cations (APHA, 1995). Because water is electrically neutral the charges should balance; however charge balance errors less than 5% generally are considered to be acceptable (Freeze and Cherry, 1979).

A simple linear regression value of ion concentrations and ratios was used. A correlation coefficient was determined for the distribution of the major ions in the five geographic areas of the Gaza Strip. The univariate regression analysis and correlation coefficient were used to combine results of water chloride concentration with the nitrate contents of the same well.

For the comparison of the results in the five regions, the results of each groundwater well were averaged then the averages of all wells of each region were averaged. The variance between the averages of the regions was higher than the variance in the average of the wells of each region. In other words, the comparison was carried out because the standard deviation and the f-test for the regions were significant.

Table (2) Analytical methods used in Gaza and Germany.

Test	Method in Gaza*	Method in Germany
Temp., pH, EC, DO	Portable field kits	Not measured
Cl	Ion Selective Electrode (ISE)	Ion Chromatograph (IC)
NO_3	UV Spectrophotometric Screening method	IC
F	Ion Selective Electrode (ISE)	IC
SO_4	Turbidimetric method	IC
PO_4	Vanadomolybdophosphoric acid colorimetric	IC
HCO_3	Tirtimetric method	Not measured
Ca	EDTA titrimetric method	ICP-OES
Na, K, Mg	Flame photometric method	ICP-OES
Heavy metals	Not measured	ICP-MS & ICP-OES

* APHA, 1995.

Meteorology, Geology and Hydrology

To explain the significantly different heavy metal levels in the groundwater and soil of the Gaza Strip, the different geological settings and actual hydrogeological conditions of the area must be considered. The geology and geochemistry of soil profiles were described by Shomar and others (2004b).

The coastal aquifer of the Gaza Strip is part of a regional groundwater system that ranges from the coastal areas of the Sinai (Egypt) in the south to Haifa in the north. The coastal aquifer is generally 10-15 km wide, and its thickness ranges from 0 m in the east to about 200 meters (m) at the coastline.

There are two well defined seasons: the wet season, starting in October and extending into April, and the dry season from May to September. The average daily mean temperature ranges from 25 °C in summer to 13 °C in winter, with the average daily maximum temperature ranging from 29 °C to 17 °C, and the minimum temperature ranging from 21°C to 9 °C, in the summer and winter, respectively. The daily relative humidity fluctuates from 65% in the daytime and 85% at night in the summer and between 60% and 80%, respectively, in the winter. The mean annual solar radiation is 2200 J/cm^2/day. There is a significant variation in the wind speed during the daytime, and the average maximum wind speed velocity is about 3.9 m/s. Moreover, storms have been observed in winter with a maximum wind speed of about 18 m/s. Peak months of rainfall are December and January; the average annual rainfall is 335 mm/y (26 year average) (CAMP, 2001).

The coastal aquifer consists primarily of Pleistocene age Kurkar Group deposits including calcareous and silty sandstones, silts, clays, unconsolidated sands, and conglomerates. Near the coast, coastal clays extend about 2-5 km inland, and divide the aquifer sequence into three or four sub-aquifers, depending upon the location. Towards the east, the clays pinch out and the aquifer is largely unconfined (PEPA, 1994).

Within the Gaza Strip, the total thickness of the Kurkar Group is about 100 m at the shore in the south, and about 200 m near Gaza City. At the eastern Gaza border, the saturated thickness is about 60-70 m in the north, and only a few meters in the south near Rafah. Local perched water conditions exist throughout the Gaza Strip due to the presence of shallow clays (MEnA, 2000).

Under natural conditions, groundwater flow in the Gaza Strip is towards the Mediterranean Sea, where fresh groundwater discharges into the sea. However, natural flow patterns have been significantly disturbed by pumping and artificial sources of recharge over the past 40 years. Within the Gaza Strip, large cones of depression have formed over large areas in the north and south. Water levels are presently below the mean sea level in many places, inducing a hydraulic gradient from the Mediterranean Sea towards the major pumping centers and municipal supply wells. From the limited available piezometer data, head differences between sub-aquifers along the coast are on the order of 0.1-0.5 m, suggesting that intervening clay layers may be sufficiently impervious in certain places to hydraulically separate the various sub-aquifers.

Long term records (>20 years) of water levels are available for more than 100 wells in the Gaza Strip. Between 1970-1993, water levels dropped 1.6 m on average, mostly in the south. This is equivalent to a decline of 5 million cubic meters per year (Mm^3/y) in overall aquifer storage on average, using a specific yield of 0.2. The water level declines are most apparent in the south, and are most likely a reflection of the lower recharge from rainfall in this area. In the north, most wells exhibit relatively slow declines with partial or complete recovery following the wetter than usual hydrological year 1991/92 (CAMP, 2001).

RESULTS AND DISCUSSION

Due to the huge amounts of data for the three-year monitoring of more than 20 parameters, this section will treat the environmentally significant results only. The results exceed the WHO standards and may have risks on human or environmental health. The average value is discussed and anomalous ones are rejected. The samples were analyzed by two separate laboratories for major anions and cations and the results varied. The values were averaged to provide the figures for this section. The variation in the concentration of the same element for the three years could be explained by personal or instrumental errors, groundwater sample collection, preservation, transportation, laboratory analysis and data reporting carry various levels of uncertainty with them that affect the reported element concentration.

General Physico-chemical Parameters (pH, EC, DO and salinity)

Generally, the depth of the old wells is ranging between 40 and 60 m, however the municipal wells are deeper than the private ones. The wells dug after the year 1995 have depths of 90 to 120 m. The average temperature of the groundwater was 20 ^oC in the summer and 24 ^oC in the winter. The pH of the groundwater (Table 3) ranges between 6.8 and 7.5 and this small variation is dependent on the geographical dimension and seasonal variation. Generally, the electric conductivity (EC) increases from the north to the south (Table 3) with some exceptions in Rafah area, this means that the water salinity also had the same trend. The best aquifer -in terms of fresh water- was located in Beit Lahia at the north western corner of the Gaza Strip; the lowest value was 520 µS/cm and the highest was about 1000 µS/cm. The most deteriorated and salty water was in the regions of Khan Yunis and Rafah with an average EC in the municipal groundwater wells of 5000 µs/cm. Within the same region of Gaza, the north wells have low EC while the south wells have high values. These findings enhance the Gaza municipality to mix water of north and south wells before supplying the consumers. The groundwater of the Gaza Strip is oxygenated and the average dissolved oxygen (DO) was 7.8 mgO_2/l in summer and 8.2 mgO_2/l in winter (Shomar et al., 2004c).

Table (3) Results of water quality-major parameters (average of three years).

Parameter	Beit Lahia	Beit Hanoun	Jabalia	Average North	Gaza	Middle	Khan Yunis	Rafah
EC (µS/cm)	769	1867	1057	1231	2156	2778	3278	1838
TDS (mg/l)	395	1183	672	750	1364	1828	2040	1194
pH	7.4	7.4	7.3	7.4	7.3	7.3	7.4	7.5
Ca (mg/l)	104	104	109	106	86	118	88	55
Mg (mg/l)	29	57	44	43	50	97	53	58
Na (mg/l)	63	184	65	104	254	340	507	282
K (mg/l)	5.0	3.2	4.4	4.6	11.8	6.0	5.8	6.6
F (mg/l)	0.7	0.4	0.8	0.6	1.1	1.4	2.0	0.8
Cl (mg/l)	90	375	128	198	431	620	684	352
NO_3 (mg/l)	58	79	115	99	107	71	191	71
SO_4 (mg/l)	28	54	52	45	104	226	278	127
Alka. ($mgCaCO_3/l$)	218	279	210	236	290	234	255	260
Hardn. ($mgCaCO_3/l$)	293	490	379	387	415	399	445	246

Ions

Except for a few wells in the north area of the Gaza Strip, all wells tested showed high to very high contents of the major ions (Table 4). The anion-cation balance of the results obtained for each well showed that the majority of cases are below 5% for each laboratory. However, this does not mean that the laboratories had identical results. In many instances the results of both laboratories have low charge balance percentages, but the differences between the results of each parameter are large. An example of this was the wells D/72 and K/21. In both instances the charge balance error was 2%, however the values were quite variable.

Table (4) Comparison of the results of major Ions and WHO standards.

Parameter	WHO*	% < WHO	% > WHO
TDS (mg/l)	1000	37	63
Cl (mg/l)	250	46	54
NO_3 (mg/l)	50	10	90
F (mg/l)	1.5	80	20
SO_4 (mg/l)	250	86	14
Ca (mg/l)	50**	11	89
Mg (mg/l)	30*	13	87
Na (mg/l)	200	47	53
K (mg/l)	10**	93	7
Hardness ($mgCaCO_3/l$)	300	30	70

*) WHO, 1998a.

**) ICON, 2001, European Community guide level.

The differences in the values may be indicative of certain laboratory practices, and therefore the averages were used also to lower the inter-laboratory variability. The differences in values were not consistent between parameters. In the examples given the values for chloride, sulfate and ammonia were quite high, but in other samples it may have been other parameters that varied. Variability between laboratories testing the same sample can be expected, but generally it was on the order of 5%. The variability in the laboratory results for this program was much higher than expected.

Major Anions (NO_3, Cl, F, SO_4, PO_4)

Approximately 85% of the wells sampled showed nitrate levels above the WHO standard (50 mg/l). The highest levels of nitrate were found in the north and the south regions (Table 4); they were 151 and 191 mg/l, respectively. All private wells, except three, showed nitrate concentrations 3-7 times higher than the WHO standards. Sources that contribute to high nitrate concentrations include the infiltration of domestic sewage through cesspits and septic tanks, solid waste leachate, manure and agriculture fertilizers. The areas which had the highest concentrations of nitrates do not have a wastewater collection system, and when present it was implemented recently. Unpublished data confirmed the good correlation between the high contents of nitrates in drinking water and the occurrence of methaemoglobinaemia in the areas where babies are not breast fed.

Chloride was the representative and correspondent parameter to the electric conductivity. The lowest value in the north area was 40 mg/l while the highest value in the eastern parts of Rafah area was 3000 mg/l. One should mention that some wells have low Cl contents but high nitrates and vise versa.

Fluorides were studied in an independent investigation (Shomar et al., 2004d). The results showed that the trend of the fluoride in the groundwater of the Gaza Strip was similar to Cl, with some exceptions in the middle area. The high fluoride contents in the groundwater (1.8 to 4 mg/l) was the main reason of the dental fluorosis disease for school children of the Gaza Strip (Shomar et al., 2004d).

The concentration of sulfate in drinking water needs to be addressed not only because of its effect on public health but also on the municipal well infrastructure. Most of the wells in Gaza have levels less than the WHO standard (250 mg/l), especially in the north area. The highest levels of sulfate appear to be in Khan Yunis and the southeast, where it was 380 mg/l. On the other hand, many popular European waters are gypsum saturated and contain over 1000 mg/l sulfate. Examples are Contrex and Contrexeville in France, Eptinger and Aproz Cristal in Switzerland, Alp Quell and Obladis in Austria and Fonti di Crodo and Santa Chianciano in Italy. In view of this, even if the WHO standard is slightly exceeded, this can hardly count as a public health problem.

Phosphates were not detected in the groundwater of Gaza with the method of vanadomolybdophosphoric acid, while the average was 1 mg/l by the IC of Germany. The test of Gaza was carried out few hours after the sampling process.

Figure 2 shows a comparison between the average contents of the major anions in the different regions.

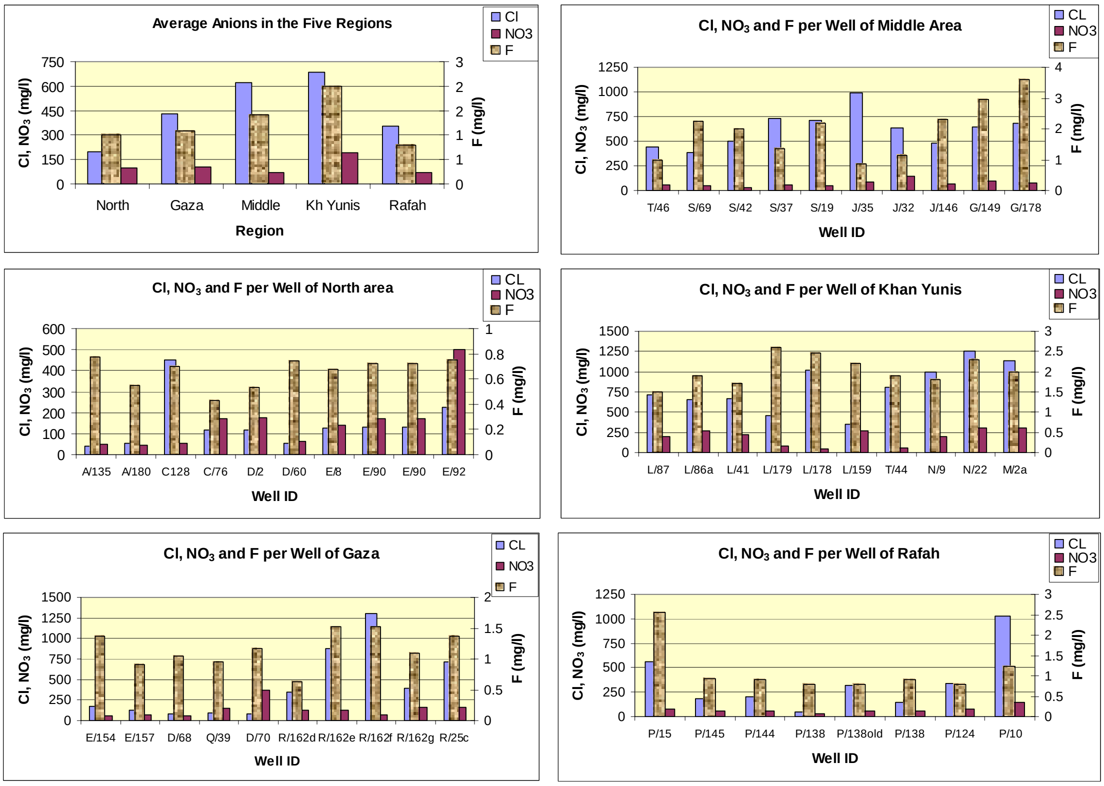

Figure (2) Average concentrations of major anions in the five regions of the Gaza Strip.

Major Cations (Na, Ca, Mg, K)

The lowest levels of sodium were in the north, and the highest levels were in the east and the south. Approximately 65 of the wells tested (>50% of the wells sampled) had sodium levels higher than the WHO standard (200 mg/l). Sodium had the same trend as Cl for all wells analyzed (Table 4).

In most of the wells tested for potassium, the value was less than 5 mg/l. However, a small number of wells have levels in excess of 15 mg/l. The wells with the highest potassium levels included R/162H, R/162C, J/35, E/154 and F/88. Neither the USEPA nor the WHO has standards or guidelines for potassium levels in drinking water.

The groundwater of most areas is hard and the average hardness represented in $CaCO_3$ for all the wells tested was 380 mg/l. The average of Ca was 93 mg/l and there was no significant difference in the results of the different seasons. The average of magnesium was 48 mg/l. The Mg/Ca ratio showed almost all points with about a 1:1 ratio. The middle region wells display the highest levels of both Ca and Mg and the results were 262 and 128 mg/l, respectively. All wells were below the seawater ratio, about 5:1 Mg to Ca.

Metal Contents (Fe, Mn, Cu, Zn, Ag, As, Pb, Cd, Cr, and Co)

Table 5 shows the results for trace elements from selected wells of the five regions. The Fe concentration was lower than the WHO standard (300 µg/l). The average content of Fe was 10-50 µg/l, although some wells in the north (Jabalia and Gaza) have Fe up to 140 µg/l. Several wells showed high contents in the year 2002, such as 6200, 1855, 1040 µg/l in wells C/127, C/76 and R/112, respectively. None of them showed similar results in the other two years. Agricultural wells showed a 3-5 times higher iron concentration than the municipal wells.

Manganese had an average of 10 µg/l as the lowest WHO standard is 100 µg/l.

All results of Cu were below the WHO standard (1-2 mg/l).The Cu ranged between 1-50 µg/l. Wells of the middle and south areas showed higher Cu contents than the north and Gaza.

The range of the Zn concentrations was 1-30 µg/l, while the WHO standard for Zn is 3 mg/l. A good indication for the quality control is the results of Zn for the well R/162L which showed similar results for the three years of monitoring (113, 117 and 102 µg/l, respectively). The results of Ag were below the USEPA standard (100 µg/l). The well R/162E showed the same results for the years 2001 and 2002 (0.5 µg/l), while the year 2003 was 7 µg/l.

The average of As contents in the wells tested was 1 µg/l, and the highest well had about 4 µg/l; most standards of As in drinking water are 10 µg/l. The results of 2001 showed an anomalous result (50 µg/l) of the well (L/178).

The range of lead standards in drinking water is 10-50 µg/l, and the results showed that all wells tested were below these standards. One municipal well (E/4) in the north area of Jabalia showed high contents of Pb (69 µg/l) in the year 2001 which was 7 times higher than the WHO standard. The results of the following years for the same well were < 2.5 µg/l.

The different standards (including the WHO) of Cd in drinking water are 3-10 µg/l. All results were below the limit of detection.

The different standards of Cr in drinking water are 50-100 µg/l and all of analyzed wells tested had less Cr than these standards. The average contents of Cr in the south area of the Gaza Strip (40 µg/l) which is higher than that of the north area (10 µg/l). The well R/162E showed similar results for the first two years (24, 27 µg/l, respectively) while the last year only showed 344 µg/l.

Although the WHO has no standard for cobalt (Co) in drinking water, the results showed very low Co contents in the wells tested. In spite of that, the private-agricultural well A/107E showed 1.5 µg/l in the year 2001 while the results of the other two years were < 0.5 µg/l.

The last group of elements showed very low contents in general. Al, Hg, and Ni were found to be less than the WHO standards for all wells and for the three years of monitoring. All wells had Ba less than the WHO (700 µg/l). The B results showed that more than 75 % of the wells had B>300 µg/l, the middle and the south areas of the Gaza Strip showed an increase in the B contents. Li results were 5-20 µg/l and few private wells only showed >30 µg/l. Sr is a typical alkaline earth element; the Sr results were 0.8-6 mg/l for all samples.

Table (5) Examples of trace elements in fifteen municipal wells of the Gaza Strip.

WHO (µg/l)	100	200	10	300	700	3		50	1000	300	1		100	20	10		3000
LD (µg/l)	0.5	10	4	10	10	1	0.5	1	1	8	2		0.5	0.5	2.5	0.01	0.5
Well ID	**Ag**	**Al**	**As**	**B**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Li**	**Mn**	**Ni**	**Pb**	**Sr**	**Zn**
E/4	<0.5	<10	<4	111	197	<1	<0.5	7.71	3.6	12	<2	3.4	1.1	<0.5	<2.5	1228	6.81
D/20	<0.5	47	<4	104	251	<1	<0.5	7.26	<1	28	<2	5.4	<0.5	<0.5	<2.5	2223	82.8
E/11C	<0.5	43	<4	348	21	<1	<0.5	11.3	1.0	19	<2	6.5	0.594	<0.5	<2.5	836	41
C/127	<0.5	13	<4	135	124	<1	0.5	9.92	<1	25	<2	3.1	0.692	<0.5	<2.5	854	19.4
D67	<0.5	15	<4	78.9	216	<1	<0.5	10.2	1.1	19	<2	2.2	<0.5	<0.5	2.99	687	8.72
R/162E	6.34	28	<4	284	219	<1	1	344	1.3	528	<2	8.1	7.04	6.45	11.6	4951	24.5
R/162B	<0.5	38	<4	202	316	<1	<0.5	16.5	1.1	22	<2	7.7	0.638	<0.5	3.24	4682	24.4
R/162H	<0.5	12	<4	1105	78	<1	0.5	25.1	6.1	29	<2	19.3	1.47	1.25	<2.5	2056	35.5
R/162G	<0.5	28	4.5	608	105	<1	<0.5	16.1	9.3	54	<2	13.4	2.34	<0.5	6.06	2536	50.5
D/72	0.5	25	5.8	92.7	268	<1	<0.5	10.3	2.9	39	<2	5.3	1.65	0.636	<2.5	1377	20.9
S/71	<0.5	20	<4	691	63	<1	<0.5	11.5	3.6	25	<2	11.4	0.72	0.603	4.11	1256	19.3
K/20	<0.5	29	<4	747	120	<1	<0.5	29.9	<1	13	<2	11.0	<0.5	<0.5	<2.5	1328	10.3
L/178	<0.5	113	6	3084	35	<1	<0.5	111	1.9	28	<2	26.2	1.79	<0.5	7.73	1561	19.3
L/43	0.8	46	<4	951	62	<1	0.7	32	6.0	66	<2	20.6	1.4	<0.5	8.86	4668	31.7
P/24	<0.5	<10	<4	469	122	<1	<0.5	30.7	<1	25	<2	11.7	10.4	<0.5	5.5	2382	12.8

Spatial and Seasonal Variations in the Concentrations of the Parameters Tested

The Gaza Strip has been classified into five regions according to their governmental system and this classification correlated with the groundwater quality in each region. With some exceptions, the Gaza Strip could be classified according to the freshness of the municipal groundwater into: north, Rafah, Gaza, middle and Khan Yunis; the ranking is based on the increase of the salinity and other major ions. Only nitrates showed another classification, in which Gaza comes after the middle area in the ranking.

For the same wells which had extremely high Cl and NO_3 concentrations, the heavy metal contents were found to be very low. The variation in the contents of the major ions, represented by the EC, is due to the variation in the precipitation levels in each area. However, the Gaza Strip is about 45 km long and each region has a different annual precipitation; the north has 500 mm/a while the south has only 250 mm/a.

There is evidence that the groundwater table in the area of the Gaza Strip has been drastically lowered, which would result in a downshift of the salinity (Shomar et al., 2004c). In spite of that, there was no relationship between the well depth and groundwater quality for the municipal wells. The story is different for the private wells, the deep wells showed less salinity and vise versa. Moreover, several private wells (A/40, A/42, F/130, F/160, and N/2) showed higher concentrations of Zn, Cd, Pb, Fe and As. These wells are located in the surroundings of heavy agricultural areas, wastewater treatment plants and solid waste dumping sites.

Ion Concentrations and Ratios

The CAMP (2001) discussed the main sources of major ions in the groundwater of the Gaza Strip with ion concentrations and ratios. The concentration of total dissolved solids in water provides the variability of the ion in the water, but it gives no indication of the source of the ion variability. Ratios of the dissolved constituents are useful in establishing chemical similarities among waters of a single aquifer (Appelo and Potsma, 1999), such as the coastal aquifer in the Gaza Strip. Ratios also make it possible to fingerprint the water sample and hopefully identify the source of ion variability. Reasons for the variability of groundwater in the Gaza Strip include seawater intrusion, chloride brines, natural water/soil interactions in the Kurkar Group materials and anthropogenic causes. Many of these causes have characteristic ratios of ions that can be applied to groundwater sampling results of the region. For example, groundwater influenced by seawater intrusion may have high levels of sodium and chloride, but since the source water is mixed with the groundwater the concentrations of sodium and chloride will be less than seawater concentrations. However, the ratio between sodium and chloride could be the same for both, therefore identifying seawater as the source. Seawater is not the only source with characteristic ratios. The ratio of calcium to magnesium is useful in studying water from limestone and dolomite, while the ratio of chloride to other ions also may be useful in studies of water contaminated with common salt (NaCl).

The same approach was used to confirm the findings of the CAMP (2001). The data above could indicate several things. In general, seawater intrusion does not seem to be the major source of the ion variability. In most regions, the ionic molar ratios were not consistent with seawater standards. Instead, ionic ratios more often resembled ratios characteristic of natural water interactions with subsurface materials. High chloride levels in the east and middle region wells could be due to brine deposits at the base of the aquifer. High sodium concentrations were more likely a result of water withdrawal from sodium-rich sedimentary rocks. Magnesium to calcium ratios resembled dolomite ratios instead of seawater ratios. Potassium ratios were below seawater standards in most wells.

CONCLUSIONS

The results indicated that water in both municipal and private wells is polluted by one parameter or another; however, the municipal groundwater wells are less polluted. The results showed that 80% of the groundwater wells are not suitable for drinking purposes because of the high contents of nitrates, chlorides and fluorides and some heavy metals which exceed 2-7 times the WHO standards. Some wells have a permissible limit of nitrates but high amounts of chloride or fluoride and vice verse. The high nitrates and fluorides in the drinking water of Gaza have a direct impact on the human health; although recent findings in the medical literature cast some doubt on the health hazards of high nitrate per se, although high nitrate is often a strong indication for fecal pollution.

The governmental classification of the Gaza Strip into five regions correlates with the quality of the groundwater of each region. The salinity and the major ions increase from the north to the south regions.

The average results of trace elements in the groundwater indicated that they do not generally pose any health or environmental hazard in the Gaza Strip. In spite of that several private wells showed concentrations of Zn, Pb, As and Cd of more than the WHO standards. These wells should not be used for drinking purposes. These wells are exposed to the contaminants of the leachate of solid waste, wastewater and manure.

The well depth does not affect its water quality, while the location does. The ion ratios indicated that the high levels of chloride and other ions do not appear to be due to seawater intrusion into the aquifer only, but other water sources, including through flow from Israel, and natural chemical changes due to soil/water interactions may cause the majority of the ion variability in the aquifer.

The results of the study and the archive of groundwater geochemistry additional to the ion ratios revealed that the reasons of the anomalous-elevated levels of Cl and other ions are the anthropogenic factors, the lateral groundwater flow and the natural chemical changes and to a lesser extent the seawater intrusion.

RECOMMENDATIONS AND ACTIONS TO BE TAKEN

The results of the study showed that the pollution of the groundwater is a major problem in the Gaza Strip. Not only there are numerous sources of pollution, but also the aquifer is highly vulnerable to pollution. The increasing chloride, nitrate and fluoride contents in most of municipal wells and the high contents of several heavy metals in several private wells illustrate the pollution problem.

Several studies should be conducted mainly on the health risk assessment and water toxicology. Examples of these studies are the methaemoglobinaemia as a result of high nitrates, the dental fluorosis as a result of high fluorides and the cancers as a result of high levels of carcinogenic pesticides.

To improve our understanding of water quality in the aquifer an integrated monitoring program should be conducted. The municipal wells should be sampled 2-4 times a year for the analysis of anions, cations, heavy metals and pesticides. The data of the groundwater quality should be centralized in a data bank or a water archive.

The risk of deterioration of water quality is an urgent theme. The objective of the Palestinian water institutions should be how to safeguard the water resources system from pollution. The protection of water quality and the reduction of the risk contamination are of great importance to a reliable and sustainable water supply. Several initiatives could be taken such as wastewater management through full collection and treatment, solid waste management to prevent leaching and infiltration into the groundwater aquifer, setting up a management system for use of pesticides and fertilizers through proper handling, storage measures and safe application, setting up groundwater protection zones in the vulnerable areas to pollution, and finally setting up an early warning and emergency response system, that will enable to take appropriate actions.

CHAPTER TWO

Fluorides in groundwater, soil and infused-black tea and the occurrence of dental fluorosis among school children of the Gaza Strip (*)

ABSTRACT

The purpose of this study was to determine the fluoride levels in water, soil and tea, and to identify the major fluoride minerals in soil that supply water with fluoride ions. Another aim was to study the prevalence of dental fluorosis in permanent dentition of the school children of the Gaza Strip.

Monitoring of fluoride levels in 73 groundwater wells and 20 topsoil samples for the last three years revealed a general trend of increasing from north to south of the Gaza Strip. A linear regression analysis found a correlation coefficient of $r = 0.93$ between the fluoride concentrations in groundwater and soil for the same geographic areas. However, the X-ray diffraction technique (XRD) results showed that none of the four major fluoride minerals were detected in the tested soil samples; the PHREEQC model showed that fluorite (CaF_2) was the main donating mineral of fluoride ions to groundwater.

A high positive correlation was found between fluoride concentrations in groundwater and occurrence of dental fluorosis. Among 353 school children of the five geographic areas of the Gaza Strip the prevalence of dental fluorosis was 60% and 40% had no signs of fluorosis in their permanent dentitions. The highest occurrence, 94%, was in Khan Yunis, followed by 82% in Rafah, 68% in the middle area, 29% in Gaza and the lowest occurrence of 9% was in the northern area. These percentages were directly proportional to the average contents of fluoride in groundwater of each area: 2.6, 0.9, 1.7, 1.2, and 0.7 ppm, respectively. The exception was Rafah where people drank from new groundwater wells that have been dug in the last 10 years.

The occurrence of the disease was due to intake of high amounts of fluorides in drinking water, tea and fish. Communication with population indicated a heavy intake of tea starting from a very young ages; not uncommonly tea is put in nursing bottles. No significant correlation was found between prevalence figures and gender or age groups. This high prevalence indicates a need to examine other sources of F including diet.

Key words: Dental fluorosis, Gaza Strip, Soil fluoride, Tea, Water fluoride

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INTRODUCTION

The fate of fluoride in soil environment and groundwater is of concern for several reasons. It is generally accepted that fluoride stimulates bone formation (Richards et al., 1994), and small concentrations of fluorides have beneficial effects on the teeth by hardening the enamel and reducing the incidence of caries (Fung et al., 1999). McDonagh et al., (2000) described in great details the role of fluoride in the prevention of dental fluorosis. At low levels (< 2 ppm) soluble fluoride in the drinking water may cause mottled enamel during the formation of the teeth, but at higher levels other toxic effects may be observed (Weast and Lide, 1990). Excessive intake of fluorides results in skeletal and dental fluorosis (Czarnowski et al., 1999). Severe symptoms lead to death when fluoride doses reach 250-450 ppm (Luther et al., 1995). It is found that the IQ of the children in the high fluoride areas (drinking water fluoride 3.15 ppm) was significantly low (Lu et al., 2000).

Fluorides enter the human diet mainly through the intake of water and, to a lesser extent foods. Among the foods rich in fluorides are fish, tea, and certain drugs (EPA, 1997). Ingested fluorides are quickly absorbed in the gastrointestinal tract, 35-48% is retained by the body, mostly in skeletal and calcified tissues and the balance is excreted largely in the urine. Chronic ingestion of fluoride-rich fodder and water in endemic areas leads to development of fluorosis in animals e.g. dental discoloration, difficulty in mastication, bony lesions, lameness, debility and mortality (Patra et al., 2000).

Children drink about one liter of water per day depending on the ambient temperature, and because water consumption is higher in areas with higher ambient temperatures, it is proposed that the recommended fluoride level in water in arid and semiarid areas would be 0.7 ppm (EPA, 1997), instead of 1.5 ppm which is the guidelines of the WHO (WHO, 1998a). Children may show dental fluorosis at an early age while skeletal fluorosis may appear at an older age (Choubisa, 2001).

Naturally occurring fluorides in groundwater are a result of the dissolution of fluoride-containing rock minerals by water (Kabata and Pendias, 1984) while artificially high soil F levels can occur through contamination by application of phosphate fertilizers or sewage sludges, or from pesticides (EPA, 1997). The F compounds added to soils by pollution are usually readily soluble. Fluorine is a typical lithophile element under terrestrial conditions, and there are not many stable F minerals; the most common are topaz ($Al_2(F,OH)_2SiO_4$) and fluorite (CaF_2). F reveals an affinity to replace hydroxyl groups in minerals, and these reactions have resulted in fluoroapatite ($Ca_{10}(PO_4)_6F_2$), the most common F mineral, and have also been responsible for increased amounts of F in amphiboles and micaceous minerals (Kabata and Pendias, 1984). The mobility of F in soils is complex and that the predominant factors controlling the level of this ion in the soil solution are the amount of clay minerals, the soil pH, and the concentration of Ca and P in soils. The greatest adsorption of F by soil mineral components is at about pH 6 to 7. The range for most normal soils seems to be from 150 to 400 ppm (Turekian and Wedepohl, 1961), but the overall variation is much broader, and in some heavy soils F levels above 1000 ppm have been found (Kabata and Pendias 1984). Much higher levels of F in uncontaminated soils are reported for provinces of endemic fluorosis.

Beside the health effects, dental fluorosis may have social and psychological consequences. There has been an escalation in daily fluoride intake via the total human food and beverage chain, with the likelihood that this escalation will continue in the future (Marier, 1977). Carbonated soft drinks have considerable amounts of fluorides (Heilman, 1999). Beers brewed in locations with high fluoride water levels may contribute significantly to the daily fluoride intake (Warnakulasuriya et al., 2002), and sweetened iced teas contain significant amounts of fluoride (Behrendt et al., 2002). A single serving of chicken sticks alone would provide about half of a child's upper limit of safety for fluoride (Fein and Cerklewski, 2001). Children's ingestion of fluoride from juices and juice-flavored drinks can be substantial and a factor in the development of fluorosis (Kiritsy et al., 1996; Whitford, 1989).

Tea is the most popular beverage in the Gaza Strip. It is well known that fluorine accumulates mainly in the leaves of the tea plants, especially in fallen leaves (Fung et al., 1999). There is one very common method of infusing tea in Gaza, by infusing tea leaves (about 10 g) for few minutes in about one liter of boiling water. People of Gaza, including babies at very early ages, consume strong and sweet tea.

The main objectives of this study were: (1) to determine the average levels of fluoride in groundwater and top soils of the Gaza Strip; (2) to determine the levels of fluoride in the prepared tea and tea leaves used in Gaza; (3) to identify the major fluoride minerals in soil that may supply groundwater with fluoride ions; and (4) to determine the dental fluorosis index (DFI) for school children of both sexes in the age range 5-16 years, and then the community fluorosis index (CFI) followed by the number of teeth with caries.

MATERIALS AND METHODS

The study area

The Gaza Strip, as one of the most densely populated areas in the world (2638/km^2; PCBS, 2000), with limited and declining resources, has already started to suffer the outcomes of environmental quality deterioration. The study area is a part of the coastal zone in the transitional area between the temperate Mediterranean climate to the east and north and the arid desert climate of the Negav and Sinai deserts to the east and south. As a result, the Gaza Strip has a characteristically semi-arid climate and the hydrogeology of the coastal aquifer consists of one sedimentary basin, the post-Eocene marine clay (Saqiya), which fills the bottom of the aquifer.

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. Ample supplies of high quality water are essential for economic growth, quality of life, environmental sustainability and, when considered in the extreme, for survival.

Wise management, development, protection, and allocation of water resources are based on sound data regarding the location, quantity, quality, and use of water and how these characteristics are changing over time. The quantity and quality of available water varies over space and time, and is influenced by multifaceted natural and man-made factors including climate, hydrogeology, management practices, pollution, etc. As the foundation for water resources decision-making, sound data must be continuous over space and time.

Previous reports on the water quality in Gaza have discussed extensively the high levels of chloride and nitrate in the drinking water (PEPA, 1994). The water quality in Gaza is affected by many different water sources including inflow of groundwater from Israel, soil- water interaction in the unsaturated zone due to recharge and return flows, mobilization of deep brines, seawater intrusion or upconing, and disposal of domestic and industrial wastes into the aquifer. The seawater intrusion and the upconing of brines in some areas may be due to water imbalance in the aquifer, since the rate of water extraction exceeds the rate of groundwater replenishment. The high concentrations of nitrates in the groundwater appear to be due to fertilizers and sewage contamination from within Gaza. Data indicate that levels of nitrate east of Gaza, in Israel, are lower than those in Gaza.

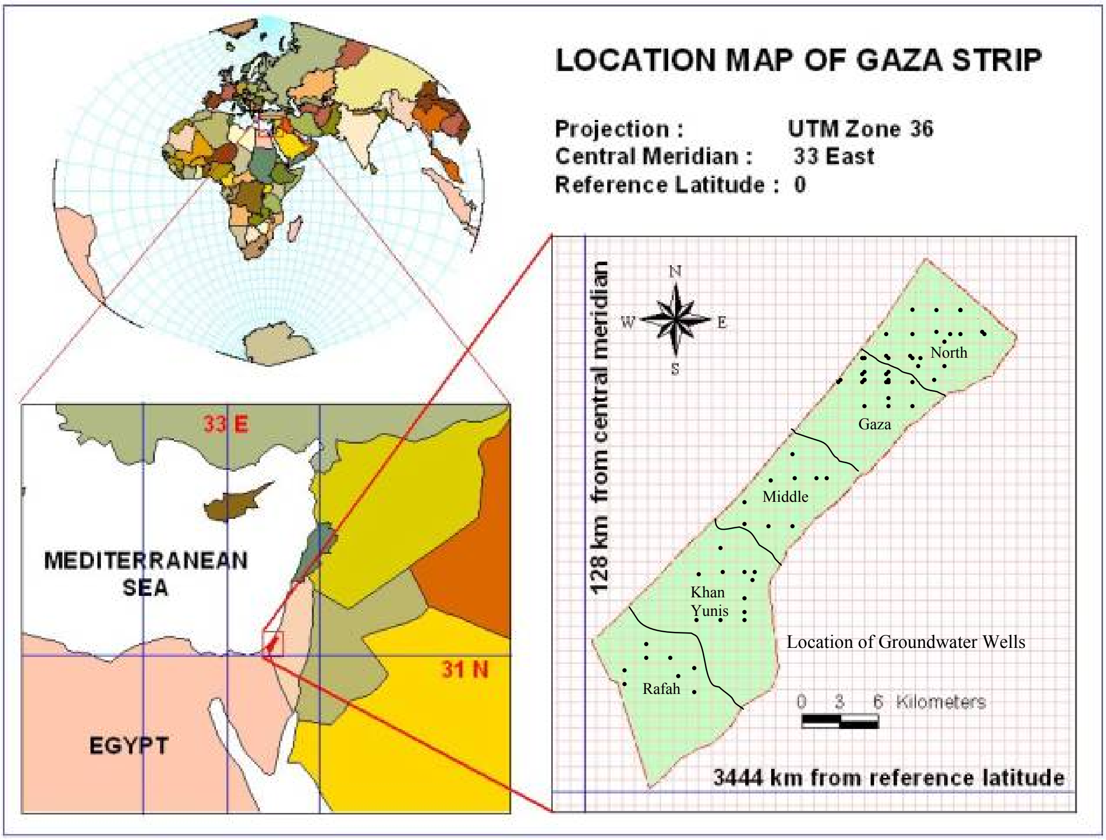

Figure (1) Five regions of the Gaza Strip and location of groundwater wells.

Sampling and analysis

The study area (Fig. 1) is divided into five geographic regions, the northern area, Gaza, the middle area, Khan Yunis and Rafah which represent the main five governorates of the Gaza Strip; moreover, the groundwater quality in terms of both salinity and nitrate contents deteriorates from north to south. Three sampling campaigns have been conducted in three years over the periods: 20 November-12 December 2000, 26 June-17 July 2001 and 25 April -17 May 2002. Soil and tea samples were collected in the last sampling campaign.

Water samples

Under the water quality testing program about 73 municipal wells and a few private wells in the Gaza Strip were sampled. The municipal wells represent groundwater in the five geographic areas of the Gaza Strip. At the municipal wells, samples were collected from a tap along the water distribution line. Prior to sampling, the injection of chlorine or sodium hypochlorite into the system was discontinued so the additive would not interfere with the analysis. In addition to the general locations of wells, Table 1 shows the ID of each well. The wells in the table are ordered from north to south where 17, 26, 7, 16, and 7 wells are chosen from the north, Gaza, the middle, Khan Yunis and Rafah regions, respectively.

In order to assure that the sample collected was from groundwater and not water standing in the well, it was originally proposed that the well should be pumped for a minimum of 1-2 h prior to the collection of the sample; however this was not always possible. The third sampling programme occurred at the end of the winter rainy season, and many private well owners were not using their wells extensively. However if it is assumed that the average private well has a 10-m depth of standing water in a 30-cm diameter pipe, the standing well volume is approximately 1 m^3. Therefore 1 h of pumping at a rate of between 45 and 70 m^3/h is sufficient to purge at least three standing well volumes; this principle is a USEPA rule of thumb for well purging.

Samples were collected from 73 groundwater wells; all are municipal and being used for drinking purposes. They represented all geographic areas: 17 in the north, 26 in Gaza, 8 in the middle, 15 in Khan Yunis and 7 in Rafah. Preservation of samples in the field was done to avoid revisiting the wells if mistakes occurred while adding the chemicals to the samples.
About 250 ml water was taken in laboratory certified clean bottles and labelled as to the sample location, date and time of sample collection. The sample was placed in a sampling ice-box and transferred to a laboratory, then the sample was filtered through 0.45 µm (Sartorius) filter; the first few ml were used for rinsing, then they were discarded, and the filtrate was transferred to clean polyethylene bottles and stored at 4 ^{o}C. The sample was divided into two sub-samples: the first 100 ml was analyzed in Gaza using an ion selective electrode (ISE) according to APHA (1995), and the other 150 ml was shipped to Germany where fluoride was analyzed by ion chromatography (IC DIONEX DX-120) with minor modifications (Yin et al., 2001). As a part of a parallel research, the same groundwater wells were sampled and analyzed for major anions and cations (see Table 2 for results from five wells in Khan Yunis).

Soil samples

Twenty composite soil samples were collected from the five regions (Table 3) from the surroundings of 20 wells. They were collected using a stainless steel dredge; approximately 0.5 kg was put in polyethylene cups and stored at 4 ^{o}C during its transport to laboratories where the soil was dried in an oven at 50 ^{o}C until it reached a constant weight. Then the samples were shipped to Germany in plastic sampling bags. The samples were sieved through a 20-µm sieve, then ground to a very soft powder by using a sand mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 50 mg of sample was placed in a nickel crucible, then 2 g of 1:1 Na_2CO_3-K_2CO_3 (anhydrous dried at 110 ^{o}C overnight) was added to the sample in the crucible. The crucibles were placed in a muffle furnace at 800 ^{o}C for 15 min.

After cooling, 15 ml of 1 M citric acid was added to the crucible and the mixture was allowed to digest until CO_2 evolution was no longer detected (3-4 h, or preferably overnight). Then 25 ml of sodium citrate buffer (1M) was added to the contents of the crucible. Finally, the mixture was transferred to a 100-ml polypropylene volumetric flask where it was diluted to the mark by deionized H_2O. The total fluoride in the soil extract was analyzed by the ISE (APHA, 1995).

The semi-quantitative X-ray diffraction technique (XR Diffractometer-SIEMENS) was used to identify the major fluoride minerals in soil samples; the four major fluoride minerals were investigated (topaz: $Al_2(F,OH)_2SiO_4$; fluorite: CaF_2; fluoroapatite: $Ca_{10}(PO_4)_6F_2$; cryolite: Na_3AlF_6). Moreover, PHREEQC (a small program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations) was applied to achieve the same purpose by using groundwater data of five wells in the area of Khan Yunis where the fluoride level is high.

Tea samples and tea consumption

To determine if the tea consumed in Gaza may have influenced the observed dental fluorosis, tea samples were collected both as a liquid and as tea leaves. Twenty teacups were collected from 20 different houses in the area of Khan Yunis. The houses were selected according to a statistical base; the first house of every ten houses was chosen in the area of Khan Yunis and eastern villages of Abasan, Bani Suhaila and Khoza'a. Tea leaves were bought from the main 10 markets of the area and infused in the laboratory by using Milli-Q water in the same manner as normally done by the Gaza population (about 10 g of tea leaves with one liter water) and it was strong and sweet. Both tea types were analyzed by the ISE.

The tea consumption was calculated from the direct answers of the tested children and from the answers given to the questionnaire distributed to the children.

Quality control

For quality control, analytical blanks and the same groundwater samples were analyzed in Gaza and Germany. The fluoride ion selective electrode and potentiometer was an ORION 868 type, USA. The calibration curve was plotted against a standard NaF solution (1000 ppm Merck-Darmstadt, Germany) containing 0.1, 0.5, 1.0, 5 and 10 mg F/l and a total ionic strength adjustment buffer was used. The mV readings were linear against the logarithm of mg/l F concentration.

Dental fluorosis index (DFI), community fluorosis index (CFI) and dental caries

The examinations were performed by two dentists and three assistants. Prior to the field work the assistants attended a one week intensive course to provide them with an understanding of the required literature and the field procedures to be used, as well as the preparation and the distribution of the questionnaires. Mouth mirrors, pliers, and dental probes were used under natural light. Key issues were taken into consideration; the examiners should note the distribution pattern of any defects and decide if they are typical of fluorosis. Considerable care should be taken to diagnose tooth-colored fillings, which may be extremely difficult to detect.

From 24 elementary and preparatory schools, 353 pupils were involved in the study. The schools represent the five regions of the Gaza Strip according to the population density and gender. There were six schools from the northern area, six from Gaza, four from the middle area, four from Khan Yunis and four from Rafah. The number of males and females was almost the same. All the 353 school children of the age group 5-16 years were examined clinically. The age group (5-16) is recommended: 5 years for primary teeth and >12 years for permanent teeth. Age -and sex- matched children of the Gaza Strip consuming water having fluoride levels within the 1.5 ppm permissible limit, according to WHO (1998a), were used as controls.

The survey of the schoolchildren in order to examine the symptoms of dental fluorosis is the first and most important step that can decide the presence or absence of fluorosis. Only when presence of dental fluorosis is confirmed in the survey, it is necessary to study further the magnitude and severity of the problem. According to the results of the dental fluorosis index (DFI), the next step is to establish the percentage incidence of fluorosis as well as the community fluorosis index (CFI).

Dental fluorosis is the most sensitive and specific index in the diagnosis of fluorosis (Jin et al., 2000). It has been classified in a number of ways. One of the most universally accepted classifications was developed by Dean (1942). In using Dean's fluorosis index, each tooth present in an individual's mouth is rated according to the fluorosis index. The index classified individuals into 5 categories, depending on the degree of enamel alteration. The recording of the DFI is made on the basis of the two teeth that are most affected. If the two teeth are not equally affected, the score for the less affected of the two should be recorded. When teeth are scored, the examiner should start at the higher end of the index, i.e. "severe", and eliminate each score until he arrives at the condition present. If there is any doubt, the lower score should be given. The DFI was determined for the permanent teeth only after brushing with toothpaste so as to reduce errors arising from dental plaque.
The dental fluorosis index was estimated according to Dean's standard method (Dean, 1942). Dean's classification index indicated that dental fluorosis comprises opaque white patches which cover less than 50% of the enamel surface. The more severe grades, 3 and 4, can involve dark brown staining and pitting of the fluorosed enamel. A cross-sectional survey was used to determine the prevalence of dental fluorosis. The dental caries was determined for each tooth. Multiple caries per tooth were considered as one.

The CFI can be calculated from the DFI. Based on the symptoms, dental fluorosis is classified into normal, questionable, very mild, mild, moderate and severe and each of these five classifications is given a numerical weight such as 0, 1, 2, 3, 4, and 5, respectively. The number of people in each category is multiplied by the corresponding numerical weight, the products thus obtained for the various categories are added up and the sum of the total divided by the total number of people surveyed, gives the community fluorosis index (CFI). Only when the CFI value is greater than 0.6, fluorosis is considered to be a public health problem in the area. Based on this procedure, the following formula was used:

$$\text{CFI} = \frac{\text{No. of individuals in each region x Statistical weight}}{\text{Total No. of Individuals tested}}$$

A simple linear regression value of soil/water fluoride was used. Twenty groundwater wells (of the 73) were selected to represent wells of each region where the 20 soil samples were taken. The univariate regression analysis and correlation coefficient were used to combine results of water fluoride concentration with the prevalence of dental fluorosis and community fluorosis index.

RESULTS

Groundwater

Table 1 shows the average concentration of fluoride in groundwater of 73 wells while Figure 2 shows the variation in fluoride contents from north to south, indicating that the highest contents were found in the Khan Yunis area (4.4 mg/l).
Drinking water that had two to three times higher than the WHO standard for fluoride (1.5 mg F/l) was found in the Khan Yunis area where dental fluorosis was easily recognized.

Table (1) Average level of fluorides in groundwater of 73 wells of the Gaza Strip.

Region	**Well ID**	**F (mg/l)**	**σ**	**Region**	**Well ID**	**F (mg/l)**	**σ**	**Region**	**Well ID**	**F (mg/l)**	**σ**
North	D/67	0.5	0.20	Gaza	R/162La	0.8	0.24	Middle	S 42	1.4	0.31
	D/73	0.9	0.71		R/162Ha	1.1	0.12		S 69	1.7	0.37
	D/74	0.5	0.02		R/162H	1.0	0.14		T 46	2.5	0.55
	E/06	0.2	0.11		R/162G	1.0	0.24	Khan Yunis	L 127	1.3	0.15
	E/10	0.4	0.06		R/162F	0.8	0.08		L 159	1.2	0.08
	E/11A	0.8	0.28		R/162E	1.0	0.18		L 176	2.0	0.24
	E/11B	0.7	0.16		R/162C	1.1	1.16		L 178A	4.4	1.13
	E/11C	0.7	0.08		R/162B	0.8	0.11		L 179	4.4	1.09
	E/138	0.9	0.51		D/71	1.6	0.06		L 41	3.0	0.53
	E/148	0.6	0.06		D/72	1.1	0.46		L 43	1.5	0.16
	E/156	0.9	0.17		R/25a	1.5	0.25		L 86	1.5	0.38
	E/4	0.8	0.19		R/25b	0.9	0.21		L 86A	4.0	1.47
	E/61	0.6	0.51		R/25c	1.5	0.16		L 87	1.7	0.16
	E/8	2.0	0.05		R/25d	1.8	0.31		M 2A	3.0	0.32
	E/90	0.6	0.18		R/112	1.6	0.24		M 2B	3.2	0.52
	E/92	0.7	0.06		R/254	1.7	0.29		N 22	2.6	0.21
	Q/40b	0.8	0.12		R/265	1.1	0.10		N 9	3.1	0.25
Gaza	E/154	0.9	0.12		R/74	1.7	0.70		T 44	2.0	0.27
	E/157	1.0	0.28		R/75	1.7	0.70	Rafah	P 10	1.3	0.21
	D/68	1.0	0.19	Middle	G1/178	2	0.06		P 124	0.8	0.11
	D/69	0.9	0.27		J 146	1.8	0.34		P 138	0.9	0.10
	D/70	1.3	0.06		J 32	1.3	0.41		P 138 old	0.8	0.10
	Q/39	0.2	0.06		J 35	1.4	0.35		P 139	0.8	0.01
	R/162L	0.9	0.17		S 19	1.2	0.14		P 144	0.9	0.08
									P 15	0.9	0.12

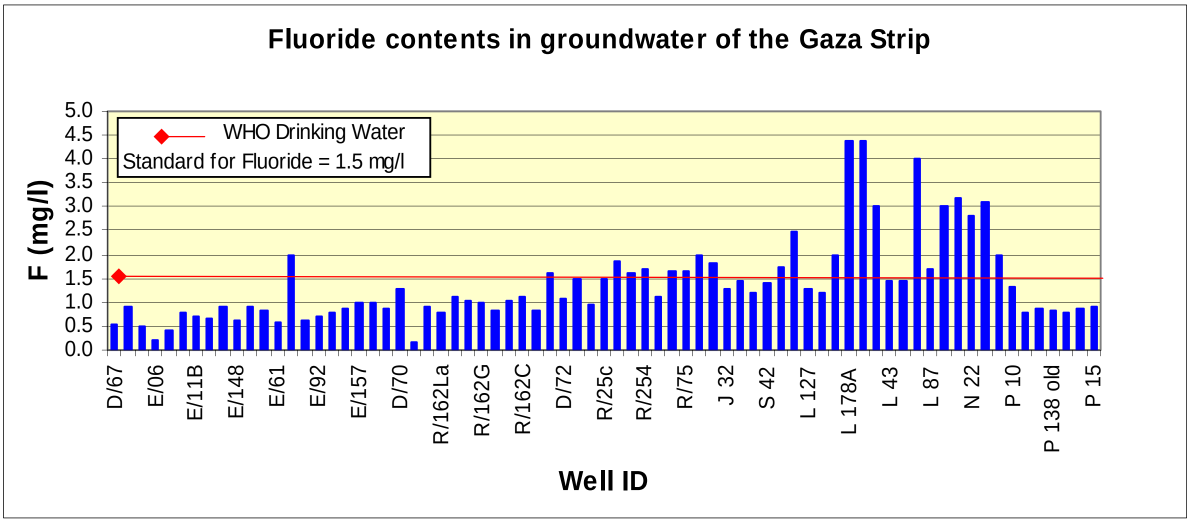

Figure (2) Variation of fluoride contents in groundwater of the Gaza Strip.

To identify the fluoride minerals supplying groundwater with fluoride ions, five groundwater wells were selected in the area of Khan Yunis. Major anions and cations were analyzed and the average of three year readings is shown in Table 2. PHREEQC was applied. It was found that the main donating fluoride mineral is fluorite (CaF_2).

Table (2) Groundwater quality of five wells in the area of Khan Yunis.

Parameter	**L 178A**	**L 179**	**L 86A**	**M 2A**	**N22**
pH	7.9	8.2	7.9	7.7	7.5
DO (mg/l)	7.4	7.5	7.7	7.2	7.6
NO_3 (mg/l)	70	126	180	190	95
SO_4 (mg/l)	604	250	250	650	568
Cl (mg/l)	1240	597	958	1288	1135
F (mg/l)	4.4	4.4	4	3	2.6
HCO_3 (mg/l)	322	240	315	308	215
Ca (mg/l)	93	70	182	126	67
Mg (mg/l)	56	46	52	56	42
Na (mg/l)	980	406	595	1058	873
K (mg/l)	8.7	4.7	6.9	9.7	6.8
Fe (µg/l)	44	70	79	113	52
Al (µg/l)	72	73	53	56	34

Soil

The results of total fluoride in soil samples are shown in Table 3 and the trend from north to south is shown in Figure 3. The figure shows the same trend of fluoride contents as the water samples, increasing in the area of Khan Yunis.

Table (3) Total fluoride contents in soil samples of five regions in the Gaza Strip.

Location	**Sample code**	**mg/kg**	**Location**	**Sample code**	**mg/kg**
North	N1	178	Middle area	M2	200
North	N2	100	Middle area	M3	243
North	N3	150	Middle area	M4	253
North	N4	144	Middle area	M5	224
North	N5	144	Khan Yunis	Kh1	475
Gaza	G1	177	Khan Yunis	Kh2	438
Gaza	G2	183	Khan Yunis	Kh3	309
Gaza	G3	137	Rafah	R1	163
Gaza	G4	156	Rafah	R2	178
Middle area	M1	236	Rafah	R3	139

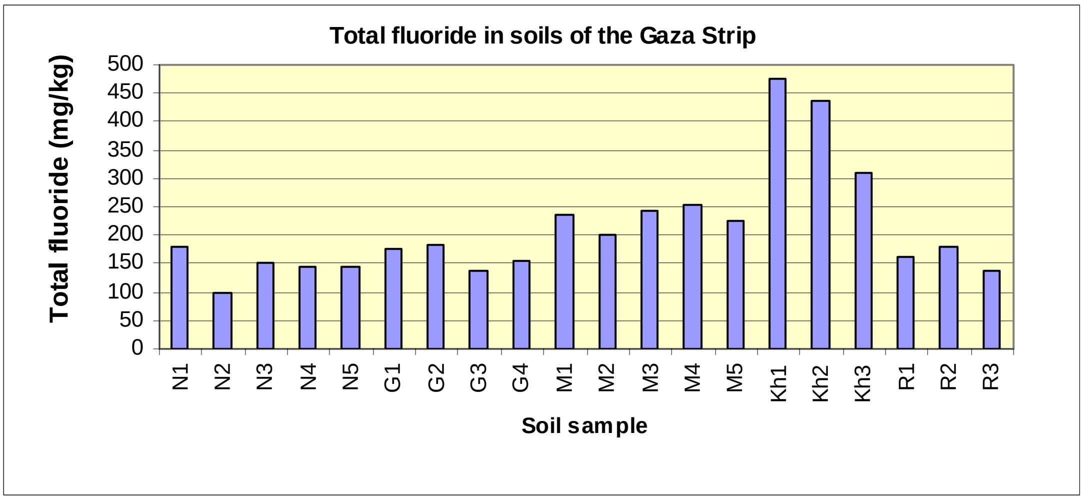

Figure (3) Levels of total fluorides in soil samples of 5 regions of the Gaza Strip.

Tea

Table 4 shows the average tea consumption during the field survey. The average number of cups drank per person per day is indicated, the highest, 3.19 cups, being in Rafah and the lowest, 2.50 cups, in Khan Yunis. For all regions of the Gaza Strip, the average number of cups drunk per day is approximately 3.

Table (4) Average tea consumption for school children in the Gaza Strip.

Region	**Average number of tea cups per person per day**
North	2.8
Gaza	3.21
Middle	2.60
Khan Yunis	2.50
Rafah	3.19

The average fluoride content in tea as a beverage, as brewed in Gaza and calculated by us, was about 4.7 ppm (Table 5). The fluoride content in the tea leaves is given in Table 6, the average is 2.7 ppm. The survey indicated an average consumption of tea of about 3 cups (each 100-120 ml) per day (Table 4).

Table (5) Fluoride contents in 20 tea liquor samples collected from 20 houses.

House No.	**F (mg/l)**	**House No.**	**F (mg/l)**
1	3.7	11	4.8
2	4.2	12	4.7
3	4.5	13	5.1
4	4.6	14	5.2
5	4.1	15	5.5
6	3.9	16	5.3
7	4.9	17	5.5
8	5.1	18	4.9
9	5.2	19	4.8
10	5.5	20	4.4

Table (6) Fluoride contents in 10 samples infused tea leaves.

Sample No.	**F (mg/l)**
1	2.2
2	2.4
3	2.1
4	2.5
5	3.0
6	3.1
7	2.8
8	2.7
9	2.9
10	3.1

DFI, CFI and prevalence of caries

The dental fluorosis index was not affected by sex or age and the results are shown in Table 7. Overall, the DFI increased going from north to south as the lowest value being in the northern area of Jabalia, 2.85, and the highest value, 4.39, in eastern villages of Khan Yunis.

Table (7) Averages DFI for each region and age group.

Region	**DFI and age groups**				
	5-7	**8-10**	**11-13**	**14-16**	**All ages**
North	3.13	3.20	2.67	2.84	2.85
Gaza	3.49	3.29	3.77	3.72	3.80
Middle	3.41	3.11	3.9	3.60	3.90
Khan Yunis	3.83	4.11	4.08	4.42	4.39
Rafah	3.50	3.20	3.37	4.21	3.50

The DFI score was weighted and a CFI was calculated. The results are presented in Table 8 where the CFI for the Gaza Strip as a whole was calculated as 2.42.

Table (8) Weighted DFI scores and estimated CFI for the Gaza Strip.

Region	Weighted DFI Score	No. Individuals
North	1.85	62
Gaza	2.76	48
Middle	2.82	117
Khan Yunis	3.15	67
Rafah	2.45	59
		CFI = 2.42

Prevalence of caries for each age group and region, presented as the number of permanent teeth with caries is given in Table 9. The number of teeth with caries ranged from 0 in the age group 5-7 to a maximum of 1.33, while it reached a maximum of 7 for the age group 14-16.

Table (9) Prevalence of caries for each age group and region.

Region	No. of permanent teeth with caries Age groups			
	5-7	8-10	11-13	14-16
North	1.00	0.75	3.34	1.14
Gaza	0.00		3.64	4.00
Middle	1.00	2.00	2.55	7.00
Khan Yunis	1.33		3.50	5.50
Rafah	0.67		4.05	6.00

DISCUSSION

The concentration of fluoride in groundwater increases from north to south, as do other parameters such as salinity and nitrate. The results showed a very good agreement between the ISE and IC results, especially for the samples which have fluoride contents exceeding 0.5 mg/l, while the IC showed more accurate results for the fluoride values less than 0.5 mg/l. Overall, there was no significant difference between the fluoride readings of winter and summer, however, in several wells there was a 5-10% increase in summer due to the overexploitation of groundwater and absence of recharge; the same percentage was found for the majority of tested anions and cations in a recent-parallel study.

Due to our knowledge of the region we suspected other factors to be involved in the development of dental fluorosis. These factors revolve around the intake of fluoride from other dietary sources such as the consumption of fish and tea. Fish also constitute a major source of dietary fluorides. Fish consumption is considered to be high (verbal communications and unpublished data from local sources). The other factor, tea, was also considered. Communication with the population indicated a heavy intake of tea starting from a very young age. Not uncommonly, tea is put in nursing bottles. Tea is made strong and sweet. The average fluoride content in tea as a beverage, as brewed in Gaza and as calculated by us was about 3 ppm. Our survey indicated an average consumption of tea of about 3 cups per day. We believe this to be on the low side and double that quantity may be more reasonable. The respondents to our survey feared a penalty from indicating the correct amount of tea drunk. In spite of that we believe that tea consumption is heavy in Gaza and is a contributing factor in the total dietary intake of fluorides.

The sources of fluorides in the groundwater of Gaza Strip are believed to be natural bedrock that supplies the fluoride ions to the water. The results of soil samples showed good correlation with the groundwater results, as the same general increase of fluoride is shown from north to south. However, the total fluoride contents of all tested soil samples are lower than the natural background of total fluoride in top soils (611 mg/kg) according to Turekian and Wedepohl (1961). For the soil samples and the wells nearby, the correlation coefficient *r* of soil/water fluoride was 0.93. None of the four fluoride minerals screened by the XRD were found in the tested soil samples. The semi-quantitative analysis and the limit of detection of the XRD showed that there were no distinguished peaks for the four major fluoride minerals tested. In spite of that the computer model suggested fluorite (CaF_2) as a donating fluoride mineral to groundwater.

DFI showed a slight increasing trend going from north to south. Linear regression analysis found a correlation ($r = 0.72$) between the level of fluorides in drinking water and the DFI. If we exclude Khan Yunis and Rafah the correlation coefficient will be 0.93. The average level of fluorides in Khan Yunis was 2.8 ppm and the DFI was found to be 4.39. In Rafah, the level of fluorides was 0.73 ppm while the DFI was 3.45. It must be noted here that dental fluorosis was formed during the tooth development period and years before the water was analyzed, suggesting that water resources have recently been altered.

It is an established fact that, in the Gaza Strip, new water wells are dug on a periodic basis to replace others where the salinity becomes high or they become contaminated as a result of human activity.

The CFI for Gaza as a whole was calculated to be 2.42. According to Dean (1942) if the CFI rises above 0.6, it begins to constitute a public health problem warranting increasing consideration. Even if the score used in the formula to calculate CFI is halved, the index will still remain far above the 0.6 figure recommended by Dean.

The number of teeth exhibiting caries was low for the Gaza population, especially in the younger age groups. It is believed that two factors are involved in that, the high DFI and the low consumption of candied products. It is a known fact that fluorides help reduce dental caries, in addition the population is of low economic status such that candied food products are a luxury and not affordable by many.

An epidemiological study of Rugg-Gunn et al., (1997) suggested that the prevalence of dental fluorosis was high among children suffering from malnutrition. Some correlation between drinking water type fluorosis and the population's socio-economic condition and nutritional status is indicated. Fluorosis prevalence increases through the agricultural towns of Khan Yunis to urban regions.

CONCLUSIONS

The levels of fluorides found in groundwater and topsoil showed a general increasing trend from northern to southern areas of the Gaza Strip. Dental fluorosis occurred in many areas especially in Khan Yunis (south and south-east) where the average level of fluoride for all tested wells was 2.6 mg F/l. The sources of fluorides in groundwater are believed to be natural bedrock that supply fluoride ions to the groundwater; however the XRD results showed that none of the major fluoride minerals tested in soil samples were detected, the computer model-PHREEQC revealed that fluorite (CaF_2) was the donating mineral of fluoride ions to the groundwater. The dental fluorosis index (DFI) showed an increasing trend going from north to south and the community fluorosis index (CFI) for the Gaza Strip as a whole was 2.42 which represents a public health problem warranting increasing consideration. Many factors were involved in the development of dental fluorosis in the area, these factors revolved around the intake of fluoride from other dietary sources such as the consumption of tea and fish; the tea is heavily consumed as sweet and strong and being consumed from a very young age where it is put in nursing bottles.

RECOMMENDATIONS

The situation in which fluorides play an important factor in public health must be addressed on an urgent basis to avoid an environmental health catastrophe. One of the recommendations we suggest is integrating the water supply for Gaza as a whole. There are a number of wells in the northern area that are low both in fluoride and salinity which when mixed with other wells will result in water of acceptable quality. This option seems to be the only feasible solution for the foreseeable future. Parents, caregivers, water quality experts and health care professionals should judiciously monitor use of all fluoride-containing dental products by children under age 5 as is the case with any therapeutic product.

CHAPTER THREE

Potential use of treated wastewater and sludge in the agricultural sector of the Gaza Strip (*)

ABSTRACT

Twelve elements (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed in 120 composite samples of influent and effluent wastewater; the results revealed that domestic wastewater influent contains considerable amounts of heavy metals and the partially functional treatment plants of Gaza are able to remove 40-70% of most metals during the treatment process. Heavy metals in 31 industrial wastewater effluents are within the ranges of international standards. All industries of Gaza are light; although they have no treatment facilities, their effluents are being discharged to municipal sewerage system and the existing treatment plants are capable of absorbing the industrial effluents with no significant impact on treatment bioprocesses.

Thirty parameters were determined in 35 sludge samples: P, AOX, C, S, $CaCO_3$, Mg, Ca, Na, K, Li, Cu, Zn, Ni, Pb, Mn, Fe, Cr, Co, Cd, As, Hg, Ti, Se, Br, Rb, Th, Sr, Y, U, and Zr. Although there are no treatment facilities for sludge within the treatment plants, the results indicated that sludge in general is clean of heavy metals. Only zinc and AOX showed anomalous concentrations; more than 85% of sludge samples showed that averages of zinc and AOX are 2,000 mg/kg and 550 mg Cl/kg, respectively, which exceed the standards of all industrial countries for sludge to be used in land application.

Key words: Heavy metals, Reuse, Sludge, Wastewater treatment plants

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INTRODUCTION

The arid and semi-arid nature of the region renders it to be a water scarce region. Population growth and agricultural and industrial development have put more pressure on the existing scarce resources. They are currently being exploited to their maximum capacity to meet the desired development. As a result, a lot of environmental problems have started to arise at all places and levels. Such problems will be more acute in the near future if the current resource utilization patterns continue. Therefore there is an essential need to start looking at the different options and mechanisms that will help overcome these escalating environmental problems.

Lack of wastewater management has a direct impact on problems related to public health, marine and coastal pollution, deterioration of nature and biodiversity, as well as landscape and aesthetic distortion in the Gaza Strip (MEnA, 2000). Currently, about 60-80% of the domestic wastewater is discharged into the environment without treatment, either directly at the source, after collection from cesspits, or through the effluent of the sewer system or the overloaded treatment plants (MEnA, 2001). Assuming that 60% of the water used for domestic usage comes back as wastewater, Gaza produces about 13 MCM annually (CAMP, 2001). About 40% (50,000 m^3/day) of the wastewater that is generated in Gaza is currently discharged into the sea; a minor part infiltrates into the soil and contaminates the groundwater.

Compared to the neighboring countries, the industrial sector in Palestine is presently rather underdeveloped. Most industries are concentrated in the city of Gaza and in the northern areas, grouped in two main industrial estates, Gaza Industrial Estate (GIE) and smaller Beit Hanoun Industrial Estate (BIE). Several industries are scattered among residential areas. The industries of greatest concern are the food industry, chemical industry, tanning industry, textile industry, and the electroplating and metal finishing industry. Industries in Gaza are light and each has 5 to 100 individuals (Shomar, 1999). Heavy metals may inhibit the activities of microorganisms within the treatment process. Regulated metals include barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, zinc and arsenic (Edwards, 1995). Industrial wastewater requires onsite pretreatment before it can be disposed into the municipal sewage network to guarantee the stability of domestic wastewater treatment plants (Safi, 1999). Because heavy metals can not be degraded in the wastewater treatment plant, either they end up in the treatment plant sludge or they pass through the plant and leave with the effluent.

Up to now there has been very little production of sludge as all existing wastewater treatment plants are deficient and operating with old technologies. The construction of new wastewater treatment plants or the rehabilitation of the existing ones in Gaza will produce a regular daily volume of sludge that will need to be disposed in landfill sites, incinerated, ocean dumped, composted or applied in agricultural lands (PEPA, 1994). Sludge treatment facilities are almost absent and the produced sludge is removed from the ponds and left to be dried, partially depending on the season and the available area close to the treatment plant (PWA, 1999). Sludge production is a function of the biological oxygen demand (BOD_5) removal rate (EPA, 1999). It is assumed that the minimum sludge production should correspond to a BOD removal rate of 95% (effluent at 30 mg O_2/l) for some treatment plants in Gaza. Next to the available data of the PWA, the field visits confirmed that the amount of sludge Gaza wastewater treatment plants produce is low.

The solids content is within the range of 16 and 22% which categorize the Gaza sludge as a dewatered sludge, although dewatered sludges have as much as 40% solids.
To guarantee and safeguard hygienic standards and have no adverse effects on the human health, environmental quality must be given the highest priority. Although opponents of sludge use have many reservations, one of their main concerns is the long-term buildup of heavy metals in the soil (Zufiaurre et al., 1998). Over time, metals such as cadmium, zinc, and copper could build up to levels high enough to damage agricultural soils (EPA, 1999). Although the use of sludge on agricultural land is largely dictated by nutrient content (N and P), the accumulation of potentially toxic elements in sewage sludge is an important aspect of sludge quality, which should be considered in terms of long-term sustainable use of sludge on land (Burica et al., 1996). The most important nutrients in the sludge are nitrogen, phosphorus, and potassium. Other nutrients that may be present include calcium, magnesium, sulfur and they add copper even though it is considered as a heavy metal (Alloway and Jackson, 1991). According to the American standards of sludge used in agriculture, the average concentration of N and P in dry weight is 2% and <1% respectively; while the total solids are 3.4% (EPA, 2002). Although sludge is a valuable source of plant nutrients, the nutrient concentrations are significantly lower than most commercial fertilizers (Sterritt and Lester, 1980). It has been suggested that determination of adsorbable organic halogens (AOX) be used as an indicator for these priority substances. Moreover, AOX determination is a relatively easy technique to use. Because AOX is an analytical parameter and represents a wide range of substances, differing not only in their chemical structure but also in their toxicological profile, a description of relevant toxicological endpoints cannot be given (Planquart et al., 1999).

The main objective of this study is to introduce the concentration of trace metals and some major parameters in domestic, industrial wastewater and sludge for the first time. Moreover, it tries to highlight the various options that aim to reuse the treated wastewater and sludge in the Gaza Strip in a manner that will ensure agriculturally sustainable development.

MATERIALS AND METHODS

The study area

There are, at the present time, four wastewater treatment plants that are either being planned, under construction or in operation. The main two operating treatment plants are: the Beit Lahia Wastewater Treatment Plant in the northern area of Gaza and the Gaza Wastewater Treatment Plant in the region of Gaza City (Fig. 1), but none is working properly. The monitoring program on wastewater of the two treatment plants is conducted by the Palestinian Water Authority (PWA) and only a few parameters (pH, solids, BOD, and COD) are recorded in a regular basis.

Beit Lahia (Northern) Wastewater Treatment Plant

The Beit Lahia Wastewater Treatment Plant, located some 1.5 km east of the town of Beit Lahia in the northern part of the Gaza Strip, was erected in stages, commencing in 1976. It serves the town of Jabalia, as well as the nearby refugee camp and the communities of Beit Lahia and Beit Hanoun. The population in the area amounts to about 150,000 people today. But, depending on an exceptionally high natural rate of growth, the population could rise to 260,000 in the year 2010 and reach over 350,000 people in the year 2020, according to the official forecasts. That means a doubling of the population in a period of 20 years (PCBS, 2000). The existing plant consists of several ponds disposed in two lines, the first two ponds of each line being aerated, and with possibilities of interconnection. The plant has no pretreatment facilities and it is designed for a peak flow of 2,600 m^3/h. The plant is located in a depression without natural outlet to the sea, although it does not lie so far (4.5 km) from it. The effluent merely overflows from the last pond of the works, spreading in a large sand dune area in the immediate vicinity of the plant, where it infiltrates to groundwater. The plant faces major operation problems, such as: no preliminary treatment; presence of sand; BOD of over 600 mg O_2/l; an overflow of used water; and the pumping station is out of operation. The average sludge production at the Beit Lahia WWTP can be estimated to be on average 8.5 tons total solids per day in the year 2010, i.e. approximately 28 m^3/day.

Gaza Wastewater Treatment Plant

This plant was originally constructed in 1977 as a two-pond treatment system. In 1986, it was expanded to a capacity of 12,000 m^3/day with the construction of two additional ponds. A project in 1994 rehabilitated the plant without capacity increase. In 1999, with USAID funding, the plant was expanded to a capacity of 32,000 m^3/day and consisted of anaerobic ponds, an aerated pond, biotowers, an effluent polishing pond, disinfection, effluent pump station/force main and sludge drying beds. The current flow to the plant is about 42,000 m^3/day from Gaza City and parts of Jabalia. The sludge produced in this plant is exposed to the sun and then accumulated and transferred to dumping sites. The plant is close to less urbanized areas and closer to agricultural areas to facilitate the distribution of reused water to farmers.

Industries

The major industries were selected to represent all industrial activities in the Gaza Strip (Tables 4, 5 and 6). Among 31 industries, 20 are located in the two major industrial estates, Gaza, and Beit Hanoun. The other 11 industries are scattered among residential areas especially in Gaza, Jabalia and few in Khan Yunis.

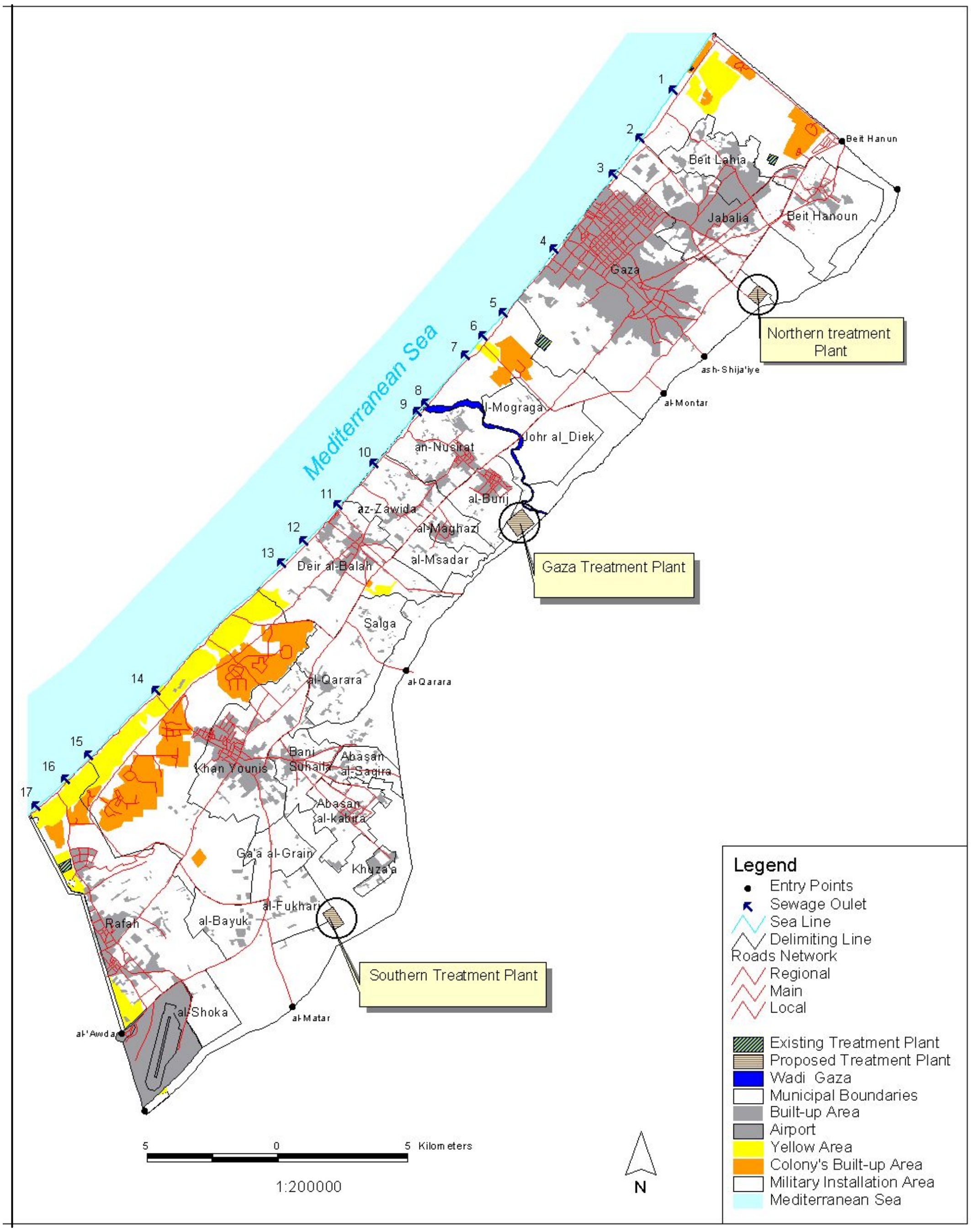


Fig. 1. Existing and proposed wastewater treatment plants and sewage outlets to the sea in the Gaza Strip.

The sampling and analysis

Domestic wastewater

The continuous presence of a trained guard in each wastewater treatment plant made the sampling campaigns easier, especially because his mandates are to protect the plant and to collect samples for the routine monitoring program of the PWA. Three sampling campaigns have been conducted in 3 years (20 influent and 20 effluent samples each year) in the periods 20 November-12 December 2000, 26 June-17 July 2001 and 25 April -17 May 2002.

A series of grab samples (8-10) were taken over 1 day (1l per 2h), starting from 6:00 am, and combined in a container to form a composite sample. Finally, 1 l of the mixture was taken in an acid-washed bottle and transferred to the laboratory, and was then filtered in an acid-washed filter holder and through a 0.45-µm Sartorius filter. The first few milliliters were used for rinsing, then they were discarded, and the filtrate was transferred to clean acid-washed polyetheylene bottles and acidified with concentrated nitric acid (Ultrapur, Merck, v/v), and stored at 4 ^{o}C until analyses by the ICP/MS (Perkin Elmer-Sciex, Elan 6000) were performed; the other part of wastewater was filtered with no additives and stored at 4 ^{o}C for anion analyses by Ion Chromatography (IC DIONEX DX-120). Several parameters were measured during the fieldwork: temperature, electrical conductivity and pH, other parameters (SS, TSS, TDS, COD and BOD_5) were measured a few hours later according to the American standard methods (APHA, 1995).

Industrial wastewater

The samples were taken from the effluent wastewater of the existing operating industries in Gaza, and they were collected in the same periods as the domestic wastewater. Although the situation in Gaza was very difficult, the sampling program went smoothly, and all but three of the industries that were initially selected were sampled, as listed in Tables 4, 5 and 6. In coordination with the staff of monitoring and inspection of the Palestinian Ministry of Environment, 31 composite samples were collected (10 in the first year, 21 in the following two years). They had the same treatment and analysis as the domestic wastewater samples.

Sludge

Thirty-five sewage sludge samples were collected during the campaigns, 5, 20 and 10 in the 3 years. Samples of sludge were collected in polyethylene containers from the different drying lagoons of the two treatment plants and from the accumulated piles in the surrounding areas. After collection, samples were freeze-dried until complete dryness; then they were ground and homogenized in an agate mortar and sieved through a mesh of 0.63-mm pore size.

About 0.5 to 1.0 g of the homogenized sample were dissolved in 10.5 ml of concentrated hydrochloric acid (37% p.a.) and 3.5 ml of concentrated nitric acid (65% p.a.) in 50 ml retorts. The samples were allowed to degas (12 h). Then all samples were heated to 160 °C on a sand bath until a complete extraction had taken place (3 h). After cooling, the solutions were diluted with distilled water in 50-ml volumetric flasks and kept in 100-ml polyethylene bottles for analysis.

Heavy metals were analyzed by two different techniques: flame atomic absorption spectrometry (AAS vario 6- analytikjena) was used for determination of Mg, Li, Ca, K, Na, Cu, Zn, Ni, Pb, Mn, Fe, Cr, Co, Cd and As. An energy-dispersive miniprobe multielement analyzer (EMMA) for direct analysis was used for K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Pb, Th and U in sludge (Cheburkin and Shotyk, 1996). The distribution of total phosphorus represented as (PO_4) was measured for all sampling stations (APHA, 1995). Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of the freeze dried samples (50-100 mg) and Hg pre-concentration on a single gold trap by means of an advanced mercury analyzer (AMA) 254 solid phase Hg-Analyzer (LECO). The total carbon and sulfur were determined directly in dried samples by using a carbon-sulfur determinator (Leco CS-225). Carbonates were measured directly via a carbonate bomb (Müller and Gastner, 1971). The TOC can be calculated by the subtraction of inorganic carbon from total carbon. AOX was determined using a Euroglas Organic Halogen Analyzery- Netherlands according to the DIN 38414 S18 Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Sludge and Sediment (Group S) Determination of AOX (DIN, 1989).

Table (1) Standards of heavy metals in wastewater and sludge.

Element	Domestic wastewater[a] (mg/l)			Industrial wastewater[b] (mg/l)		Sewage sludge[c] (mg/kg)		
	EPA[1]	China[2]	Ayers & Westcot[3]	WHO[4]	Jordan[5]	USA[6]	Germany[7]	France[8]
Ag				0.03	1			
Al			5					
As	0.05	0.05	0.1		0.05	41		
Cd	20	0.005	0.01		0.01	39	1.5	2
Co	2		0.05					
Cr	5	0.1	0.1	5	0.05	1200	100	150
Cu	0.2	1	0.2	1	1	1500	60	100
Fe			5					
Mn	10		0.2		1			
Ni	0.2		0.2	1	0.1	420	50	50
Pb	0.05	0.1	5	0.1	0.1	300	100	100
Zn	2	2	2	5	15	2800	200	300
Hg		0.001			0.001	17	1	1

[a]: *Standards for reuse.*

[b]: *Standards for discharging into municipal sewerage system and to the environment.*

[c]: *Limit values for heavy metals in sludge for use in agriculture.*

[1]: *EPA, 1999.*

[2]: *China National Regulations for Agricultural Irrigation, 1992.*

[3]: *Ayres and Westcot, 1985.*

[4]: *WHO, 1998b: Concentration of heavy metals inhibiting aerobic biological treatment processes.*

[5]: *Ministry of Municipal and Rural Affairs & the Environment-Jordan, 1991.*

[6]: *EPA, 2002: pollutant concentration limit (mg/kg) for Land Application in the United States, Dry Weight Basis.*

[7]: *ICON, 2001: Standards for agricultural application and McGrath, 1995.*

[8]: *McGrath, 1995.*

Quality control

For quality control, analytical blanks and two samples with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents. For wastewater analysis, Standard Reference Material 1643c was used for determination of trace elements (NIST, 1991). For sludge samples, the accuracy was evaluated by two Sewage Sludge Standard Reference Materials (DIN, 1997). As an independent check on the trace element measurements of the sludge, these were also measured in solid samples using the energy-dispersive miniprobe multielement analyzer EMMA-XRF. As a boundary and a reference of the expected results, about nine international standards of heavy metals in domestic wastewater, industrial wastewater and sludge were chosen (Table 1).

RESULTS AND DISCUSSION

Domestic Wastewater

In a 2-week monitoring of general parameters, the performance of the two plants was recorded (Table 2), while the performance of the plants with respect to the heavy metals in 3 years is shown in Table 3. The general parameters indicated that the two plants under the existing treatment facilities were working well and they were able to remove >92%, >88%, >60% of BOD_5, COD and both total P and total N, respectively.

Table (2) Performance of wastewater treatment plants in the Gaza Strip (4-19 July 2001).

Parameter*	German standards	Beit Lahia WWTP** Influent	Beit Lahia WWTP Effluent	Removal (%)	Gaza WWTP Influent	Gaza WWTP Effluent	Removal (%)
pH		7.04	7.43	-6	7.5	7.7	-3
Temperature (^oC)		22.3	22.3	0	25.5	26	-2
Settleable Solids SS (Ml/l)		6	0.1	98	9	0.1	99
Total Dissolved Solids (TDS) mg/l		895	1007	-13	1470	1536	-4
Total Suspended Solids (TSS) mg/l		1288	1024	20	440	20	95
Chloride (mg/l)		270	250		555	480	
Fluoride (mg/l)		0.6	0.6		1.2	1.4	
Sulfate (mg/l)		242	250		314	320	
Total P (mg/l)	2	15	6	60	23	9	61
Total N (mg/l)	18	17	6	65	19	7	63
NO_2 (mg/l)		63	16	75	71	20	72
NH_4-N (mg/l)	10	64.4	61.4	5	62	60	3
COD (mg O_2/l)	110	884	108	88	940	89	91
BOD_5 (mg O_2/l)	25	420	35	92	520	25	95

** Average value of each parameter.*
*** WWTP: Wastewater Treatment Plant*

The heavy metal removal was not constant due to the many factors affecting the treatment process. A good example was the shortage in aerator performance, and this affected the oxygen contents in the aeration lagoons and the latter affected the form of the metals and their solubility; this could explain the maximum and minimum variations of some parameters sensitive to dissolved oxygen such as Fe, Mn and As.

Table (3) Average concentrations of heavy metals in influent and effluent wastewater.

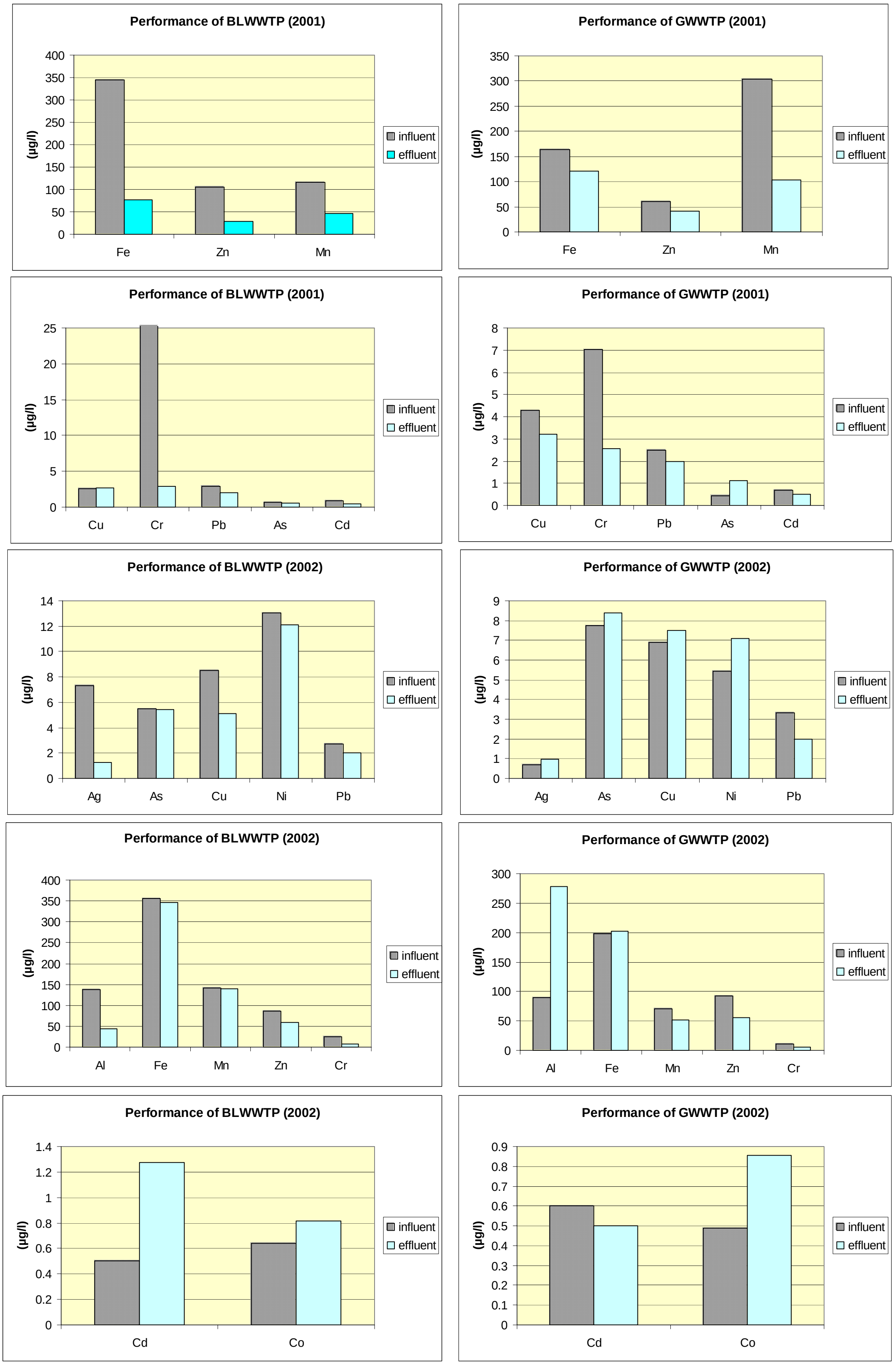
	LD[a]	Beit Lahia Wastewater Treatment Plant					
		Inf 2000	Eff 2000	Inf 2001	Eff 2001	Inf 2002	Eff 2002
Ag µg/l	0.5	0.7	0.6	NM[b]	NM	7.3	1.3
Al µg/l	25	73	39	NM	NM	138	44
As µg/l	5	5.6	5.1	0.7	0.6	5.5	5.4
Cd µg/l	0.5	< 0.5	0.8	0.1	< 0.5	< 0.5	1.3
Co µg/l	0.3	0.3	0.8	NM	NM	0.6	0.8
Cr µg/l	2.5	38.9	7.6	25.3	2.9	25.2	8.4
Cu µg/l	1	6.0	6.7	2.5	2.7	8.5	5.1
Fe µg/l	15	373	114	344	76	356	347
Mn µg/l	1	120	96	116	47	142	139
Ni µg/l	0.5	21.9	11.8	NM	NM	13.1	12.1
Pb µg/l	2.5	2.6	< 2.5	2.9	< 2.5	2.7	< 2.5
Zn µg/l	10	120	35	105	29	87	59
Gaza Wastewater Treatment Plant							
		Inf 2000	Eff 2000	Inf 2001	Eff 2001	Inf 2002	Eff 2002
Ag µg/l	0.5	0.8	0.8	NM	NM	0.7	1.0
Al µg/l	25	71	61	NM	NM	89	278
As µg/l	5	6.6	7.0	0.4	1.1	7.8	8.4
Cd µg/l	0.5	0.5	< 0.5	0.1	0.1	0.5	< 0.5
Co µg/l	0.3	0.4	0.7	NM	NM	0.5	0.9
Cr µg/l	2.5	11.3	4.8	7.0	2.6	11.3	5.9
Cu µg/l	1	7.0	7.0	4.3	3.2	6.9	7.5
Fe µg/l	15	137	132	163	121	198	202
Mn µg/l	1	76	68	303	103	70	52
Ni µg/l	0.5	5.5	6.8	NM	NM	5.4	7.1
Pb µg/l	2.5	2.6	2.6	2.5	< 2.5	3.3	< 2.5
Zn µg/l	10	75	54	61	41	92	56

[a] Limit of detection

[b] NM: not measured

The results indicated that the concentrations of major anions (Cl, F, NO_3 and SO_4) and major cations (Na, Ca, Mg and K) in wastewater were similar to their values in the groundwater of the area of each treatment plant. Many metals have a high affinity to react with anions and this affects their mobility within the treatment process and their final contents in effluent and sludge. Anomalous results of some elements indicated that their concentrations in the effluent were higher than those in the influent; despite the fact that there is no clear explanation, it is assumed that the accumulation of these elements in water has occurred in the final sedimentation lagoons of each plant. There was no steady state behavior of each element in the 3 years of monitoring; the same phenomenon appeared independently for each treatment plant. On the other hand; major indicating parameters (BOD_5, COD and TSS) were removed to the maximum and all tested heavy metals in the effluent complied with different standards.

All tested elements showed similar concentrations in the influent in the 3 years monitored and no significant difference was observed between the values of both treatment plants; the effluents showed a similar situation; only Ag showed anomalous results in the influent of 2000 and 2002 for the Beit Lahia treatment plant. The wastewater effluent had good characteristics close to the guidelines and standards of many developed countries (Table 1), and in general the results revealed that there was no significant difference between the performances of the two treatment plants in terms of heavy metal removal (Fig. 2). Moreover, the wastewater effluent of the two treatment plants was suitable for all purposes and applications such as agriculture and industry. Generally the results showed that heavy metals in the effluent are low and they comply with the standards of reused wastewater in agriculture.


Performance of BLWWTP (2001)

Performance of GWWTP (2001)

Performance of BLWWTP (2001)

Performance of GWWTP (2001)

Performance of BLWWTP (2002)

Performance of GWWTP (2002)

Performance of BLWWTP (2002)

Performance of GWWTP (2002)

Performance of BLWWTP (2002)

Performance of GWWTP (2002)

Fig. 2. Performance of Beit Lahia wastewater treatment plant (BLWWTP) and Gaza wastewater treatment plant (GWWTP), heavy metals in influent and effluent wastewater.

Industrial Wastewater

From the field surveys, it was found that the industrial wastewater was disposed of to the municipal sewage system when the latter was present, or to septic tanks constructed for each industry, or directly to the surrounding areas which are in some cases wadies. Treatment processes were almost absent, and in the best case they were very simple, represented by sediment tanks. There was no periodic inspection, and if present there were no scientific rules regarding the discharge standards or quality control. Tables 4, 5, and 6 show the heavy metals in the effluent of 31 industries. The tables confirmed important conclusions: unlike the domestic wastewaters, it is very difficult to generalize about the industrial wastewaters; the characteristics of the industrial wastes vary not only with the type of industry, but also from plant to plant, due to differences in manufacturing processes and, to a lesser degree, the quality of the original raw water used. Under the worst-case scenario of the industrial wastewater production in terms of quality and quantity, the treatment plants are able to absorb all amounts of pollutants and the final effluent is considered clean for agriculture and other reuse applications.

Table (4) Heavy metals in the effluents of 10 industries in the Gaza Strip (µg/l), year 2000.

Industry	Fe	Zn	Cu	Mn	As	Pb	Cr	Cd
Pharmaceutical Industry	97	259	2.68	40	0.92	<2.5	<2.5	<0.5
Cosmetics Industry	127	109	4.262	45	0.36	4.1	5.52	<0.5
Jeans washing	775	1369	500	124	1.2	6.61	16.43	<0.5
Electroplating Factory	5450	29500	4000	219	3.58	102	15859	70.15
Galvanic Factory	2900	3096	14.95	26	2.36	10.3	797	9.40
Detergent Factory	1619	1730	1	71	7.77	110	1073	8.65
Cloth Washing Factory	277	503	500	57	1.9	6.52	50.65	<0.5
Ice Cream Factory	222	251	100	26	1.44	<2.5	50.95	0.86
Soft Drinks Factory	825	143	400	64	1.34	4.25	22.32	<0.5
Car Washing Machine	1308	212	100	75	2.12	27.3	23.13	<0.5

Table (5) Heavy metals in the effluents of 10 industries in the Gaza Strip (µg/l), year 2001.

Industry	Fe	Zn	Cu	Mn	As	Pb	Cr	Cd
Pharmaceutical Industry	97	259	2.68	40	0.92	<2.5	1.89	0.06
Cosmetics Industry	127	109	4.26	45	0.36	4.10	5.52	0.09
Jeans washing	775	1369	500	124	1.20	6.61	16.43	0.03
Electroplating Factory	5450	29500	4000	219	3.58	102	15859	70.15
Galvanic Factory	2900	3096	14.95	26	2.36	10.3	797	9.40
Detergent Factory	1619	1730	0.67	71	7.77	110	1073	8.65
Cloth Washing Factory	277	503	500	57	1.9	6.52	50.65	0.28
Ice Cream Factory	222	251	100	26	1.44	<2.5	50.95	0.86
Soft Drinks Factory	825	143	400	64	1.34	4.25	22.32	0.19
Car Washing Machine	1308	212	100	75	2.12	27.30	23.13	0.44

Table (6) Heavy metals in the effluents of 11 industries in the Gaza Strip (µg/l), year 2002.

Industry	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Industry of Detergents (1)	2.79	925	31	0.7	2.2	103.5	174	645	12	27	10.7	269
Industry of Detergents (2)	35.05	1010	29	2.3	2.3	281.0	48	375	16	5	7.9	174
Metal coating – Galvanization	21.55	104	8	< 0.5	3.4	71.5	385	565	3	5	< 2,5	10200
Jeans-Washing Industry	8.9	59	5	0.6	0.8	7.6	39	380	111	5	< 2,5	940
Pharmaceuticals	1	313	14	0.8	3.5	102.5	54	3200	221	22	53.0	605
Cosmetics and perfumes	0.5	33	8	< 0.5	0.5	11.4	11	379	42	5	< 2,5	426
Jeans-Washing Industry	1.755	38	10	< 0.5	0.5	34.1	25	281	32	13	< 2,5	102
Paintings	< 0.5	1440	15	0.5	2.2	8.7	51	585	45	6	453.0	173
Soft Drinks	2.05	466	14	0.8	1.0	27.3	32	1330	21	14	84.5	63
Industry for Plastics	< 0.5	920	5	< 0.5	0.3	6.9	10	395	22	2	17.2	53
Metal Electroplating	0.94	143	< 5	0.7	3.6	48050	1585	1270	80	74	7.0	1085

Sludge

Table 7 summarizes the statistical analysis of sludge quality and the average value is considered to represent each parameter, bearing in mind that the median value is very close to the average.

Table (7) Averages of trace metals and major parameters in sludge of three years.

Parameter	Gaza WWTP 2000	BLWWTP 2001	Gaza WWTP 2001	BLWWTP 2002	Gaza WWTP 2002
	Mean	Mean	Mean	Mean	Mean
PO_4 [g/Kg]	10	10	21	13	25
AOX [mg/kg]	490	467	523	480	495
C [%]	15	31	31	34	24
S [%]	0.5	2.0	2.0	3.8	2.6
$CaCO_3$ [%]	23	17	23	17	22
Mg [%]	0.9	1.2	1.3	1.0	1.0
Ca [%]	7	4	4	8	11
Na [mg/Kg]	2230	1257	3076	4145	7095
K [mg/Kg]	2425	1158	1447	1890	1746
Li [mg/kg]	3.3	3	3	3.1	2.9
Cu [mg/Kg]	110	200	251	257	276
Zn [mg/Kg]	897	1646	1909	2000	2281
Ni [mg/Kg]	24	60	25	46	25
Pb [mg/Kg]	49	77	121	92	140
Mn [mg/Kg]	206	148	235	158	244
Fe [%]	1.1	1.7	1.2	1.4	1.4
Cr [mg/Kg]	50	120	82	98	93
Co [mg/Kg]	4.1	6.5	5.3	2.8	2.5
Cd [mg/Kg]	0.9	2.4	1.3	2.0	1.8
As [mg/Kg]	18.2	35.0	21.2	6.4	4.1
Hg [mg/Kg]	3.1	2.0	2.6	2.4	3.3

Heavy metals

According to the results of the wastewater, the majority of metals transfer to sewage sludge, although 20% may be lost in the treated effluent, depending on the solubility and this may be as high as 40%-60% for the most soluble metal, Ni. It is important to mention that the quality of the wastewater effluent has a direct relationship with the quality of the sludge produced from the same plant. This means that when the total solids in the effluent are high the sludge has low solid contents and the treatment process is not efficient and vise versa.

In addition to the common metals analyzed (Table 7) in sludge samples in many parts of the world, an extra nine elements were determined (Table 8) and, although these elements are of lesser importance, seven of them have low concentrations and only titanium (Ti) and strontium (Sr) as an alkaline earth metal showed considerable amounts in the tested samples.

Table (8) Other elements in sludge produced from Gaza (mg/kg), by using EMMA.

Parameter	LD*	Sludge quality of Beit Lahia WWTP, April 2002					Sludge quality of Gaza WWTP, April 2002				
		max	min	mean	median	σ	max	min	mean	median	σ
Ti		3336	2457	2835	2846	328	3213	2276	2719	2854	416
Se	0.6	2	1	1.2	1.0	0.5	5	3	3	3	1.0
Br	0.7	20	18	19.2	19	0.7	27	17	23	23	3.9
Rb	0.7	13	8	10.5	11	2.1	12	8	10	10	1
Sr	0.8	363	335	349	352	11.5	984	540	709	651	168
Y	1.0	9	6	8.0	9	1.2	8	6	7	7	1.0
Zr	0.5	86	59	71.0	69	10.5	185	96	129	103	42
Zn	1.0	1597	1383	1495	1472	98	1642	1107	1341	1261	239
Th	2.5	9	5	7	7	1.8	3	0	2	2	1.4
U	2.5	5	3	4	4.3	0.8	11	6	9	9	2.0

*) Limit of Detection

The results of Zn in more than 90% of sludge samples revealed that this metal is present in high amounts and this is a very serious fact. Zinc in sludge of Gaza exceeds that of all standards of developed and industrial countries (Table 1). This raises the question about the main sources of Zn in sludge. Based on the field surveys, the Zn sources are expected to be domestic and commercial in origin. Domestic sources of Zn are corrosion and leaching of plumbing, water-proofing products, anti-pest products, wood preservatives, deodorants and cosmetics, medicines and ointments, paints and pigments, printing inks and coloring agents. The commercial sources are galvanization processes, brass and bronze alloy production, tires, batteries, paints, plastics, rubber, fungicides, paper, textiles, taxidermy, building materials, special cements, and also cosmetics and pharmaceuticals.

As mentioned above, the effluent wastewater showed low contents of Zn and the average of Zn removal in the treatment process was 55%; this ratio finds its way to the sludge and this may explain the high contents of Zn in sludge. For further quality assurance, the same samples were analyzed by the EMMA, and the Zn average was 1400 mg/kg which is the same as the American standard. Under the best-case scenario of Zn contents in sludge and taking the EMMA reading, it is recommended not to apply this sludge on agricultural land before detailed investigations.

A brief comparison between the sludge of the two plants revealed that Mg, Ca, Li, Cu, Zn, Fe, Cr, Co and As have similar concentrations and no significant changes occurred during the 3 years of monitoring; however the results for As and Zn were 2-3 times higher in the years 2001 and 2002, respectively. Nickel was 2-3 times higher in Beit Lahia WWTP while Mn and Pb were 2 times higher in the sludge of Gaza WWTP; the reason is expected to be the fluctuation of industrial activities and the irregular production load of these elements in the industrial wastewater. The high concentrations of Na in the sludge of Gaza (2-3 times) may be connected to the same ratio of Na in groundwater and wastewater for the two areas.

Nutrients (N and P)

The averages of calculated total organic carbon TOC (total carbon – inorganic carbon) for sludge are 17-22 % for Beit Lahai and Gaza, respectively, while the results of nitrogen for the two plants showed averages that are less than 2% (the American standards); nitrogen in Beit Lahia WWTP was 1.35% while it was 1.6 in Gaza WWTP. This range puts the sludge of Gaza in an acceptable ranking for land application.

The average of phosphorus in the sludge of Gaza plant was 0.7% while it was only 0.4% in the sludge of the Beit Lahia plant. Both results are less than the standards of the USA (1%) and other developed countries. All other values of K, Ca, Mg etc. are shown in Table 7 and they are all within the international standards.

Adsorbable organic halogens (AOX)

In this survey of contamination levels of sludge of Gaza, it was found that concentration of AOX is in the range of 200-600 mg Cl/kg, while the German and EU standard is 500 mg Cl/kg. AOX is not a measure for toxicity, and according to the site visits the main sources are expected to be paper pulp industry. Even though the wastewater effluent of the paper industries was not examined, it is proposed that the main source of AOX in sludge was the 26 paper industries distributed in Gaza and the northern area. These industries were using old technologies and they represented the largest consumer of chlorine and the greatest source of toxic organochlorine discharges directly into waterways. Large quantities of toxic organochlorine byproducts, including dioxin and thousands of other substances, were being discharged into the municipal sewage system. Many organochlorines resist natural breakdown processes, so they build up over time in the sludge, and this explains the high AOX ratio in the sludge of Gaza. Based on the results of the heavy metals and of the other major parameters obtained in this study, the application of sludge should comply with the soil physical, chemical and biological characteristics. Protection of soil organisms and microbially mediated soil processes is important. Regular monitoring systems for sludge and soil should be implemented and risk assessment programs should be adopted prior to and after sludge application.

Variation of heavy metal contents in wastewater and sludge

The fluctuation of heavy metal contents in wastewater and sludge could be explained as follows: firstly, the majority of industries in Gaza are connected to the treatment plants and they represent a major source of heavy metals in wastewater; these industries work neither to a regular time schedule nor in a steady state of wastewater production; secondly, around 35% of population and industries in Gaza are not connected to the wastewater collection network and they use septic tanks for wastewater disposal, these septic tanks have different sizes and they used to be emptied into the treatment plants by special tankers, the quantity and the quality of the transported wastewater is not stable; and thirdly, Gaza is located in a semi-arid zone where the rainy season is very short (4-5 months) and the seasonal variation plays an important role in the variation of wastewater characteristics. The three sampling campaigns were conducted in three different seasons; the weather and the rain intensity were varying even from day to day and this affects the concentration of heavy metals in both influent and effluent wastewater. Moreover, the wastewater treatment plants are open lagoons and they directly receive rain water on the rainy days and this affects the quality of wastewater and sludge.

CONCLUSIONS

1. The existing wastewater treatment plants in Gaza show a similar performance, and although they are partially functional, the heavy metal contents of the effluent are less than that of the standards of neighboring countries, and the treated wastewater could be used in agriculture with respect to heavy metals.
2. The industries in Gaza are light and they have no treatment facilities. Some individual industries produce high amounts of heavy metals in their effluents but the wastewater treatment plants have the capability to absorb the industrial effluents with no significant impact on the treatment bioprocesses.
3. The existing plants produce small amounts of sludge with low contents of all tested heavy metals except Zn, which exceeds the standards of all industrial countries. This is additional to the AOX which is found to be more than 500mg Cl/kg in some sludge samples of Gaza treatment plant while more than 85% of the samples have less than 500mg Cl/kg.
4. In addition to total metal concentrations the determination of specific chemical forms of heavy metals and their mode of binding in soil is very important in order to estimate their mobility, bioavailability and related ecotoxicity. Education, information, and training of farmers also play an important role in promoting sensible reuse practices.
5. Gaza Strip is a good example for similar studies in all neighboring countries which have similar conditions of metrology and climate, environment and natural resources, population growth, water scarcity, wastewater management problems and finally socio-economic situations. The findings and conclusions of wastewater reuse and sludge application could be imitated in these similar areas not only in the region but also in many developing countries.
6. By the reuse of treated wastewater, Gaza can not only reduce the pollution load of the Mediterranean Sea by wastewater contaminants but also consider wastewater as a precious source of water which could be used in agriculture.

CHAPTER FOUR

Geochemical characterization of soil and water from a wastewater treatment plant in Gaza (*)

ABSTRACT

The aim of the study was to determine the interaction between the natural geochemistry and the anthropogenic effects through trace element profiles in one of the environmentally significant areas of the Gaza Strip. Five boreholes were dug in the area of the Gaza wastewater treatment plant. The geology, mineralogy, and geochemistry of the soil profiles were studied; and the geochemistry of wastewater, sludge, soil, and groundwater was identified by several analytical techniques. The study introduced the environmental baselines and the infrastructure needed for further research for the first time: the natural infiltration potential, the artificial recharge, and the agricultural activities of water and wastewater. The results of the geochemical investigations confirmed that the upper 40 cm of soil was found to be the affected zone by wastewater and sludge. Among 26 elements analyzed, only a few metals: As, Cd, Cr, Hg, Zn, and to a lesser extent Pb showed relevance from the human health point of view. The metal accumulations in the soils were characterized by a large spatial variability, with some ‘hot spots’ of Cu and Zn reaching topsoil concentrations of up to 240 and 2005 mg/kg, respectively. In spite of that, the results of the groundwater revealed that none of them was detected at concentrations that exceeded the WHO (World Health Organization) standards. Moreover, it was shown that both anthropogenic activities as well as seawater intrusion caused the high levels of nitrate and salinity.

Key words: Gaza, Geochemistry, Soil profile, Wastewater treatment plant

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(*) *The study was accepted in the Soil and Sediment Contamination: an International Journal as:*

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INTRODUCTION

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. The groundwater aquifer of Gaza is extremely susceptible to surface-derived contamination because of its largely unconfined nature and highly permeable sands and gravels. In the past decade, the aquifer has become the focus of experts and public concern. This concern has resulted from widespread salinity, nitrate and fluoride; from the detection of agricultural pesticides and fertilizers; and from increased pressures for urban development above the aquifer. As a first step to determine the reference levels of contaminants, it is necessary to know their contents in various environmental compartments. A few studies have been conducted in the area of wastewater and sludge but none in soil and groundwater. Studies of the interaction between environmental components of Gaza are completely lacking. Soils are one of the most precious natural resources of Gaza and they are prone to contamination from atmospheric and hydrological sources, but direct waste disposal causes a major impact on this limited natural resource, posing serious environmental concerns. Information on the soil macro- and micronutrient levels and trace elements could be of great interest for agricultural usage and artificial recharge of the groundwater aquifer (McBride et al., 1997; Roemkens and Salomons, 1998; Wilcke et al., 1998; Whittle et al., 2002).

Metal mobility in soils depends on two main factors: (1) water transfer through the soil and (2) physicochemistry or biogeochemistry of the trace metals with the solid phase of the soil (sorption/desorption, precipitation/dissolution, complexation by the organic matter). Water transfer and chemical reactions depend on the chemical, mineralogical, and physical/hydrological properties of the different soil horizons (Cornu et al., 2001; Abrahams, 2002). As a matter of fact, pollution problems may arise if toxic metals are mobilized into the soil solution and are either taken up by plants or transported to the groundwater (Planquart et al., 1999). The concentrations of several potentially harmful contaminants, such as metals commonly found in sludges, limit their application on land. The high contents of Zn and Adsorbable Organic Halogen (AOX) in the sludges of Gaza are examples of such contaminants (Shomar et al., 2004e). By spreading sewage sludge on fields, the metal content of the soil drastically increases (Smith et al., 1996), inducing a potential risk of groundwater pollution, increased toxic metal mobility (e.g. organic complexing of the transition metals), plant toxicity, and metal contamination through the food chain (Mikac et al., 1998; Cornu et al., 2001). Many investigations on the distribution of metals in relation to depth in the profiles of sludged soils have shown that, in the short term, relatively little downward movement of metals occurs below the depth of cultivation or of sludge application (Alloway and Jackson, 1991). Increases in metal concentrations below the depth of 30 cm did not appear to be significant compared to background values, suggesting that the movement of metals downward in the soil profile was minimal. However, several authors have reported a more pronounced movement of metals within the profiles of amended soils.

Darwish and Ahmad (1997) have shown that sludge-borne Zn, Cu, Cd, and Pb moved down to a depth of 40 cm in soils referred to as saline, non-saline, sodic, and calcareous (except Zn in the calcareous soil). Although several trace metals have clearly migrated within the profiles, and therefore must have been in a soluble form at some time, their present concentrations in the leachates are very low. This indicates that after migration they have become fixed in more stable and insoluble forms (Planquart et al., 1999; Cornu et al., 2001; Hoffmann et al., 2002).

The main goals of this study were: (1) to introduce all relevant information from the study area on hydrogeology, geochemistry, and geology; and (2) to study the geochemical characteristics of an on site column of wastewater, sludge, soil, and groundwater in the area of the Gaza central wastewater treatment plant.

METEOROLOGY, GEOLOGY AND HYDROLOGY

There are two well-defined seasons: the wet season, starting in October and extending into April, and the dry season from May to September. The average daily mean temperature ranges from 25 °C in summer to 13 °C in winter, with the average daily maximum temperature ranging from 29 °C to 17 °C, and the minimum temperature ranging from 21°C to 9 °C, in the summer and winter, respectively. The daily relative humidity fluctuates from 65% in the daytime to 85% at night in the summer and between 60% and 80%, respectively, in the winter. The mean annual solar radiation is 2200 J/cm^2/day (MEnA, 2000). There is a significant variation in the wind speed during the daytime, and the average maximum wind speed velocity is about 3.9 m/s. Moreover, storms have been observed in the winter with a maximum wind speed of about 18 m/s. Peak months of rainfall are December and January; the average annual rainfall is 335 mm/y (26 year average) (CAMP, 2001).

The coastal aquifer consists primarily of Pleistocene age Kurkar Group deposits, including calcareous and silty sandstones, silts, clays, unconsolidated sands, and conglomerates. Near the coast, coastal clays extend about 2-5 km inland, and divide the aquifer sequence into three or four sub-aquifers, depending upon the location. Towards the east, the clays pinch out and the aquifer is largely unconfined (PEPA, 1994). Within the Gaza Strip, the total thickness of the Kurkar Group is about 100 m at the shore in the south, and about 200 m near Gaza City. At the eastern Gaza border, the saturated thickness is about 60-70 m in the north, and only a few meters in the south near Rafah. Local perched water conditions exist throughout the Gaza Strip due to the presence of shallow clays (MEnA, 2000).

From the results of pump tests carried out in the Gaza Strip, aquifer transmissivity values range between 700 and 5,000 square meters per day (m^2/d). Corresponding values of hydraulic conductivity are mostly within a relatively narrow range, 20-80 meters per day (m/d). Most of the wells that have been tested are municipal wells screened across more than one subaquifer. Hence, little is known about any differences in hydraulic properties between these sub-aquifers. Specific yield values are estimated to be about 15-30% while specific storativity is about 10^{-4} from tests conducted in Gaza (CAMP, 2001).

Under natural conditions, groundwater flow in the Gaza Strip is towards the Mediterranean Sea, where fresh groundwater discharges into the sea. However, natural flow patterns have been significantly disturbed by pumping and artificial sources of recharge over the past 40 years. Within the Gaza Strip, large cones of depression have formed over large areas in the north and south. Water levels are presently below mean sea level in many places, inducing a hydraulic gradient from the Mediterranean Sea towards the major pumping centers and municipal supply wells (PEPA, 1994). Between 1970-1993, water levels dropped 1.6 m on average, mostly in the south. This is equivalent to 5 million cubic meters per year (Mm^3/y) decline in overall aquifer storage on average, using a specific yield of 0.2 (CAMP, 2001).

It is estimated from available data that less than 10% of the Gaza's aquifer resource contains groundwater that meets the WHO drinking water standard for chloride (250 mg/l); primarily in the north and along the coastal sand dune areas of the Mawasi (southwest). The major documented water quality problems in the Gaza Strip are elevated salinity and nitrate concentrations in the aquifer. Depending on location, rates of salinization may be gradual or sudden. In Gaza City/Jabalia, chloride values are increasing at rates up to 10 mg/l per year in several wells. The lateral inflow of brackish water across the 1948 borders (chloride concentrations varying from 800 to 2000 mg/l) affects the water quality of a significant portion of the Gaza coastal aquifer, and is of a natural origin. Nitrate in 90% of the groundwater wells is more than 50 mg/l (CAMP, 2001).
Rates of aquifer replenishment are one of the most difficult parameters to derive. There is no simple method that can be applied to estimate recharge from rainfall in the Gaza Strip. This is primarily a function of the extreme climatological variability observed between rainfall stations and numerous influencing factors, such as soil types and irrigation practices. A pragmatic approach has been used for the Gaza regional model, which translates supporting information from other similar areas to the Gaza situation, and is guided by groundwater modeling (CAMP, 2001; MEnA, 2000).

STUDY AREA, MATERIALS AND METHODS

Location of the study area

The study area is the central wastewater treatment plant of the Gaza Strip which lies to the southwest of Gaza City. The specific location within the plant is the drying lagoons which are being used as filtration basins. Treated wastewater and produced sludge are disposed to open areas a few meters beside the plant itself. The plant is close to less urbanized and agricultural areas. Figure 1 shows the location of the Gaza Strip and a schematic illustration of the wastewater treatment plant as well as the five boreholes. The area has a long history of exposure to wastewater and sludge. Large areas have been used for the disposal of raw sewage effluents and untreated sludge from 1977 up to date. Due to the lack of functional and effective wastewater treatment plants associated with the absence of a wastewater management system, the area of 50 ha was converted to a pure sewage disposal field and receives up to 10,000 m^3/day of untreated or partially treated wastewater.

Sampling and analysis

Sampling considerations

As an independent project, 13 test borings were drilled at specified locations determined by an approved surveyor. The sampling locations were selected according to many justifications fitted to Gaza. The aquifer system, groundwater flow, available geological data, meteorological conditions, natural and anthropogenic factors, etc., are examples of these justifications. Because of the high cost of transportation and analysis, five test borings were chosen for this specific study to represent all locations Figure 1.

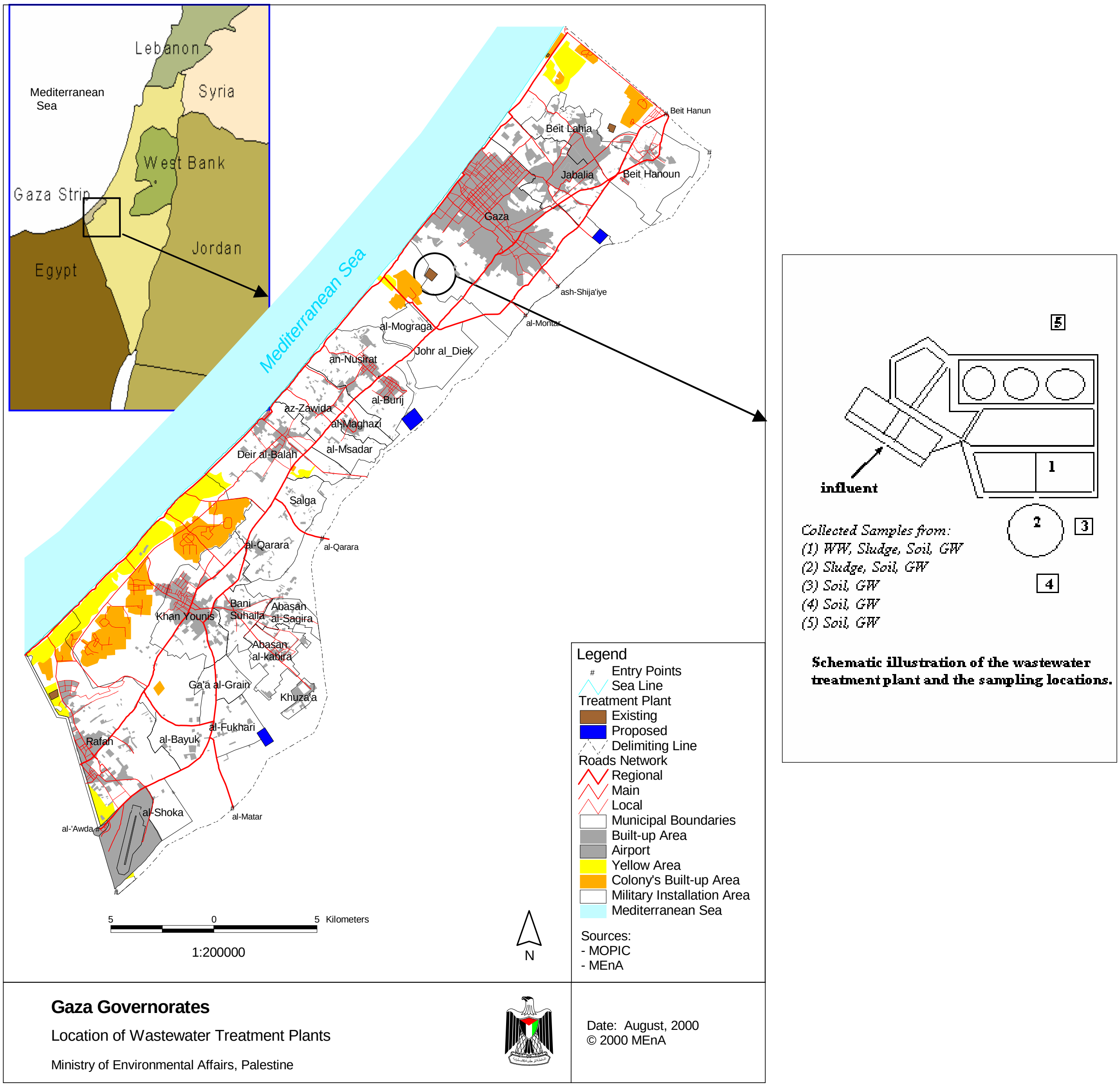
The five boreholes were selected to be: one borehole inside the existing treated wastewater pond, one borehole inside an old sludge drying pond, and three boreholes from the surrounding area. Each borehole is considered as a vertical study area starting from the surface, which is in some cases treated wastewater followed by sludge, then soil and finally groundwater. The ground surface at the site is covered with sand dunes of yellowish, fine sand.

Wastewater samples

The sampling campaign was conducted in the period of 10 October-25 December, 2002. The average depth of wastewater in the sampling site was 30 cm. A series of grab samples (8-10) were taken from two lagoons 1-2 days before the drilling process. The grab samples were combined in a container to form a composite sample. Finally, one liter of the mixture was taken in an acid-washed bottle and transferred to the laboratory, where it was filtered in an acid-washed filter holder and through 0.45 µm pore size Sartorius membrane filters; the first few milliliters were used for rinsing, then discarded, and the filtrate was transferred to clean acid-washed polyethylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v) to pH <2 and stored at 4 ^{o}C until analyses by the inductive coupled plasma mass spectrometer (ICP/MS - Perkin Elmer-Sciex, Elan 6000) were performed. The other part of the wastewater was filtered with no additives and stored at 4 ^{o}C for anion analyses by ion chromatography (IC DIONEX DX-120). Several parameters were measured during the fieldwork: temperature, electric conductivity, and pH; other parameters (settleable solids SS, total suspended solids TSS, total dissolved solids TDS, chemical oxygen demand COD, and biochemical oxygen demand BOD_5) were measured a few hours later according to the American standard methods (APHA, 1995).

Sludge samples

A continuous layer of sludge (15-25 cm depth) was found directly under the wastewater column of one site. The other four samples were collected from the neighboring sludge drying areas. Samples were collected in polyethylene containers. After collection, samples were freeze-dried to complete dryness; then they were ground and homogenized in an agate mortar and sieved through a mesh of 63-mm pore size. About 0.5 to 1.0 grams of the homogenized sample were dissolved in 10.5 ml concentrated hydrochloric acid (37%) and 3.5 ml concentrated nitric acid (65%) in 50 ml retorts. The samples were degassed (12 hours), then heated to 160 °C for 3 h. After cooling to room temperature, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for analysis.



Collected Samples from:
(1) WW, Sludge, Soil, GW
(2) Sludge, Soil, GW
(3) Soil, GW
(4) Soil, GW
(5) Soil, GW

Schematic illustration of the wastewater treatment plant and the sampling locations.

Figure (1) Location of the Study Area.

Elements were analyzed by different instruments; a flame atomic absorption (AAS vario 6-Analytik Jena) for determination of Ca, Cu, K, Li, Mg, and Na; an ICP/OES (VARIAN, VISTA-MPX) for determination of As, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, and Zn; and an energy-dispersive miniprobe multielement analyzer (EMMA-XRF) (Cheburkin and Shotyk, 1996) for determination of Br, Rb, Se, Th, U, Y and Zr. Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of freeze-dried samples (50-100 mg) and Hg pre-concentration on a single gold trap by means of an AMA 254 solid phase Hg-Analyzer (LECO).

Total carbon and sulfur were determined directly in dried samples by using a carbon-sulfur determinator (LECO CS-225); and finally carbonates were measured directly by a carbonate bomb (Müller and Gastner, 1971). The total organic carbon (TOC) was calculated by the subtraction of inorganic carbon from total carbon. Adsorbable organic halogen (AOX) was determined by a Euroglas organic halogen analyzer- The Netherlands according to the DIN 38414 S18 Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Sludge and Sediment (Group S) Determination of AOX (DIN, 1989).

Soil samples

Soil samples were obtained continuously from the five boreholes throughout the drilled depth. Three-inch size split spoon sampling tubes (3" diameter x 24" long) were used to collect the samples. The samples were examined, described, and classified by geologists and geotechnical engineers. Natural beeswax was used to cap the ends of the sample tubes, as requested. The samples were properly labeled and placed in waterproof plastic bags before being placed in wooden boxes. Approximately 0.5 kg of soil was put in polyethylene cups and stored at 4 ^{o}C during transport to laboratories where soil was dried in an oven at 50 ^{o}C until constant weight. Then they were shipped to Germany in plastic sampling bags. The samples were sieved through a 20-µm sieve and ground to a very fine powder by using a sand mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 1-2 grams of the homogenized sample were dissolved with 10.5 ml of concentrated hydrochloric acid (37%) and 3.5 ml of concentrated nitric acid (65%) in 50 ml retorts. The digestion process of the soil samples was the same as the above-mentioned process for sludge samples. Al and Ba were analyzed by inductively coupled plasma optical emission spectroscopy (ICP/OES). AOX was analyzed by the same method as the sludge samples. In order to determine soil mineralogy, a semi-quantitative X-ray Diffraction technique (XR Diffractometer, SIEMENS) (Moore and Reynolds, 1989) was used.

Groundwater samples

Groundwater depth measurements were taken whenever groundwater was encountered in the boreholes, using a water-level indicator instrument. Groundwater samples were collected from the boreholes at the specified depths; they were sampled about one meter below the groundwater surface. Five groundwater samples were collected from the five boreholes. One-liter samples were collected and treated as the wastewater samples above. Several parameters were measured during the fieldwork: temperature, turbidity, electric conductivity, and pH. Elemental analysis was measured in the lab.

Quality control

For quality control, analytical blanks and two standard reference materials with known concentrations of metals were prepared and analyzed using the same procedures and reagents. Precision for the results of soil and sludge samples was estimated using the reproducibility between the duplicates, and a coefficient of variation of less than 5% was found. The accuracy was evaluated using 20 aliquots of two river sediment standard reference materials-RS1 and RS3-Deutsche Industrie Norm (DIN, 1989, 1997). As an independent check of the trace element measurements of the soil and sludge, these were also measured in solid samples using the energy-dispersive miniprobe multielement analyzer (EMMA-XRF). A deviation of less than 5% from the certified values was found. The coefficient of variation for triplicates (2 samples and one standard) was less than 2% for all parameters. For the wastewater and groundwater analysis, standard reference materials 1643c and 1643d were used for the determination of trace elements (NIST, 1991, 1994) and SPS-WW2, wastewater level 2 (SPS, 2002).

RESULTS

Wastewater

Table 1 shows the average values of parameters of the wastewater effluent. The general parameters indicate that the treatment plant was able to remove >92%, >88%, >60% of BOD_5, COD, and both total P and total N, respectively, under the existing treatment facilities. The table shows the metal content of the collected five composite wastewater samples, and these results agree with the findings of a three-year monitoring program conducted by Shomar et al. (2004e).

Table (1) Chemical Characteristics of Wastewater Effluent.

Parameter	Average	SD (σ)
pH	7.7	0.3
Temperature (°C)	26	1.7
Settleable Solids SS (ml/l)	0.1	0.03
Total Dissolved Solids (TDS) mg/l	1536	62
Total Suspended Solids (TSS) mg/l	20	2.6
Chloride (mg/l)	480	50
Fluoride (mg/l)	1.4	0.1
Sulfate (mg/l)	320	26
Total P (mg/l)	9	0.3
NO_3 (mg/l)	20	6.1
COD (mgO_2/l)	89	7.7
BOD_5 (mgO_2/l)	25	1.3
Ag (µg/l)	0.7	0.0
Al (µg/l)	52	2.9
As (µg/l)	8	1.3
Cd (µg/l)	< 0.5	0.1
Co (µg/l)	0.8	0.4
Cr (µg/l)	5	1.0
Cu (µg/l)	7	0.8
Fe (µg/l)	163	3.2
Mn (µg/l)	48	4.2
Ni (µg/l)	6	1.7
Pb (µg/l)	< 2.5	0.2
Zn (µg/l)	42	12

** Average value of each parameter.*

Sludge

In addition to the common metals analyzed in the sludge samples in many parts of the world, an additional eight elements were determined (Table 2). Seven of them had low concentrations and only strontium (Sr) showed considerable amounts in the tested samples. Zinc in the sludge of Gaza (> 2100 mg/kg) exceeds that of all standards of developed and industrialized countries for land application. As a very general parameter, the average AOX in the tested samples reached the mean value of 550 mg Cl/kg.

Table (2) Average Chemical Composition of Five Sludge Samples (n=3).

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
AOX (mg Cl/kg)	610 ± 68	600 ± 55	530 ± 62	510 ± 44	495 ± 52
As (ppm)	5.5 ± 0.8	2.1 ± 0.8	3.5 ± 0.7	5.4 ± 0.8	4.3 ± 0.6
Cr (ppm)	89 ± 6	68 ± 5	89 ± 7	111 ± 6	108 ± 11
C (%)	27 ± 0.7	19 ± 0.5	27 ± 0.8	26 ± 0.8	22 ± 1
Ca (%)	12.7 ± 0.3	9.0 ± 0.2	13.3 ± 1	10.5 ± 0.8	11.5 ± 0.4
Cd (ppm)	2.2 ± 0.8	1.5 ± 0.7	1.7 ± 0.3	2.0 ± 0.1	1.8 ± 0.3
Co (ppm)	3.3 ± 0.3	3.6 ± 0.2	0.9 ± 0.1	2.5 ± 0.2	2.4 ± 0.2
Cr (ppm)	89 ± 7	68 ± 5	89 ± 6	111 ± 11	108 ± 8
Cu (ppm)	304 ± 11	220 ± 8	288 ± 13	286 ± 14	281 ± 12
Fe (%)	1.5 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.5 ± 0.2	1.3 ± 0.1
Hg (ppm)	3.5 ± 0.5	2.6 ± 0.5	4.5 ± 1	3.2 ± 0.6	2.8 ± 0.5
K (ppm)	1836 ± 36	1808 ± 42	1673 ± 40	1810 ± 37	1605 ± 38
Li (ppm)	3.0 ± 0.2	2.5 ± 0.2	2.6 ± 0.2	3.4 ± 0.3	3.2 ± 0.3
Mg (%)	1.1 ± 0.3	0.9 ± 0.2	1.0 ± 0.1	1.0 ± 0.1	0.9 ± 0.1
Mn (ppm)	227 ± 8	188 ± 5	270 ± 7	261 ± 8	273 ± 10
Na (ppm)	9894 ± 26	10312 ± 42	7720 ± 35	3191 ± 22	4359 ± 25
Ni (ppm)	28 ± 5	21 ± 4	24 ± 5	26 ± 6	25 ± 5
Pb (ppm)	154 ± 5	111 ± 6	140 ± 11	156 ± 9	136 ± 8
Rb (ppm)	10.6 ± 0.7	11.5 ± 1	9.0 ± 0.5	9.9 ± 0.8	8.2 ± 1
S (%)	3.0 ± 0.3	2.1 ± 0.4	2.8 ± 0.2	3.1 ± 0.3	2.1 ± 0.1
Se (ppm)	2.6 ± 0.2	2.6 ± 0.2	5.0 ± 0.4	3.2 ± 0.4	3.0 ± 0.5
Sr (ppm)	651 ± 7	540 ± 9	984 ± 15	643 ± 32	730 ± 62
Th (ppm)	3.1 ± 0.2	0.0 ± 0	2.0 ± 0.2	2.4 ± 0.1	0.0 ± 0
U (ppm)	8.8 ± 0.6	5.7 ± 0.5	10.7 ± 1	10.5 ± 2	8.5 ± 0.4
Y (ppm)	7.1 ± 0.4	8.3 ± 0.5	5.8 ± 0.2	6.9 ± 0.3	8.1 ± 0.4
Zn (ppm)	2443 ± 46	1820 ± 66	2230 ± 84	2527 ± 72	2385 ± 78
Zr (ppm)	185 ± 5	164 ± 11	96 ± 9	103 ± 7	98 ± 11

Soil

Due to the large set data obtained from the analysis of 160 soil samples, each having 26 parameters, this section will cover mostly the fifth soil profile which represent the five profiles. The upper 40-50 cm represent a mixture of sludge and fine sand and its color starts from dark black in the surface layer up to very light dark downward. A well-distinguished soil appears from 20 cm depth and more.

The four examples of X-ray diffractograms (Fig. 2) show that the soil mineralogy is mainly composed, in order of abundance, of quartz, calcite, kaolinite, and some feldspars. The soil texture, including the major components of each layer, is shown in Figure 3.

Table (3) Geochemical Characteristics of Sludge Covered Soil Profile under Wastewater Lagoon.

Parameter	**0 cm**	**5 cm**	**10 cm**	**15 cm**	**20 cm**	**25 cm**	**30 cm**	**35 cm**	**40 cm**	**45 cm**	**50 cm**
Org. C (%)	26.1	26.1	23.7	21.6	20.8	20.1	1.6	1.9	1	1.2	0.4
Ca (%)	12.8	10.0	10.1	13.4	12.5	10.0	11.9	1.4	0.59	0.5	0.45
Cu (mg/kg)	237	237	157	120	77	45	18	12.7	5.3	1.3	1.8
Fe (%)	1.3	1.6	1.8	0.4	0.2	0.4	0.3	0.3	0.4	0.2	0.2
Ni (mg/kg)	41	38	34	13	11	6.0	3.2	2.3	2.3	2.2	1.9
Pb (mg/kg)	114	76	58	33	8	3	2.0	0.8	0.6	0.1	0.5
Zn (mg/kg)	2197	1276	999	217	10.7	8	7.2	3.5	2.7	4.8	5.1

Table (4) Geochemical Characteristics of Sludge Covered Soil Profile under Sludge Drying Area.

Parameter	**0 cm**	**5 cm**	**10 cm**	**15 cm**	**20 cm**	**25 cm**	**30 cm**	**35 cm**	**40 cm**	**45 cm**	**50 cm**
Org. C (%)	25.7	25	21	20.2	20	19.2	1.9	2	0.9	1.3	0.5
Ca (%)	12.1	12.8	10.0	13.5	11.5	3.19	2	0.59	0.7	0.5	0.8
Cu (mg/kg)	240	210	180	132	95	52	20	17	6	2	1.2
Fe (%)	1.7	1.5	1.7	0.5	0.3	0.4	0.3	0.4	0.3	0.3	0.2
Ni (mg/kg)	42	39	28	14	10	6.0	3.2	2.3	1.8	2.9	2.5
Pb (mg/kg)	115	82	60	27	11	2.5	1.8	0.9	0.7	0.2	03
Zn (mg/kg)	2005	1700	1102	350	42	22	9	5.2	3.4	2.6	2.5

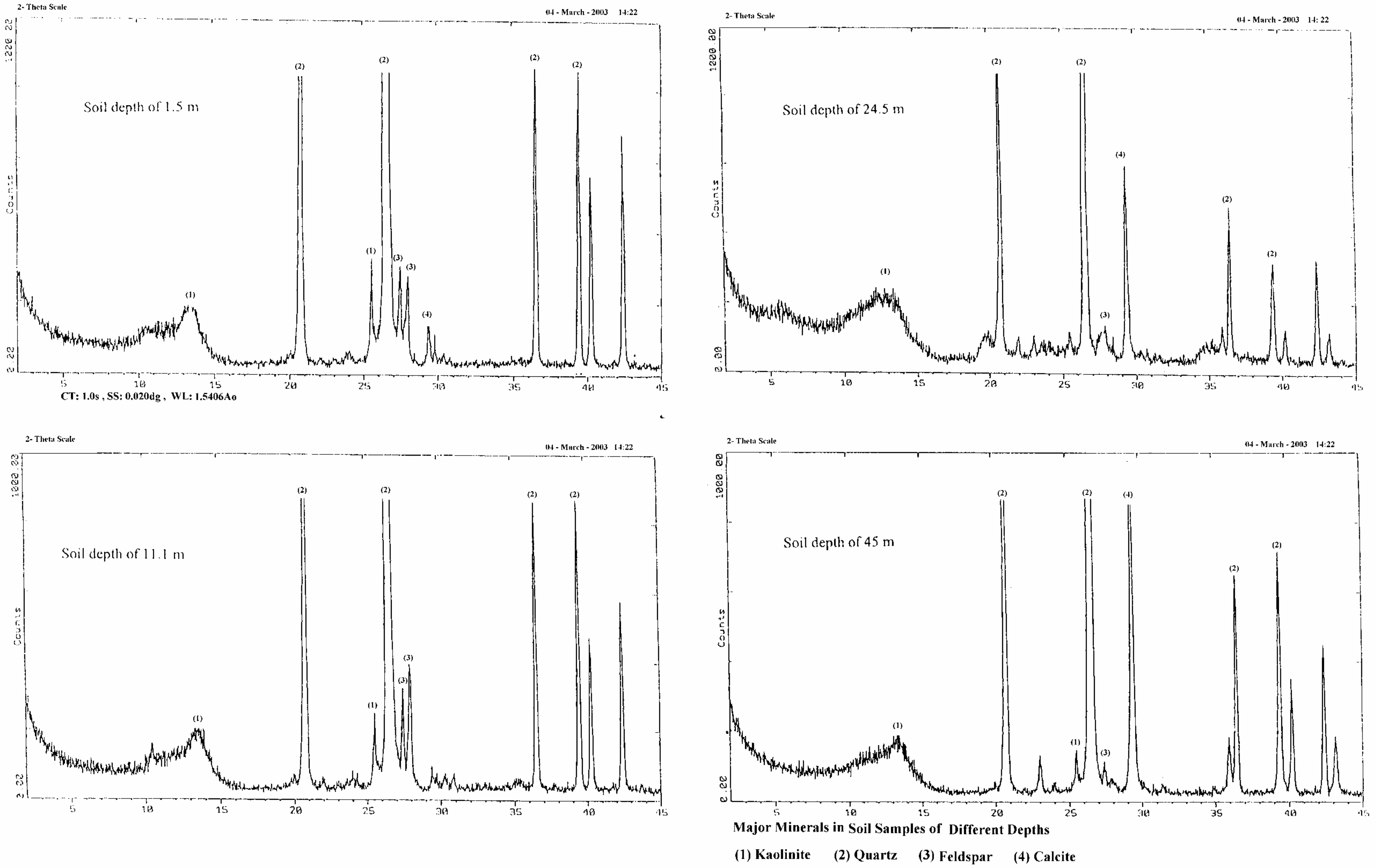


Figure (2) Some Examples of XRD Results of the Fifth Soil Profile.

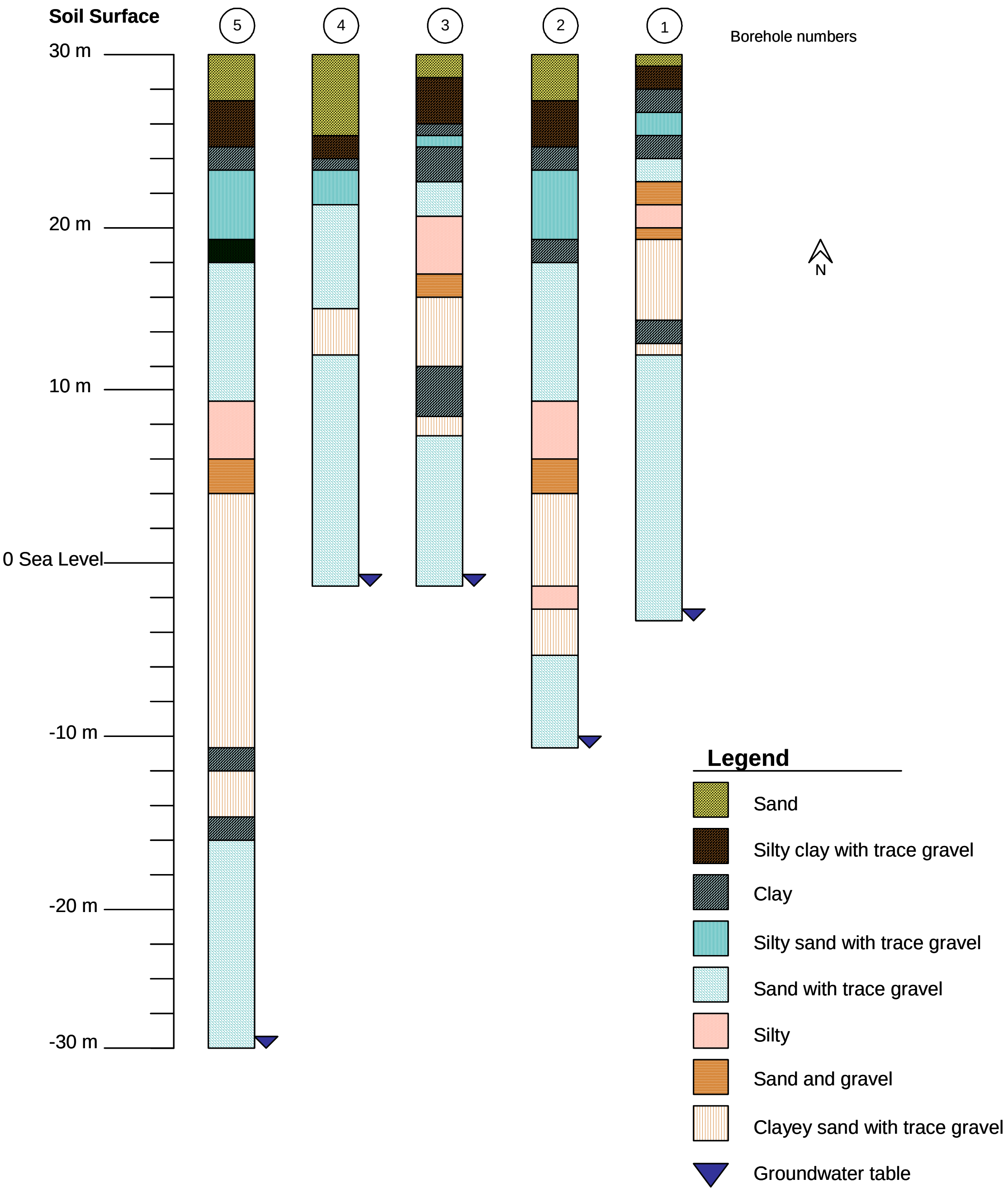


Figure (3) General Geological Features of the Five Soil Profiles.

The soil-wastewater/sludge interaction and the trend of major parameters could be found in two profiles (1 and 2). The first is under the treated wastewater lagoon (Table 3) and the second is under the sludge old drying area (Table 4). Selected depths of soil profile and their metal contents are shown in Table 5 and Figure 4.

The organic content of the soil decreased with depth from 26% organic carbon by weight in the surface sludge to less than 0.05% of 55 m depth, while the AOX in general is very low in the deep layers (less than 5 mg Cl/kg). The soil at the study plot was neutral to basic (pH 7.2-8 in 0.4-60 m), while the upper 40 cm of the sludge-covered soil was acidic (pH 4.8) due to high inputs of nitrate and sulfate loads from wastewater and sludge which increase the acidity through the intensive mineralization and nitrification processes.

Table (5) Chemical Composition of Soil for Selected Depths of the Fifth Profile (Aver.± SD).

Element	**UC***	**LC****	**0.6 m**	**7.5 m**	**24.5 m**	**35 m**	**55 m**
Al (%)	7.74	8.21	0.3 ± 0.1	1.7 ± 0.2	1.0 ± 0.1	0.7 ± 0.1	0.1 ± 0.1
As (mg/kg)	2	1.3	2.8 ± 0.2	2.1 ± 0.3	0.8 ± 0.1	3.6 ± 0.2	4.7 ± 0.4
Ba (mg/kg)	668	568	32 ± 4	79 ± 16	67 ± 11	66 ± 12	12 ± 2
Br (mg/kg)	1.6	0.28	0.0 ± 0	4.3 ± 0.8	1.4 ± 0.1	1.2 ± 0.3	1.0 ± 0.1
C (%)	0.32	0.06	0.9 ± 0.2	2.4 ± 0.4	0.8 ± 0.1	1.6 ± 0.2	1.3 ± 0.1
Ca (%)	2.95	4.86	3.2 ± 0.4	7.4 ± 1	2.2 ± 0.2	4.6 ± 0.8	4.2 ± 0.7
Cd (mg/kg)	0.102	0.101	0.06 ± 0	0.07 ± 0	0.04 ± 0	0.08 ± 0	0.1 ± 0
Co (mg/kg)	11.6	38	2.7 ± 1	9.8 ± 2	6.9 ± 2	4.3 ± 0.4	1.3 ± 0.1
Cr (mg/kg)	35	228	8 ± 1	34 ± 7	11 ± 3	12 ± 3	4 ± 1
Cu (mg/kg)	14.3	37.4	2.5 ± 0.6	26.1 ± 7	8.5 ± 3	3.6 ± 1	4.6 ± 2
Fe (%)	3.1	5.7	0.4 ± 0.1	1.7 ± 0.2	0.8 ± 0.2	0.7 ± 0.1	0.3 ± 0.1
Hg (µg/kg)	56	21	2.0 ± 0.4	2.0 ± 0.2	2.0 ± 0.2	2.0 ± 0.1	1.0 ± 0.1
K (%)	2.86	1.31	0.07 ± 0	0.17 ± 0.1	0.14 ± 0	0.07 ± 0	0.02 ± 0
Li (mg/kg)	22	13	1 ± 0.2	4.8 ± 1	3.9 ± 0.3	2.1 ± 0.2	0.5 ± 0.1
Mg (%)	1.35	3.15	0.1 ± 0.1	0.6 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.1 ± 0
Mn (mg/kg)	527	929	94 ± 11	251 ± 34	219 ± 80	148 ± 47	64 ± 14
Na (%)	2.57	2.12	0.12 ± 0	0.05 ± 0	0.05 ± 0	0.04 ± 0	0.03 ± 0
Ni (mg/kg)	18.6	99	6 ± 0.2	17 ± 4	13 ± 2	7 ± 1	2 ± 1
Pb (mg/kg)	17	12.5	0.8 ± 0.1	2.8 ± 0.3	1.7 ± 0.4	1.1 ± 0.4	0.6 ± 0.2
Rb (mg/kg)	110	41	10 ± 2	20 ± 4	20 ± 5	17 ± 4	7 ± 2
S (%)	0.95	0.41	0.01 ± 0	0.01 ± 0	0.01 ± 0	0.01 ± 0	0.01 ± 0
Sr (mg/kg)	316	352	95 ± 12	133 ± 41	95 ± 24	63 ± 13	77 ± 9
Th (mg/kg)	10.3	6.6	0.0 ± 0	2.5 ± 0.8	0.0 ± 0	2.7 ± 0.7	0.0 ± 0
Y (mg/kg)	20.7	27.2	9 ± 2	21 ± 6	32 ± 8	14 ± 3	8 ± 1
Zn (mg/kg)	52	79	8 ± 2	26 ± 8	26 ± 7	14 ± 4	13 ± 4
Zr (mg/kg)	237	165	342 ± 44	254 ± 51	354 ± 58	188 ± 46	107 ± 28

(*) Upper Crust, and (**) Lower Crust: Turekian and Wedepohl, 1961.

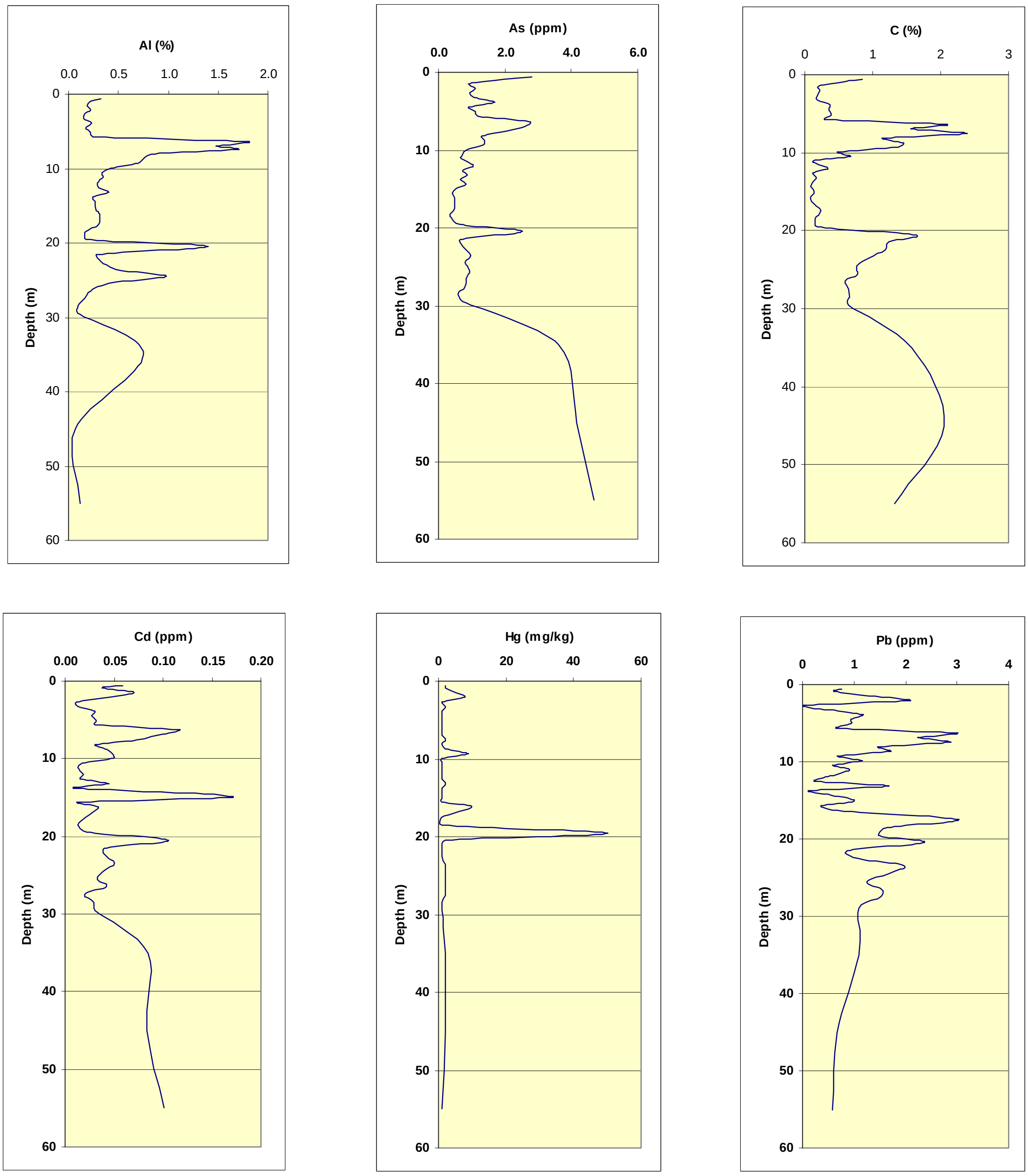


Figure (4) Examples of Element Profiles.

Groundwater

Table 6 shows the concentration of the major anions and cations in the five groundwater samples. The average total dissolved solids (TDS) of groundwater is 1800 mg/l; and major ions of Cl, F, NO_3, SO_4, CO_3, PO_4, Na, Ca, Mg, and K are high. Tested groundwater of the area showed sulfate averages of 190 mg/l (Shomar et al., 2004c). Although it is assumed that fluoride is a natural constitutional of the groundwater of the Gaza Strip (Shomar et al., 2004d), F averages of the tested wells are 1.8 mg/l. The results of the fluoride contents by using IC are consistent with the results of the ISE. Phosphates were below the detection limit of the vanadate molybdate spectrophotometric method. Groundwater is oxygenated and Fe and Mn are in the oxidized soluble forms. The average dissolved oxygen (DO) was 6.7 mgO_2/l. Previous studies of the groundwater quality in the surrounding area revealed that many parameters (EC, TDS, Cl, NO_3, SO_4, F, Ca, Mg, and Na) are affected by seasonal variation; they are 30-60% higher in the summer (Shomar et al., 2004c).

Table (6) Groundwater Quality of Five Boreholes (Average ± SD σ).

Parameter	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**WHO***	**LD** (µg/l)**
Temp. (^{o}C)	22 ± 0.5	22 ± 0.6	23 ± 0.4	24 ± 0.7	21 ± 0.4		
pH	6.7 ± 0.2	6.8 ± 0.3	7.1 ± 0.2	6.9 ± 0.2	6.7 ± 0.2	6.5-8.5	
DO mgO_2/l	6.4 ± 0.2	6.3 ± 0.2	6.9 ± 0.2	6.7 ± 0.3	7.1 ± 0.4		
EC mS/cm	2.65 ± 0.1	2.59 ± 0.2	2.6 ± 0.1	2.61 ± 0.2	2.65 ± 0.2		
Cl (mg/l)	560 ± 32	590 ± 35	505 ± 28	602 ± 34	595 ± 33	250	
NO_3 (mg/l)	77 ± 7	85 ± 11	76 ± 9	89 ± 14	64 ± 7	50	
SO_4 (mg/l)	135 ± 14	140 ± 17	160 ± 16	110 ± 9	123 ± 11	250	
F (mg/l)	1.7 ± 0.1	1.8 ± 0.2	1.7 ± 0.1	2.0 ± 0.1	1.9 ± 0.2	1.5	
PO_4 (mg/l)	< 1 ± 0.0	< 1 ± 0.1	< 1 ± 0.1	< 1 ± 0	< 1 ± 0.1		
Na (mg/l)	320 ± 22	201 ± 24	370 ± 29	198 ± 18	231 ± 27	200	
Mg (mg/l)	90 ± 14	87 ± 9	110 ± 7	106 ± 10	119 ± 10		
Ca (mg/l)	128 ± 19	140 ± 20	133 ± 22	122 ± 19	143 ± 23		
Ag (µg/l)	< 0.5 ± 0.1	< 0.5 ± 0.1	< 0.5 ± 0	< 0.5 ± 0.1	< 0.5 ± 0		0.5
Al (µg/l)	28 ± 4	34 ± 7	27 ± 6	< 25 ± 4	29 ± 7	200	25
As (µg/l)	5 ± 1	10 ± 1	9 ± 2	7 ± 1	7 ± 2	10	2.5
Cd (µg/l)	0.7 ± 0.1	< 0.5 ± 0	< 0.5 ± 0.1	< 0.5 ± 0	< 0.5 ± 0	3	0.5
Co (µg/l)	<0.3 ± 0	<0.3 ± 0	<0.3 ± 0.1	<0.3 ± 0.1	<0.3 ± 0		0.3
Cr (µg/l)	11 ± 2	29 ± 3	45 ± 3	23 ± 2	30 ± 3	50	2.5
Cu (µg/l)	< 1 ± 0.1	9 ± 1	3 ± 0.5	4 ± 0.2	2 ± 0.1	2000	1
Fe (µg/l)	26 ± 4	1855 ± 245	28 ± 4	16 ± 2	26 ± 3	300	
Mn (µg/l)	< 1 ± 0.1	15 ± 3	< 1 ± 0.1	< 1 ± 0	< 1 ± 0.1	500	1
Ni (µg/l)	3 ± 0.2	6 ± 0.2	4 ± 0.1	3 ± 0.4	2 ± 0.2	20	0.5
Pb (µg/l)	< 2. 5 ± 0.2	2.6 ± 0.2	< 2.5 ± 0.3	< 2.5 ± 0.3	< 2.5 ± 0.5	10	2.5
Zn (µg/l)	< 10 ± 2	12 ± 2	< 10 ± 1	12 ± 2	23 ± 3	3000	10

** WHO: World Health Organization Guidelines.*
*** LD: Limit of Detection by the ICP/MS in (µg/l).*

The results for the metals indicate that all of them are within the WHO drinking water standards. Arsenic and iron for borehole number 2 are high; As is the same as the tentative new WHO standard (10 µg/l), while Fe is 1855 µg/l which is about 6 times higher than the WHO standard (300 µg/l).

DISCUSSION

The wastewater treatment plant was able to remove >92%, >88%, >60% of BOD_5, COD, and both total P and total N, respectively. This indicates that the majority of the metals have been transferred from the wastewater to the sewage sludge where Zn, Pb, Cu, and Cr in the sludge were 2100, 125, 240, and 75 mg/kg, respectively. The new results agree with the findings of Shomar et al., (2004e), however, 20% may be lost in the treated effluent, depending on the solubility, and this may be as high as 40-60% for the most soluble metal, Ni (Scancar et al., 2000). The average of Zn removal in the treatment process was 55%; this ratio finds its way to the sludge and this may explain the high contents of Zn in the sludge (>2100 mg/kg).

The most affected zone by wastewater and sludge is the upper 40-50 cm of the soil profile and the metal content decreased with depth. Element mobility sequence was Ni>Ca>Cu>>Fe where the concentrations in the upper 5 cm were 40 mg/kg, 10%, 240 mg/kg, and 1.5% and in the lower 40 cm were 2, 0.5, 5, and 0.3, respectively. This result agrees with that of Legret (1993) and Cornu (2001). Nickel is the most soluble metal in sludge, and thus the most mobile (Henry and Harrison, 1992). The general trend of the total Ni concentrations in each soil profile was a slight increase with depth. The distribution of Ni in a soil profile is related to the clay fractions; the higher the clay content, the greater the accumulation of Ni. The percent clay in the soil profiles increased due to the claylenses in the 6.3 and 9.3 m depth, as did the total Ni concentrations. This could be supported by the explanation of the EPA (1995) that stated that Ni tends to accumulate in arid and semiarid soils as well. The sludge-covered soils were exposed to rainfall over the course of the study which may have resulted in the leaching of Ni to the lower depths. It has been shown that soils with higher pHs have higher potentials for fixing Ni in less soluble forms than in soils with lower pHs (Abdel-Sabour, 1991). A mean comparison of total trace element concentrations in the upper 40 cm depth indicated that the uncovered soil had significantly lower Cu and Ni concentrations than the sludge-covered soils. In addition, the comparison of means from each soil profile indicated there were no significant differences among the mean of most tested elements.

In soil, Ca is the most mobile, while Fe is the least mobile element (Sparks, 2002). The pH of the upper 40 cm for the sludge-covered soils increased slightly with depth. The results of the upper 40 cm of the soil profile were anticipated as the sludges that covered the soil surface contained low concentrations of the tested elements. The trend showed a definite increase in Cu within the upper 40 cm of all sludge-covered soils. This could be explained by the fact that the organic compounds of the sludge increased the solubility of Cu (Kabata-Pendias and Pendias, 1992). Total soil Cu concentrations were somewhat variable in the individual profiles.

The solubility, mobility and concentration of Pb and Zn are controlled by several mechanisms like organic matter, pH and soil structure (Sims and Patrick, 1978; Pepper et al., 1983; Milner and Barker, 1989). The total Pb concentrations of the soil were basically uniform throughout the soil profiles. The heavy precipitation, in combination with the acidic environment of the upper sludge layer of pH 4.8 and the high contents of organic matter (26%) enhances the solubility and leaching processes of Pb from sludge. Pb concentration is high in the upper layers and decreases with depth. Even although the pH of the sandy layers was high, the concentrations of Pb and Zn were low due to the lack of organic matter and the effect of the downward water flow. Pb reached its minimum concentration (2.7 mg/kg) in the sandy soil at a depth of 40 cm. The leached Pb accumulated in the deep layers of clay at a depth of 5.5 and 25 m, where its concentrations are 4.2 and 3.6 mg/kg, respectively. The Pb profile in soil is similar to the Fe profile as well as to the organic matter profile. In comparison with Zn, organic matter is relatively more important in adsorbing Pb, but clay minerals are relatively more important in adsorbing Zn. Zn showed similar trend as Pb.

It was found that the soil metal content was affected by soil structure. Clay layers showed higher contents of major elements than soil layers. In clay layers Cd, Cr, Fe, Mn, Ni, Pb, and Zn were 0.1 mg/kg, 23 mg/kg, 6%, 930 mg/kg, 100 mg/kg, 13 mg/kg, and 80 mg/kg, respectively while they were 0.04, 10, 0.7, 70, 8, 1, and 13, respectively in other soil structures. Generally speaking, a trend of increase of most elements was observed from fine sand, sandstone, loose sandstone, sand clay, and clay. This conclusion agrees with the findings of several studies (Premovic et al., 2001; Navas and Machin, 2002; Pearson et al., 2002; USGS, 2004). Except for the upper half-meter of the soil profile which is directly affected by sludge, the lateral distribution of elements was dependent on the physicochemical characteristics of the soil and not on depth.

The total contents of studied elements indicate that the concentrations of Zn, Mn, Cu, Fe, and partly As and Pb correlate with the clay content in the individual soil profile. The total content of Mn, Fe, Zn, and Cu in the individual soil horizons is proportional to their clay content (Martinek et al., 1999). The trend showed that the layer of 6.3-9.3 m deep had high contents of Al, Ca, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Y, Zn, and Zr, and to a lesser extent of Cd, Co, and Hg. Also, the soil samples of 35-55 m depth showed an increase in the contents of most elements. The Al figure shows the same trend of Ba, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Sr, Th, Y, and Zn. The figure of Cd shows the trend of Rb. The Pb figure shows the same trend of S and Zr.

There is no significant difference between the mineralogy of the different depths of the fifth profile. Although the five boreholes were dug in around a 1 km^2 area, the layers were not continuous and this could be explained by the irregular deposition, sedimentation, and weathering rates. The stability rate under weathering conditions in the study area is gravel>sand>clay, where the clay layer is impermeable.

However, the results of groundwater revealed that it is highly polluted and all major parameters exceed regional and international standards, it was hard to judge that the major source of pollution is the leaching of these pollutants from the upper surface to the aquifer.

It is believed that the high concentrations of nitrate (>75 mg/l) in the area is caused by leaching of nitrate from wastewater to the aquifer (CAMP, 2001; Shomar et al., 2004e). The results for the metals indicate that all of them are within the WHO drinking water standards (1998a). Arsenic and iron for borehole number 2 are high; As is the same as the tentative new WHO standard (10 µg/l), while Fe is 1855 µg/l which is about 6 times higher than the WHO standard (300 µg/l).

CONCLUSIONS

A very good agreement was observed between soil physical characteristics and the vertical distribution of metals. The trend of most elements was: clay>sandclay>loose sandstone>sandstone>fine sand. The trend showed that the clay layer of 6-9 m depth had high contents of Al, Ca, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, Th, Y, Zn, and Zr, and to a lesser extent of Cd, Co, and Hg.

Except for the upper half-meter of the soil profile which is directly affected by waster and sludge, the lateral distribution of elements was dependent on the physical characteristics of the soil and not on the depth.

The treated wastewater is a promising water resource for agriculture, and regular monitoring systems on soil, crops and groundwater should be adopted. Sludges, on the other hand, have high Zn (>2000 mg/kg) and AOX (>500mg Cl/kg) concentrations, which exceed the standards of all industrialized countries for land application.

Although the groundwater samples were collected from the aquifer below the wastewater treatment plant, no anomalous concentrations were found with respect to metals. However, several studies showed that elevated salinity, nitrate, chloride, and sulfate are believed to be a result of both anthropogenic and natural sources.

CHAPTER FIVE

Seasonal variations of chemical composition of water and bottom sediments in the wetland of Wadi Gaza, Gaza Strip (*)

ABSTRACT

Water and sediment samples were collected from 18 sampling stations in Wadi Gaza for two successive years in order to: (1) Establish a baseline condition of the geochemistry of surface water and sediments; (2) assess the impact of seasonal variation on distribution of heavy metals and major ions; and (3) identify possible natural and anthropogenic sources of pollution. The heavy metal concentrations in the sediments of the lake (downstream) were higher than those of the eastern eight stations (upstream) where the water was shallower. The discharge of olive oil mill wastewater was recorded in the Ca, Na, Mg, K and P concentrations in sediments of one of the sampling stations.

Water in shallower areas showed greater temporal variation than deeper areas. Several elements (P, Fe, Mn and As) showed the greatest temporal variability. For example, in the winter rainy season these elements decreased 2-10 times compared to their values in summer. Moreover, Ca, Na, Cl, PO_4, and NO_3 decreased 3, 3, 5, 2, 4 times, respectively. Some of the trace metals were more abundant in these waters compared to the domestic wastewaters of the study area. The averages of Cd and Co were 6 and 43 µg/l, respectively and they were 50 times higher than the domestic wastewater results.

Key words: Heavy metals, Seasonal variation, Wadi Gaza, Water and sediment quality.

(*) *The study was published in the Journal of Wetlands Ecology and Management as:*

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INTRODUCTION

The Gaza Strip is one of the most densely populated areas in the world (2638 People/km^2; PCBS, 2000). With limited and deteriorated resources, it has already started to suffer the outcomes of environmental quality deterioration. The shortage and pollution of resources, coupled with high population growth and insufficient job opportunities have created many environmental hazards. The shortage of water and the deterioration of water quality constitute a limiting factor in the economic development of Palestine (MEnA, 2000). Because of these problems, the Wadi Gaza is under threat (MEnA, 2000). Moreover, the Wadi is closed from both upper (inlet) and lower (outlet) streams. There is urgent need to obtain background geochemical data for this site, as no data are currently available.

The capacity of sediment to accumulate contaminants makes them one of the most important tools to assess environmental impact on aquatic ecosystems (Silva and Rezende, 2002). In fact, lake sediments can serve as an information archive of environmental changes through time (Haworth and Lund, 1984). Chemical speciation studies have shown that heavy metals display different degrees of affinity for either organic or inorganic compounds and that this is an important factor influencing metal distribution (Lu et al., 1983). In aquatic ecosystems research, the role of sediments in the cycling of chemical elements has often been underestimated, and the exchange of elements (especially nutrients) between sediment and water is a crucial topic (Alloway and Ayres, 1997; Kelderman et al., 2000). Seasonal variation may also affect the exchange process directly and indirectly. Anaerobic conditions in summer period were shown to cause a rapid phosphorus release from the sediment to the hypolimion of the water body. This mechanism is still one of the key examples of sediment-water interaction (Kelderman, 1985). Many factors affect the sediment-water exchange of nutrients such as sediment type and grain size, aerobic and anaerobic conditions, temperature and pH (Rippey, 1977; Holdren and Armstrong, 1980; Nixon et al., 1980; Kelderman, 1996).

The main goal of this paper was to establish a baseline study of water and sediment quality of the Wadi Gaza. A secondary objective was to identify the extent to which the relevant water and sediment quality parameters vary seasonally.

MATERIALS AND METHODS

The study area

Wadi Gaza* is the only major watercourse in the Gaza Strip (Fig.1). Its catchment covers 3,500 km^2 most of which is in the Israeli territory, with only the last 7 km of its course in the Gaza Strip (MEnA, 2002a). The Gaza section, which lies some 7-8 km south of Gaza City, is a sandy valley 20-50 m wide, with steep cliffs 6-8 m high. The river flow has eroded the Wadi banks, expanding to a permanent, brackish, water body several hundred meters wide (forming a lake) shortly before it reaches the Mediterranean Sea. No data are available on flood-flow frequency, height or volume; yet it is evident that occasional or regular flash floods sweep down the Wadi bed, although their frequency may be reduced by the suspected presence of small dams, or diversion schemes, in the catchment.

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* *The part of the Wadi located in the Gaza Strip.*

The study area is a part of the coastal zone of the Gaza Strip and the hydrogeology of the coastal aquifer consists of one sedimentary basin, the post-Eocene marine clay (Saqiya), which fills the bottom of the aquifer. Wadi Gaza as well as the whole Gaza Strip area is located in the transitional zone between the temperate Mediterranean climate to the East and North and the arid desert climate of the Negav and Sinai deserts to the East and South. As a result, the Wadi Gaza area has a characteristically semi-arid climate. There are two well defined seasons: the wet season starting in October and extending into April, and the dry season from May to September.

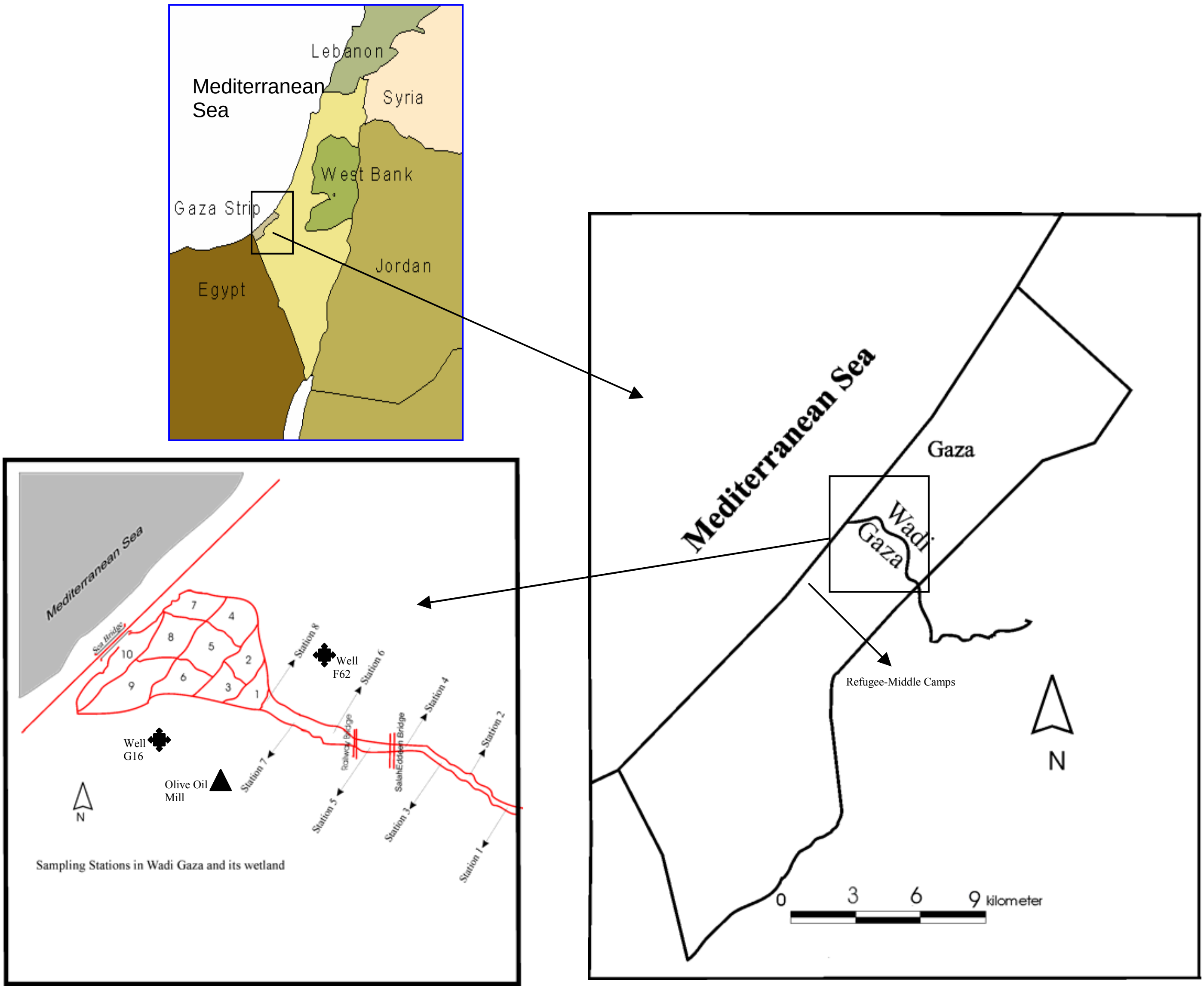


Fig. 1. Location of the Wadi Gaza and schematic illustration of the sampling stations.

The average daily mean temperature ranges from 25 °C in summer to 13 °C in winter, with the average daily maximum temperature ranges from 29 °C to 17 °C, and the minimum temperature range from 21 °C to 9 °C in the summer and winter respectively. The daily relative humidity fluctuates between 65% in the daytime and 85% at night in the summer and between 60% and 80% respectively in the winter. The mean annual solar radiation is 2200 J/cm^2/day. There is a significant variation in the wind speed during the daytime, and the average maximum wind speed velocity is about 3.9 m/s. Moreover, storms have been observed in winter with a maximum wind speed of about 18 m/s. Peak months of rainfall are December and January; the average annual rainfall is 335 mm/y (26-year average). There is a constant flow of untreated domestic sewage water and agricultural runoff into the Wadi from the Refugee–Middle Camps with the main outlet at the southern bank of the Wadi under Salahedden Bridge (Fig. 1). This maintains a trickle of water in the Wadi bed, and feeds the permanent stagnant pool that covers several hectares at the mouth of Wadi Gaza, hence maintaining an extensive water body during the dry season (CAMP, 2001). Fish are known to occur in this pool, although it is dominated by dense algal growth in summer season. No surface water quality data are available, but several wells around the Wadi appear to have unacceptable levels of bacterial contamination, indicating that the pollution is extending to the groundwater in this area (MEnA, 2002a). Three bridges cross the Wadi (two roads and one rail) and numerous dry season tracks criss-cross the Wadi bed where it widens near the refugee camps. At the southern side of the Wadi there is a three stage olive mill which disposes the wastewater and the marc directly to the Wadi. On either side of the Wadi, farmland extends with olives, vines, fruits and vegetables, some of which are probably flooded during major storm events. At the eastern road bridge, farmers dam the river in summer using earth, and pump the water for irrigation; this water is affected by algal blooms and has a bright green color. The vegetation in the Wadi is dominated by *Tamari*x growing on the dunes and sand deposits in and around the Wadi bed. The wetter areas have stands of *Typha* which also fringe the water body near the outlet to the sea (Issac et al., 1997). Around 125 hectares of saltmarshes recorded in the Gaza Environmental Profile of 1994 have disappeared following construction of the new bridge at the Wadi Gaza outflow in 1996. This has disrupted the outlet, affected windblown sand deposition, improved access to the public and generally modified the ecology and geomorphology of Wadi Gaza estuary. Local staff reports indicated that the foundations of the bridge have also blocked the river course and therefore raised the level of the pond. While this may be the case, it is evident that sand accumulation, either brought down by the Wadi Gaza in recent floods, or deposited during sea storm events is another proximate cause of the blockage (MEnA, 2002b). During westerly storms, seawater may be pushed over the sand barrier into the Wadi, maintaining brackish conditions in the downstream part of the system.

The sampling and analysis

The study area (Fig. 1) is divided into nine parts, each about 1-km long, numbered from east to west (K1 to K7). The eighth part (En 8) represents the entrance of the Wadi to the lake and the ninth is the lake. The lake is divided into 10 areas (W1 to W10). During the sampling period, the water depth varied between 0.4 and 1.5 m due to change in the total wastewater discharged to the Wadi; the topographic depression of wetland has an average depth of 1.8 m. The two sampling campaigns were conducted at the end of summer dry season 2001 and at the end of winter rainy season 2002.

Water samples

A total of 17 composite water samples were collected in late summer (November, 2001) and 18 in late winter (April, 2002). Water samples were collected from the six eastern parts (Stations 2-7): the first Station was dry in summer, and another sample from Station 8 which represents the entrance of the Wadi to the lake. Ten water samples were collected from the lake. One-liter samples were collected, then divided into two subsamples, the first (500 ml) was filtered in acid-washed filter holder and through 0.45 µm pore size membrane filters, the first few milliliters were used to rinse then they were discarded, and the filtrate was transferred to clean acid-washed polyetheylene bottles and acidified by concentrated nitric acid (Ultrapur, Merck, v/v), and stored at 4 ^{o}C until analyses of total metal contents by ICP/MS (Perkin Elmer-Sciex, Elan 6000) were performed; the other part of water was filtered with no additives and stored at 4 ^{o}C for anion analyses by Ion Chromatography (IC). Several parameters were measured in the water samples during the fieldwork: temperature, turbidity, electric conductivity and pH, other parameters were measured in the lab. As excessive fluoride concentrations are known to be problematic in this area, fluorides were measured also, using Ion Selective Electrode (ISE) according to the American standard methods (APHA, 1995). One wastewater composite sample was collected from the open canal directly before entering the Wadi and two groundwater samples were collected from the wells F62 and G16 which are located 50-100 m away from the Wadi.

Sediment samples

Thirty six sediment samples were collected from the same stations in the two sampling campaigns. They were collected using a stainless steel dredge; approximately 0.5 kg was put in polyethylene cups and stored at 4 ^{o}C during its transport to laboratories. Sediments were sieved through a 20-µm sieve with deionized water, and then were dried in an oven at 50 ^{o}C until constant weight. Samples were ground in an agate mortar. Approximately 1-2 grams of the homogenized sample were dissolved with 10.5 ml of concentrated hydrochloric acid (37% p.a.) and 3.5 ml of concentrated nitric acid (65% p.a.) in 50 ml retorts. The samples were allowed to degas (12 hours). Then all samples were heated to 160 °C on a sand bath until complete extraction (3 hours). After cooling, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for analysis. Trace metals were analyzed using a Flame Atomic Absorption (AAS vario 6- Analytik Jena). The distribution of phosphorus as (P_2O_5) was measured for all sampling stations (APHA, 1995). Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of freeze dried samples (50-100 mg) and Hg pre-concentration on a single gold trap by means of an AMA 254 solid phase Hg-Analyzer (LECO). Total carbon and sulfur were determined directly in dried samples by using a Carbon-Sulfur Determinator (Leco CS-225). Carbonates were measured directly by a carbonate bomb (Müller & Gastner, 1971).

Quality control

For quality control, analytical blanks and two samples with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents (Avila-Perez et al., 1999). For the surface water, groundwater and wastewater analyses, Standard Reference Materials 1643c and 1643d were used for the determination of trace elements (National Institute of Standards and Technology NIST, Gaithersburg, 1991 and 1994) and SPS-WW2, Wastewater Level 2 (SPS, 2002).

Precision was estimated evaluating the reproducibility between the duplicates and a coefficient variation of lower than 5% was found. The accuracy was evaluated by two River Sediment Standard Reference Materials-RS1 and RS3-Deutsche Industrie Norm (DIN, 1997, 1989). As an independent check on the trace element measurements of the sediments, these were also measured in solid samples using the Energy-dispersive Miniprobe Multielement Analyzer EMMA-X-Ray Fluorescence Spectrometry (Cheburkin and Shotyk, 1996).
The EMMA was calibrated and standardized for trace elements in sediments using a variety of certified, standard reference materials. These materials were used in the AAS measurements. A rigorous quality control program was implemented to check the results obtained from the two methods (AAS and EMMA). From the statistical point of view, a simple comparison (in percentage) was calculated between the results for the same parameter of the two methods.

RESULTS AND DISCUSSION

Many parameters were not detected in any of the water samples, while other parameters (Hg and Cd) in the sediments were found to be less than the background. Consequently data from these elements are not presented in figures 2 and 4.

Water Quality

Table 1 shows the results of all water samples from all stations in summer and winter and Figure 2 indicates the trend of each parameter along the Wadi.

Temperature, pH, Electric Conductivity and Dissolved Oxygen

Both Table 1 and Figure 2 show the seasonal variation of water temperature, pH, DO and EC. The latter has the same trend of Cl. The rainy winter season reduced EC and Cl by diluting the waters of the Wadi.

Major ions

The average total dissolved solids (TDS) in groundwater, wastewater and Wadi's water was 1800 mg/l and major ions of Cl, F, NO_3, SO_4, CO_3, PO_4, Na, Ca, Mg, K were higher than their concentrations in several surface water bodies in the world (Song and Müller, 1999). The western stations of the wetland are exposed to the sea waves especially in summer and this resulted in the high concentrations of Cl, Na, Ca, Mg, SO_4 in area 10 of the lake.

In the winter, the concentrations of these ions were influenced by rainwater and wastewater; while in summer their concentrations were influenced only by wastewater. In the winter, rainwater inputs decreased NO_3 concentrations; moreover the lake was eutrophic in summer and not in winter. Groundwater concentrations of sulfate averaged between 240 and 190 mg/l in summer and winter, respectively and SO_4 contents were not affected by seasonal variation (Fig. 2c). Although it was assumed that fluoride is a natural constitute of the groundwater of the Gaza Strip (Shomar et al., 2004d), F decreased to the half in winter. The results of fluoride analysis using IC were consistent with the results of the ISE and only few samples showed a difference of around 5%. Phosphates in the same figure fluctuated along the Wadi due to the different factors affecting the existence of phosphate in the river. Phosphate contents in the groundwater of the area were very low, while they were much higher in domestic wastewater (25 mgPO_4/l).

Table (1) Water Quality of Wadi Gaza.

	Summer, November 2001				Winter, April 2002				Fresh-water*	Domestic Wastewater**	LD*** (µg/l)
	Max	Min	Mean	σ	Max	Min	Mean	σ			
Temp. (^oC)	24	21	23	0.8	17	15	16	0.7		25.5	
pH	9	6.5	7.6	0.5	8.6	8	8.3	0.2		7.5	
DO mgO_2/l	7	3.9	5.3	0.8	9.6	4.3	8.4	1.3			
EC mS/cm	4.8	2.9	4.2	0.8	2.8	1.7	2.18	0.3		3	
Cl (mg/l)	1142	450	924	296	700	320	478	107		650	
NO_3 (mg/l)	21	2	8	5.3	31	17	22.7	4.2	0. 22		
SO_4 (mg/l)	2536	14	236	614	305	80	184	82	11.1		
F (mg/l)	31	1	4.4	7.9	3.2	0.8	1.8	0.6	0.1	1.2	
PO_4 (mg/l)	85	5	49	19.2	42	12	24.7	11.4	0.06	25	
Na (mg/l)	8233	19	678	2015	160	102	124	15.9	6	380	
Mg (mg/l)	303	53	89	60.4	95	42	65.7	15.9	4	36	
Ca (mg/l)	348	68	136	62.8	124	67	102	16.8	15	43	
Fe (µg/l)	776	192	382	174.1	6600	223	909	1666	500	200	15
Zn (µg/l)	206	1	82	45.1	1560	13.6	148	408	15	100	10
Cu (µg/l)	10	1	4	2.9	123	5.5	16.4	30	3	6	1
Mn (µg/l)	580	320	423	64.9	385	38.3	266	85	8	300	1
As (µg/l)	9.4	0.5	1.7	2.1	27.6	7.6	12.7	4.6	0. 5	0.4	5
Pb (µg/l)	30	1	12	10	135	5.1	40.8	63	3	2	2.5
Cr (µg/l)	139	3	65	38.3	130	4.6	20.6	34	1	7	2.5
Cd (µg/l)	12	1	6	3.4	3.4	0.5	1.6	1.3	0.1	0.5	0.5
Co (µg/l)	70	15	43	19.6	8.1	1.1	2.3	1.7	0.2	0.3	0.3

** Elemental composition of freshwater (Bowen, 1979).*

*** Elemental composition of domestic wastewater discharged to the Wadi.*

**** LD: Limit of Detection by the ICP/MS in (µg/l).*

Fe and Mn

Water of Wadi Gaza was oxygenated and the Fe and Mn were in the oxidized soluble forms. The measurement of DO of water samples collected from Wadi Gaza showed an average of 9.6 mgO_2/l, keeping in mind that the sampling program was carried out under windy conditions in winter. Groundwater wells in the same area had lower Fe and Mn contents than the Wadi Gaza samples. Figure 2e shows stability of Mn concentrations in the eastern stations of the Wadi, while there was a gradual increase of Mn in the lake from east to west. Fe, on the other hand, decreased from east to west, remained constant in 8 stations of the wetland, and only Station 6 had higher Fe compared with other stations.

Trace elements (Zn, As, Pb, Cr, Co, Cd, and Cu)

These elements come to the Wadi from the wastewater and generally were high in summer and low in winter. Groundwater samples of wells F62 and G16 have considerable amounts of these elements (Fig. 3). The impact of seasonal variation was recorded for As and Cd and they showed opposite behavior, while Pb, Co, and Cu were not significantly affected.

Human inputs in the Wadi Gaza

Figure 3 shows the comparison between wastewater, water of sampling stations 7 and area 3 of the lake and groundwater of the two wells nearby. Untreated wastewater is directly discharged to the Wadi and has high amounts of microorganisms, which during summer increase the biodegradation activity, reduce DO and pH, and affect the redox processes of Fe, Mn, As and P. In summer, wastewaters also expressed an increase in NO_3, SO_4, F, Cu, Al, Ni, Zn, Pb, Cr and Cd concentrations in Wadi Gaza. Some industrial wastes of detergents and fertilizers increase P contents, while metallic wastes and construction materials in the area increase Ca, Na, Mg, Fe and Mn concentrations. The three stage olive oil extraction mill generates oil and two by-products: wastewater and marc (solid waste formed by olive stone and pulp wastes). The amount of waste generated ranges between 0.5 and 1.4 l/kg of processed olive. The wastes of the olive oil mill reduced the pH of surface water in summer and increased the Na, Mg, Ca and P concentrations in station 7. The groundwater in the area showed high amounts of Cl and NO_3, especially in summer. Well F62 had 989 mg Cl/l and 117 mg NO_3/l and well G16 had 890 and 110 mg/l of the same anions.

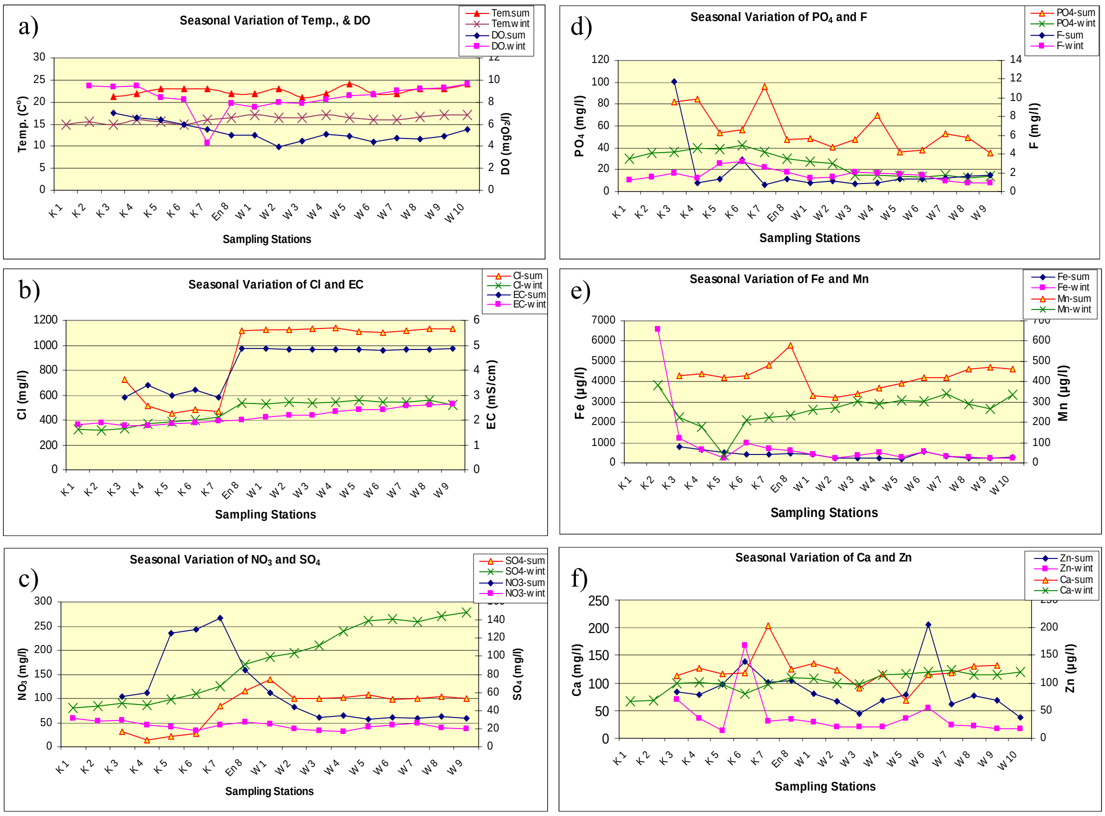
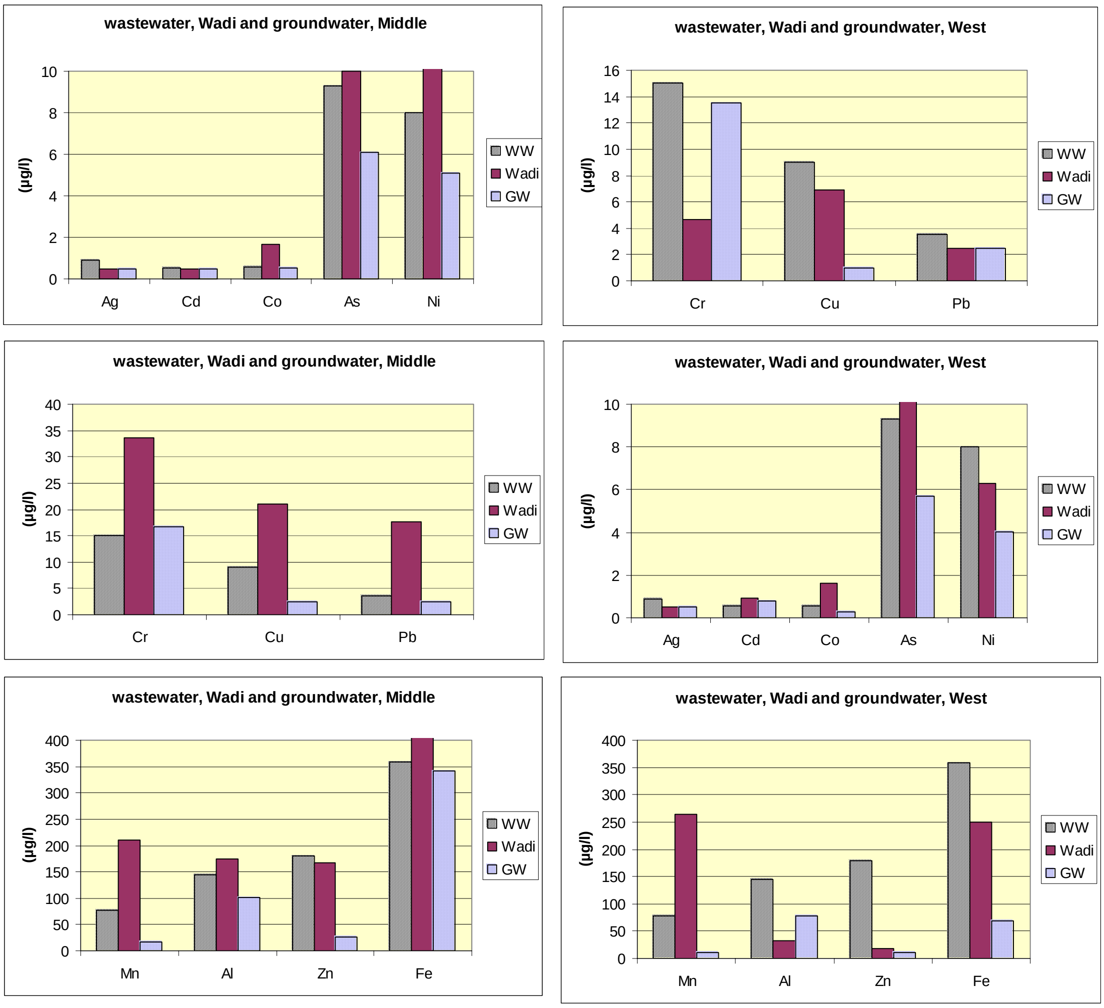


Fig. 2. (a) Temp., and DO, (b) Cl and EC, (c) NO_3 and SO_4, (d) PO_4 and F, (e) Fe and Mn , (f) Ca and Zn in water samples of the Wadi Gaza.

Sediment metal concentration

The coefficient of variation for two independently prepared aliquots of the same sample was less than 2% for all parameters. The agreement between the certified and experimentally established concentrations in Standard Reference Materials was less than 2% for all parameters except for Cd which was more than 6%. The difference between the Standard Reference Materials (RS1 and RS3) supplied by DIN was used to estimate the accuracy of the method analyzed. The difference rates (%) were: $CaCO_3$=0.9, Mg=0.44, Ca=1.05, Cu=0.7, Zn=0.72, Ni=0.77, Pb=0.65, Mn=0.73, Fe=0.67, Cr=1.26, Cd=6.7 and As=0.66.



wastewater, Wadi and groundwater, Middle

wastewater, Wadi and groundwater, West

wastewater, Wadi and groundwater, Middle

wastewater, Wadi and groundwater, West

wastewater, Wadi and groundwater, Middle

wastewater, Wadi and groundwater, West

Fig. 3. Comparison between trace metals in domestic wastewater (WW) discharged to Wadi Gaza, water of Wadi (W) in two sampling stations and groundwater (GW) of two wells in the middle (F62) and the western (G16) areas of Wadi Gaza.

Phosphorus

Phosphorus in sediment followed an opposite trend to P in water; P in sediment was high in winter and low in summer. Figure 4a shows the trend of P along the Wadi. The eastern stations were shallow and the P content in the lake was higher than its values in these stations. Moreover, the water flow in summer was very slow, eutrophication phenomena appeared in the western lake, and limited algal blooms appeared in the eastern stations. The major source of phosphorus in the area is wastewater, containing detergents and fertilizers applied in the surrounding agricultural areas. The relationship between P and Fe is discussed under the results of Fe in water and sediments. Table 2 and Figure 4a show the variation of P in summer and winter. Generally P increased by a factor of 2 in winter compared with summer in the western lake. The decay of water plants in winter may have increased the P in sediment and decreased the P in water. Moreover, the sediments release P to water in summer and sorb it in winter (Kelderman, 1996).

Table (2) Chemical characteristics of sediments by flame AAS.

Parameter	Summer, November 2001				Winter, April 2002				*Background
	Max	Min	Mean	σ	Max	Min	Mean	σ	
P g/Kg	1.6	0.3	1.0	0.4	2.3	0.2	1.3	0.7	
C[%]	9.7	0.6	4.0	2.4	5.1	1.2	3.56	1.3	
S[%]	1.2	0.0	0.5	0.4	1.92	0.0	0.78	0.6	
$CaCO_3$ [%]	32.0	7.0	24.6	7.8	28	7	19.3	7.0	
Mg [%]	2.1	0.2	1.4	0.7	2.0	0.3	1.34	0.6	
Ca [%]	12.9	3.0	10.1	2.8	13.1	3.4	9.40	3.4	
Na mg/Kg	28714	196	6586	7302	43072	81	11762	13814	
K mg/Kg	10964	624	7370	3597	9207	655	5336	3348	
Cu mg/Kg	28.0	4.0	20.5	8.7	28.6	3.8	20.88	8.7	45
Zn mg/Kg	104.0	7.0	70.4	30.2	101.1	13.9	74.77	31.0	95
Ni mg/Kg	48.0	1.0	30.4	17.3	47.4	3.5	31.14	15.8	68
Pb mg/Kg	16.0	4.0	11.6	3.6	17.7	0.1	10.91	5.8	20
Mn mg/Kg	739	85	502	228	671.0	88.2	483.7	217.2	850
Fe [%]	7.5	0.6	4.3	2.5	3.9	0.4	2.53	1.3	4.7
Cr mg/Kg	59.0	6.0	35.8	17.8	62.5	5.1	37.28	20.6	90
Co mg/Kg	18.0	2.0	11.4	4.9	16.5	0.9	11.43	5.3	19
Cd mg/Kg	0.4	0.0	0.2	0.1	0.4	0.0	0.21	0.1	0.3
As mg/Kg	10.1	1.8	5.9	2.2	4.6	0.5	2.62	1.3	
Hg mg/Kg	0.9	0.0	0.1	0.2	0.1	0.004	0.05	0.03	0.4

* *Turekian & Wedepohl, 1961.*

Carbon and Sulfur

The field survey indicated that the sources of carbon in the Wadi Gaza include not only natural sources but also different construction materials dumped to the Wadi. There was no significant difference in the contents of C and S in summer and winter and only two sampling stations showed sudden increases in C summer samples.

$CaCO_3$, Ca, Mg and Na

Figure 4b shows the trend of $CaCO_3$ and Ca in the summer and winter. Sampling station 6 has a sudden increase in the Ca contents in the summer presumably from the accumulated wastewater produced from the olive oil mill opposite to this station. The wastewater was very rich in Ca and may have percolated to the sediment of that area. The $CaCO_3$ showed the same trend as Ca. Generally, seasonal variation affected the contents of $CaCO_3$ and it was higher in summer than winter. The results of Mg and Na in summer and winter were similar, especially in the eastern sampling stations, and the reason of the fluctuation of Na in 3 stations within the lake was not clear. The lake showed higher Na in winter than summer, while the Mg remained the same in all stations.

Cu, Zn, Cr, Ni, Pb, Co, As, Hg and Cd

The analysis of Cu and Zn in sediments of the Wadi Gaza showed similar values in summer and winter with no major difference. The two metals displayed the same trend in summer and winter and also in all sampling stations (Fig. 4c). Cu started low in the east and increased gradually in the west.

The concentration of each metal remained the same within the lake's 10 areas. Chromium had the same trend in summer and winter; it started in the eastern sampling stations then increased in the lake. As shown in Figure 4d, the concentrations of Ni and Pb were the same in summer and winter.

Only sampling Station 6 showed an increase in Ni in winter while the others remained the same. Cobalt fluctuated in summer and winter but both results had the same range (Fig. 4e). As, on the other hand, was two times higher in summer than in winter especially in the lake where the water depth was about 1.8 m; the eastern stations showed less difference as the water was shallow (30-60 cm depth).

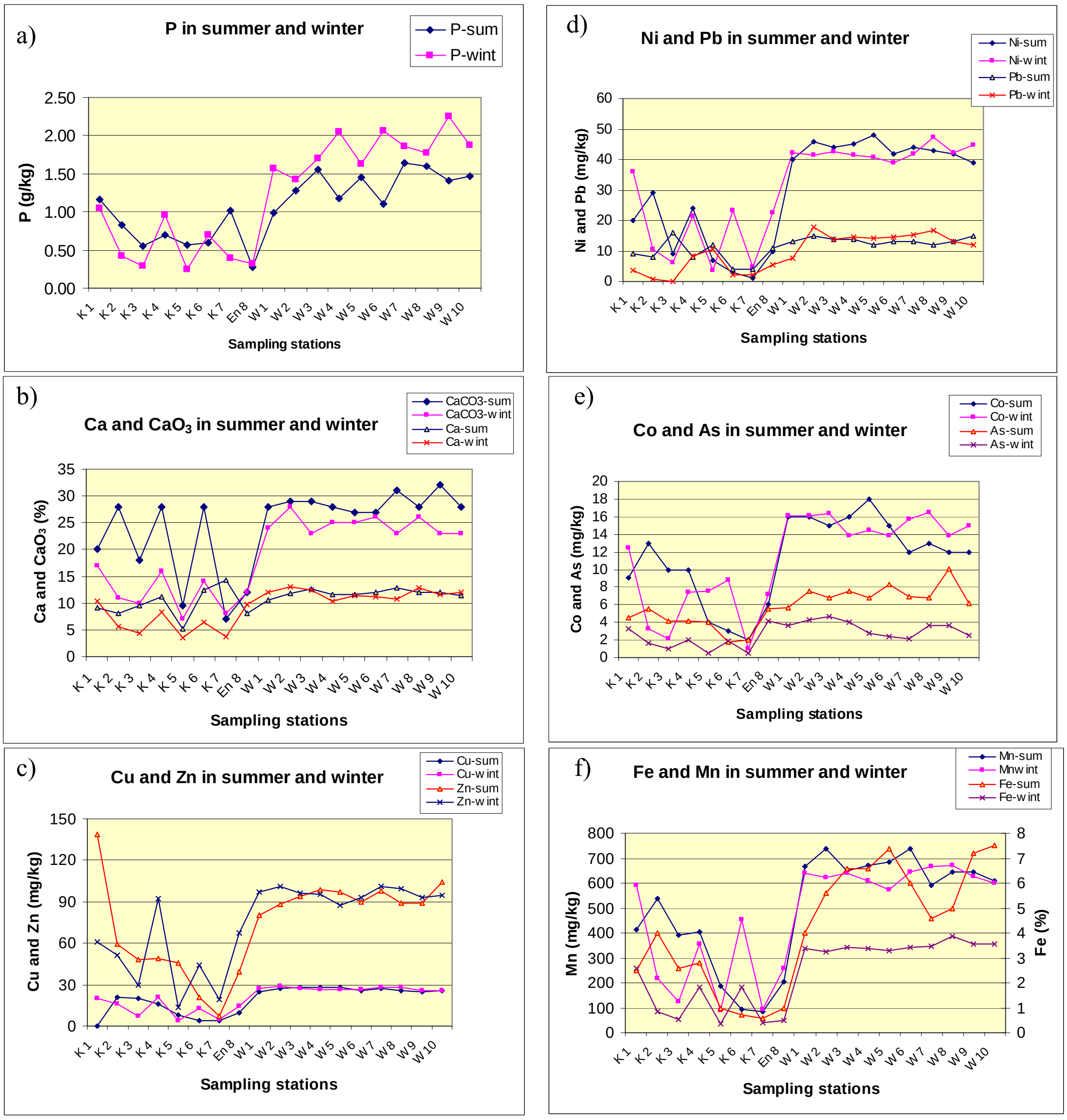


Fig. 4. (a) P, (b) Ca and $CaCO_3$, (c) Cu and Zn, (d) Ni and Pb, (e) Co and As, (f) Fe and Mn in the sediment samples of Wadi Gaza.

During the summer sampling, some medical wastes were found in the area, as a result of the disposal activities by local clinics. The recent observations agreed with the findings of Zoarob (1997) who identified Wadi Gaza as a disposal site of medical wastes. This is probably the main source of Hg in the area. Mercury values were not affected by seasonal variation. They remained low and two anomalous readings only appeared in Station 1 and area 5 (W5) of the lake in summer sediments. Hg levels were still below the German and the European standards for sediments (Oka-Elbe Project, 2000). Cadmium was low but fluctuated in all sediment samples with no significant differences along the Wadi.

Fe and Mn

Fe and Mn represented the major metals in sediment samples of Wadi Gaza. Fe and Mn in the sediments were also much higher than the Fe and Mn contents in the soils of the other areas in the Gaza Strip. As mentioned before, most of the metallic solid wastes dumped into Wadi had high amounts of Fe. The results showed that both Fe and Mn followed similar trends (Fig. 4f). The summer season had many impacts on water and sediment and the sediment-water exchange of P was much dependent on the season. In the summer the sediment released P whereas in the winter, a P accumulation took place. In the summer season this phosphorus was used as a main source of nutrients needed for water plants covering the Wadi. Higher temperatures could lead to anoxic conditions in sediment resulting in Fe and P release. In winter the sediments are oxygen-rich, and Fe is in the Fe(III) form, which forms an insoluble bond with phosphate. Under anaerobic conditions of summer (to be more specific, at redox potentials below 150 mV), the Fe(III) was reduced to Fe(II). Since Fe(II)-phosphates are 100 times more soluble than Fe(III)-phosphates, this gave rise to a P release from Fe-P bondings.

Table (3) Chemical characteristics of sediments by EMMA.

Parameter	Summer, November 2001				Winter, April 2002			
	Max	Min	Mean	σ	Max	Min	Mean	σ
K [%]	2.4	0.6	1.8	0.6	2.6	0.9	2.0	0.6
Ca [%]	12.0	4.4	10.2	1.8	12.9	5.8	10.3	2.1
Ti [%]	0.6	0.4	0.5	0.1	0.8	0.3	0.5	0.1
Cr mg/Kg	117.1	32.3	76.1	25.4	117.2	32.1	85.8	26.6
Mn mg/Kg	672.8	122.9	475.1	171.3	597.7	145.5	465.1	147.4
Fe [%]	4.1	0.8	3.0	1.1	4.2	1.0	3.1	1.2
Ni mg/Kg	59.9	4.5	35.5	17.2	52.0	7.7	34.1	14.2
Cu mg/Kg	566.1	4.7	50.9	128.8	34.3	6.7	24.2	9.0
Zn mg/Kg	140.4	14.7	81.0	30.4	118.5	18.0	86.5	34.0
Ga mg/Kg	13.9	2.3	10.0	3.7	15.4	2.1	10.8	4.6
As mg/Kg	7.6	0.0	3.8	2.6	6.1	0.0	3.7	2.0
Se mg/Kg	0.9	0.0	0.1	0.3	0.0	0.0	0.0	0.0
Br mg/Kg	84.1	2.4	23.2	22.3	168.3	1.6	36.7	43.7
Rb mg/Kg	45.6	11.0	34.4	12.9	46.2	10.3	34.4	13.6
Sr mg/Kg	385.3	140.6	284.6	64.9	455.6	106.0	285.4	93.2
Y mg/Kg	26.4	8.0	20.3	7.0	25.9	5.6	19.0	7.2
Zr mg/Kg	511.3	144.6	246.9	130.0	330.9	103.3	175.1	67.5
Pb mg/Kg	193.3	2.5	21.1	43.1	18.8	3.8	12.5	3.8
Th mg/Kg	8.1	0.0	4.2	2.2	6.3	0.0	3.9	2.4

AAS and EMMA

Tables 2 and 3 and Figure 5 show the results obtained from the flame AAS and the EMMA. The agreement between the two methods was generally good and was compatible with the findings of Cheburkin and Shotyk (1996). The shared parameters between the two methods were Ca, Fe, Mn, Cu, Zn, Ni, Pb, Cr, As and K. The flame AAS showed levels 5% and 10 % higher than the EMMA for Ca and As respectively and 6-8% higher than the Mn concentrations. Both systems have a difference of 5% for Cu, Zn and Pb. They showed < 2 % difference for Fe. The Cr and Ni were 40 and 20% higher in the EMMA to the AAS results, respectively, probably because of an incomplete dissolution of the soil samples during the digestion process by acids. Additional metals were measured by the EMMA and Table 3 showed the contents of these metals (Ti, Ga, Se, Br, Rb, Sr, Y, Zr and Th) in summer and winter.

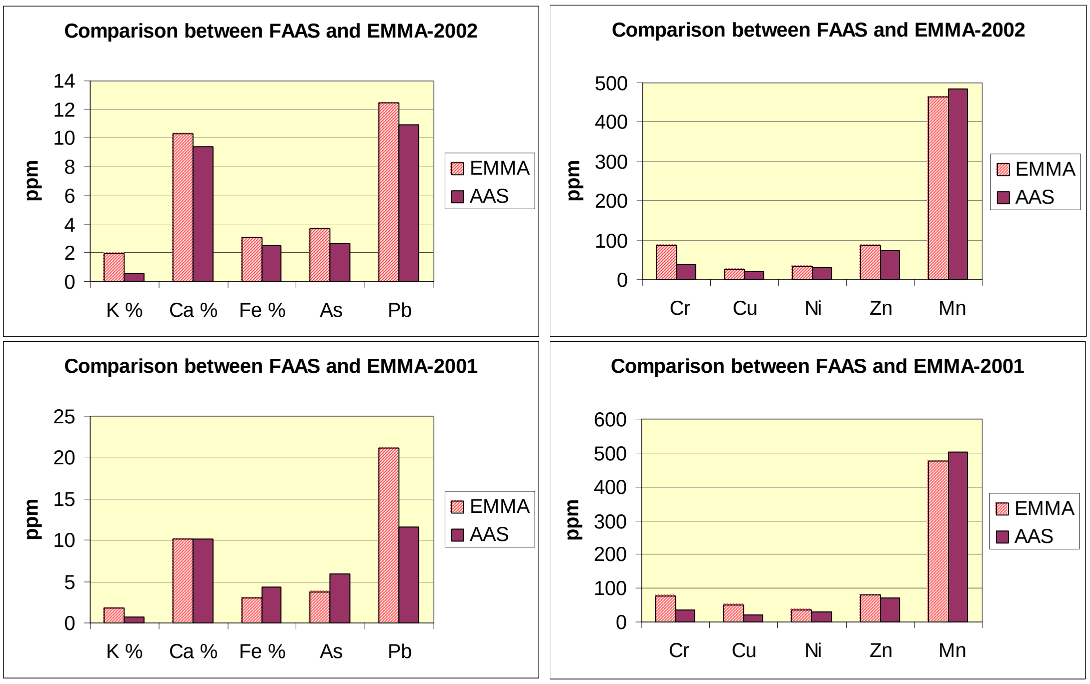


Fig. 5. Comparison between the results of AAS and EMMA for sediment samples of Wadi Gaza for two successive years.

CONCLUSIONS

1) The results obtained served to increase our knowledge of the geochemistry of water and sediment of the Wadi Gaza. In spite of this, the study has highlighted the need for further research, by increasing sampling density and regularity to better characterize the geochemical conditions of the Wadi.

2) Excluding Station 7, no major contamination of Fe, Zn, Cu, Mn, As, Pb, Cr, Cd, and Co was found in water at most of the stations. Sediments in only two stations had high Hg, Cd, Fe and Zn compared to background values of Turekian & Wedepohl (1961). Heavy metal contents in sediment samples were low in the eastern stations and higher in the lake.

3) The various anthropogenic inputs may lead to the enrichment of many metals in the sediments of Wadi Gaza. Pollution of several sites was found to be considerably high for Hg, Cd, Fe and Zn and to a somewhat lesser extent for As, Pb, Ni, Cu and Co, whereas anthropogenic input of Ga, Se and Th seems to be less important.

4) The chemical composition of water and sediments exhibited seasonal variation. The human inputs affect the concentrations of the tested parameters in summer; while the precipitation inputs in winter diluted pollutants to minimum levels.

RECOMMENDATIONS AND MANAGEMENT STRATEGIES

Wadi Gaza is the only wetland in the Gaza Strip and its unique habitat and species warrant careful management. The opportunity exists to apply measures which can bring both ecological and socio-economic benefits. Measures to clean up and restore the wetland would bring ecological, landscape and visual improvements. This may improve the health and the environmental conditions for local people, bring new opportunities in education, recreation, tourism and research, as well as maintain a range of cultural, social and historical heritage values.

The main pressures should be reduced in short, medium and long term measures. These pressures include overgrazing, pollution from the untreated wastewater, discharge of oils and pesticides, cutting and burning of natural vegetation, building roads, agricultural encroachment, hunting and poaching. By reduction of these pressures, the ecosystem functions and productivity will be restored. Examples of short term measures would be to open the mouth of the Wadi to the Mediterranean Sea and to stop the use of oil and pesticides for combating mosquitoes. Examples of medium and long term measures would be to stop the discharge of raw wastewater to the Wadi and to cooperate with the upstream regions in management of the Wadi water resources. Because the Wadi is subject to many jurisdictions, local, governmental, and nongovernmental institutions should all play a role in protecting and conserving the Wadi. The efforts should aim to support the conservation of the wetland by implementing activities such as: (1) cleaning campaigns, (2) removal of construction debris, (3) development of recreational areas, (4) building of bridges of culverts, hiking trails, observation towers, and water retention structures and (5) planting of trees in the site.

CHAPTER SIX

Geochemical Features of Topsoils in the Gaza Strip: Natural Occurrence and Anthropogenic Inputs (*)

ABSTRACT

The aims of this study were to establish the current contents of trace metals and major elements in agricultural soils of the Gaza Strip, and to identify the main anthropogenic inputs affecting trace metal contents. An extensive soil survey was conducted in agricultural and non-agricultural areas. One hundred seventy sites were selected which represent a broad range of soil types and locations. The results revealed that soils fall within the range of the uncontaminated to slightly contaminated category. Up to 90% of the tested soils had trace metal contents representing the international background values. 10% showed slight contamination mainly by Zn, Cu, As and Pb due to anthropogenic inputs, and their mean concentrations were 180, 45, 13 and 190 mg/kg, respectively. The trace metal contents vary with the highest contents detected in the southern regions (clay soil and low precipitation) and the lowest in the northern areas (sandy soil and high precipitation). The soil geochemistry is dependent on soil type and location and to a lesser extent on crop pattern and fertilizer and fungicide application. Anthropogenic inputs lead to the enrichment of Zn, Pb, Cu and Cd in the agricultural soils. Pollution of several investigated sites was found to be most severe for Zn, Pb, Cu and Cd and to a somewhat lesser extent for As, whereas anthropogenic input of Hg, Ni and Co seem to be less important. The application of Cd-containing phosphate fertilizers coupled with Cu-containing fungicides may be important sources of Cd and Cu in several soils. High Zn levels (1000 ppm) in several soils may be caused by sewage sludge that has an average Zn content of 2000 ppm. Saline-sodic soils were found in the central and southern regions where the soils are characterized by high contents of Na and salty groundwater. Elevated Cl, Na, Zn and Pb contents in some areas need further investigation for their ecological and health implications.

Key words: Anthropogenic inputs, Gaza Strip, Soil pollution, Trace elements.

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INTRODUCTION

Due to the scarcity of land and rapid urbanization in the Gaza Strip, most agricultural areas are located near industrial areas and the environmental hotspots of wastewater treatment plants and solid waste dumping sites. The soils of these agricultural areas are subject to potential pollution from various sources (Abrahams, 2002). Soils are prone to contamination from atmospheric and hydrological sources, but direct waste disposal causes a major impact on this natural resource, posing serious environmental concern (Navas and Machin, 2002). At current rates of atmospheric deposition concentrations of potentially toxic trace metals in soils of several countries worldwide may already be close to exceeding their critical capacity for pollution (Nriagu, 1990). Most trace metal contamination in the surface environment is associated with a cocktail of contaminants rather than one metal (Jung, 2001). It has been noted that roadside soils near heavy traffic and urban soils are polluted by Cd, Cu, Pb and Zn and other metals (Li et al., 2001). In the polluted soil, the trace metal concentrations in crop plants were found to vary between plant species (Lee et al., 2001). Balances between removed and supplied quantities of trace elements indicate slow depletion of the micro nutrients Zn, Cu and Mn in farming based on cash crops and conventional fertilization. The soil levels of Cd, Hg and Pb are slowly increasing due to additions of commercial fertilizers (Andersson, 1992; Bowen, 1979).

Soil salinity and sodicity can have a major effect on the structure of soils. Soil structure, or the arrangement of soil particles, is critical in affecting permeability and infiltration (Sparks, 1995). Saline irrigation water, low soil permeability, inadequate drainage, low rainfall, high potential evapo-transpiration and poor irrigation management all cause salts to accumulate in several soils of Gaza, which deleteriously affects crop growth and yields (Sparks, 1995).

In the Gaza Strip, there is not enough water to leach soluble salts from soil. Consequently, the soluble salts accumulate, resulting in salt-affected soils. The major cations and anions of concern in saline soils and waters are Na^+, Ca^{2+}, Mg^{2+} and K^+ and the primary anions are Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} and NO_3^-. Carbonate ions are normally found only at $pH \geq 9.5$.
Crop rotation and fertilization vary between different regions depending on climate and soil conditions, and, similarly, there is a variation in the rate of precipitation from south (250 mm/a) to north (400 mm/a) over the Gaza Strip.

The main goal of this study was to establish the topsoil geochemistry in the Gaza Strip. A secondary objective was to identify the major anthropogenic inputs affecting soil geochemistry.

MATERIALS AND METHODS

Soil Types

The Gaza Strip is 360 km^2, has several major soil types (Fig. 1). Arenosolic, Calcaric, Rhegosolic and Calcaric Fluvisolic soils are examples of these soils (Table 1). Arenosolic (Sandy) soils of dune accumulations are Regosols without a marked profile. The soils are moderately calcareous (5-8% $CaCO_3$), with low organic matter, physically suitable for intensive horticulture.

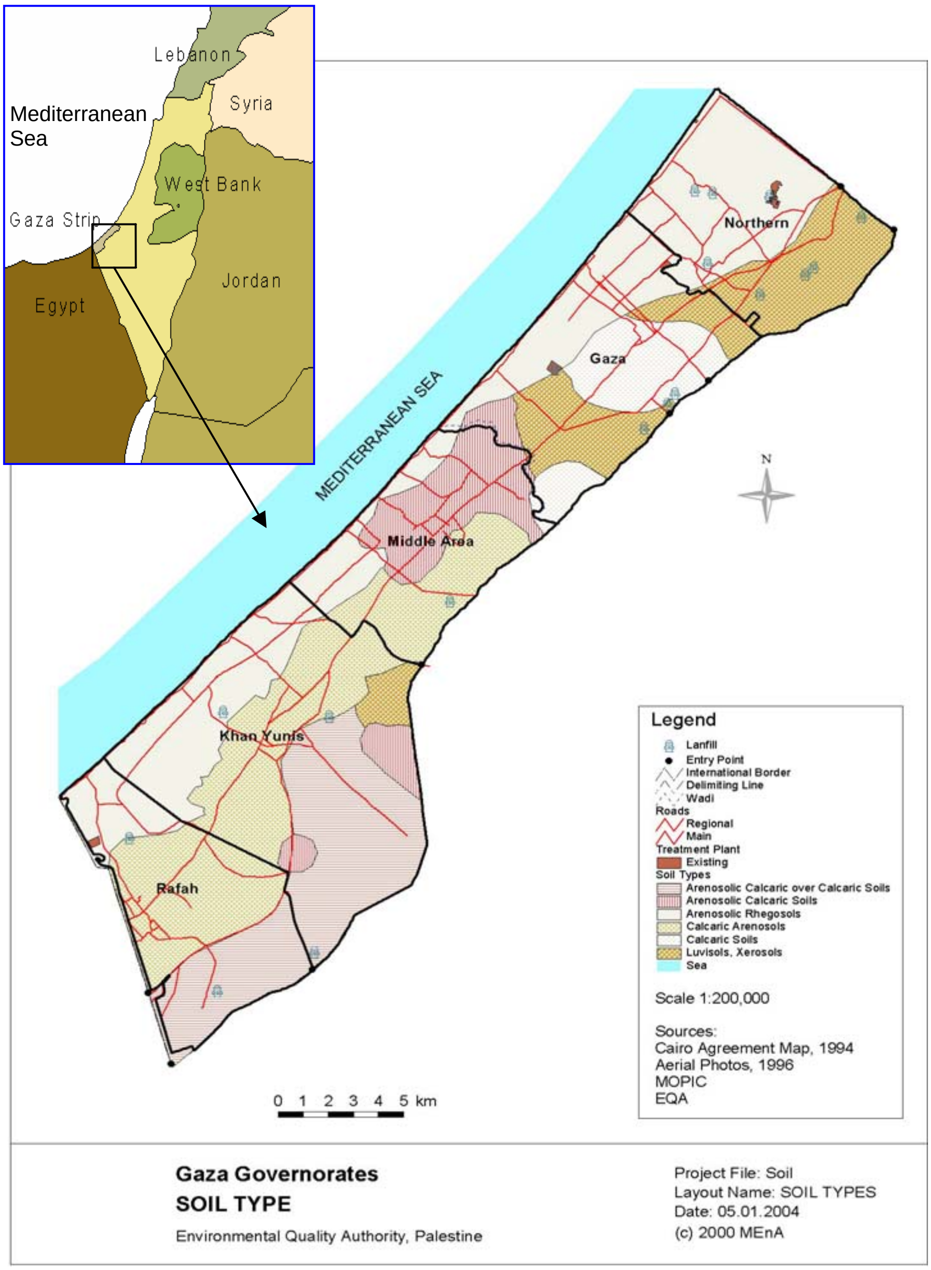

Fig. 1. Location of the Gaza Strip and Soil Type Distribution.

Calcaric Arenosols (Loessy sandy soils) can be found some 5 km inland in the central and southern part of the Strip, in a zone along Khan Yunis towards Rafah, parallel to the coast. This belt forms a transitional zone between the Arenosolic soils and the Calcaric (Loess) soils. Typical Calcaric soils are found in the area between the city of Gaza and the Wadi Gaza and they contain 8-12% $CaCO_3$. Arenosolic Calcaric (Sandy loess) soils are transitional soils, characterized by a lighter texture. These soils can be found in the depression between the Calcareous (Kurkar) ridges of Deir El Balah. Apparently, windblown sands have been mixed with Calcareous deposits. Deposition of these two types of windblown materials originating from different sources has occurred over time and more or less simultaneously. These soils have a rather uniform texture. Another transitional form is the Arenosols over Calcaric soils. These are loess or loessial soils (sandy clay loam), which have been covered by a layer (0.20 – 0.50 m) of dune sand. These soils can be found east of Rafah and Khan Yunis.

Table (1) Soil Types, land form and dominant land use of the Gaza Strip.

Soil Type	Land Form	Dominant Land Use
Arenosolic Rhegosols	Active steep dunes Undulating stabilized dunes Calcareous ridges	Irrigated horticulture in greenhouses Irrigated horticulture in tunnels and open fields El Mawasy rainfed vegetables/fruit Rainfed grapes
Calcaric Arenosols	Flat/rolling interdune areas	Open horticulture, tunnels
Arenosolic Calcaric Soils	Flat/rolling plains or depressions	Dates Citrus plantation Some irrigated vegetables, fieldcrops
Calcaric Soils	Rolling plains	Citrus plantations
Arenosolic Calcaric over Calcaric Soils	Gently rolling plains	Rainfed fieldcrops Almonds, olives Some irrigated vegetables
Luvisols, Xerosols	Ancient alluvial valleys Depressions and slopes	Citrus orchards Rainfed fieldcrops Non-rainfed vegetables

Fluvisols (Alluvial) and Vertisols (Grumosolic), dominated by loamy clay textures are found on the slopes of the northern depressions between Beit Hanoun and Wadi Gaza. Borings east of El Montar ridge have revealed that alluvial deposits of about 25 m in thickness occur. At some depth, calcareous concentrations are present. The $CaCO_3$ content can be approximately 15 – 20%. Some of the soils have been strongly eroded and the reddish brown subsoils may be exposed on top of ridges and along the slopes. The alluvial sediments are underlain by a calcareous layer.

Sampling and Sample Preparation

The soil sampling campaigns were conducted according to the European soil sampling guidelines (Theocharopoulos et al., 2001). The criteria for the sampling area, specific site, and point selection were mainly based on pedology, land use and geology. The depth of sampling varied between 0-10 cm for the open and grass soils; 20 cm for the vegetable soils; and up to 30 cm for the ploughed soils.

One hundred seventy soil samples were collected in October/November 2001, April/May 2002, and January/February 2003: 35 samples from the green houses (vegetables) of three different geographic areas, 25 from fruit farms (olive, peach, guava), 25 from citrus farms of northern and southern areas, 20 from open vegetable farms, 15 from strawberry farms, 20 from the vegetable farms near wastewater treatment plants, 20 from the vegetable farms near solid waste dumping sites and 10 from non-agricultural isolated areas representing local reference sites.

At each sampling station, a circle of 2-5-m diameter was identified and 10 sub-samples were collected within the perimeter and mixed to form a composite sample. Samples (0.5 kg) were collected and placed into polyethylene cups and stored at 4 °C. The soils were dried in an oven at 45 °C until constant weight. They were then shipped to Germany in plastic sample bags.

Analyses

Samples were freeze-dried until complete drynessm and sieved through a 2-mm sieve and ground to a powder by using a ring mill (FRITSCH-Labor Planeten Mühle, pulverisette 5). Approximately 0.5 to 1.0 g of each homogenized sample was dissolved in 10.5 ml of concentrated HCl (37% p.a.) and 3.5 ml of concentrated HNO_3 (65% p.a.) in 50 ml retorts. The samples were degassed (12 h) then heated to 160 °C on a sand bath until a complete extraction had taken place (3 h). After cooling, the solutions were diluted with distilled water in 50 ml volumetric flasks and kept in 100 ml polyethylene bottles for analysis.

Samples were analyzed by ICP/OES (VISTA-MPX, VARIAN) for alkali and alkaline-earth elements Mg, Li, Ca, K, and Na, heavy metals Cu, Zn, Ni, Pb, Mn, Fe, Cr, Co, Cd, and the metalloid As. Energy-dispersive miniprobe multielement analyzer-X-ray fluorescence (EMMA-XRF) was used for K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Pb, Th and U (Cheburkin and Shotyk, 1996). The distribution of total P represented as (PO_4) was measured according to APHA (1995). Mercury concentrations were determined using atomic absorption spectroscopy after thermal combustion of the freeze dried samples (50-100 mg) by an advanced mercury analyzer (AMA) 254 solid phase Hg-Analyzer (LECO). The total C and S contents were determined in dried samples by using a Carbon-Sulfur Determinator (Leco CS-225). Carbonates were measured via a carbonate bomb (Müller and Gastner, 1971). The TOC was calculated by the subtraction of inorganic C from total C.

The adsorbable organic halogens (AOX) were determined using a Euroglas Organic Halogen Analyzer. Analytical procedures DIN 38414 S18 followed that in the "Deutsche Einheitsverfahren zur Wasser, Abwasser und Schlammuntersuchung, Sludge and Sediment (Group S) Determination of AOX" (DIN, 1989). The AOX in soil was analyzed according to Asplund et al., (1994). Ten to 50 mg milled soil sample was added to an acidic nitrate solution (20 ml, 0.2 M KNO_3, 0.02 M HNO_3) and shaken on a rotary shaker (200 rpm) for at least 1 h. The suspension was filtered through a 0.45 m polycarbonate filter. The filter with the filter cake were then combusted under a stream of O_2 at 1000 °C in an Euroglas AOX-analyser (model 1200) in which the formed hydrogen halides were determined by microcoulombmetric titration with Ag ions. Each sample was analyzed in duplicate. Blanks were analyzed according to the same procedure but without addition of soil.

Quality control

Analytical blanks and two Standard Reference Materials with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents (Avila-Perez et al., 1999). Precision for the results of soil samples was estimated using the reproducibility between the duplicates, and a coefficient of variation of less than 5% was found. The accuracy was evaluated using 20 aliquots of two River Sediment Standard Reference Materials-RS1 and RS3-Deutsche Industrie Norm (DIN, 1997, 1989). Geochemical reference materials were also analyzed by EMMA techniques. A deviation of less than 5% from the certified values was found. The coefficient of variation for triplicates (2 samples and one standard) was less than 2% for all parameters except for Cd which had a coefficient of variation higher than 6%. The difference between the Standard Reference Materials (RS1 and RS3) supplied by DIN was used to estimate the accuracy of the analytical method (ICP/OES) and the data accuracy rates came within: $CaCO_3$ 0.9%, Mg 0.44%, Ca 1.05%, Cu 0.7%, Zn 0.72%, Ni 0.77%, Pb 0.65%, Mn 0.73%, Fe 0.67%, Cr 1.26%, Cd 6.7% and As 0.66%. The accuracy rates with EMMA were: Cu 1.1%, Zn, Ni, Pb, Mn and Cd1%, and As, Fe, Cr 0.9%.

Fertilizers and Fungicides

Samples of commonly used fertilizers and fungicides were collected from private stores in Gaza. They were freeze-dried and ground to powder. Fertilizer and fungicide samples were measured using EMMA-XRF for K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb. The analyzer used monochromatic excitation with an energy of 19.6 keV. The software includes a possibility to normalize the peak area of each element by the intensity of incoherent scattering radiation. This feature allows the elimination of the matrix effect for samples with a different matrix. However, with the extremely wide range of matrices for fungicide samples even such normalizing does not work well. Several fungicide samples have a very heavy matrix due to the presence of high concentration of Mn, Cu, Zn and Br.

The EMMA-XRF analyzer was calibrated using different Standard Reference Materials. The analytical data for trace elements in the fungicides are semi-quantitative and may have a relative error up to 30%. As the results of the EMMA-XRF were semi-quantitative, a quantitative determination was carried out after a full digestion procedure by using the ICP/OES (VISTA-MPX, VARIAN) instrument for analyzing Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sc, Sr and Zn. The detection limit of the ICP/OES was estimated as 10% less than the lowest measurable standard used for calibration.

RESULTS

Due to the large data set obtained from the analysis of 170 soil samples, each having 26 parameters, this section will cover mostly elements that are environmentally significant in Gaza. Mercury was detected in 56 samples while Sb was only detected in 8 of them. The levels of Ti, Br, Rb, Sr, Y and Zr were low to very low and consequently data from these elements are not presented in Table 2. The statistical median of similar soils was considered and 11 soil categories were used to represent all samples (Table 2).

Among a total of 27 elements analyzed, only a few trace elements showed environmental relevance in Gaza: As, Cd, Cr, Hg and to a lesser extent Pb. The trace metal accumulations in the soils affected by sludge were characterized by a large spatial variability, with some 'hot spots' of Cu and Zn with concentrations of up to 45, 1800 mg/kg, respectively (Shomar et al., 2004a).

Non-parametric Spearman correlation coefficient was calculated for the raw data of 170 soil samples and the results are presented in Table 3.
Fertilizers are expected to be another source of trace elements apart from the natural occurrence. Table 4 shows the contents of some trace metals in selected commercial fertilizers commonly used in the Gaza Strip. The results of Ni, As, Se, Rb, Y and Zr were below the detection limit of the analytical procedure and, consequently they are not included in Table 4. Table 5 shows examples of the fungicides used in Gaza and their content of trace metals.

Table (2) Concentrations of Trace Metals and Other Elements in Selected Soils of the Gaza Strip

Soil taken from	C %	AOX mg/kg	P g/kg	Mg mg/kg	Ca %	Na mg/kg	Fe %	Mn mg/kg	Cr mg/kg	Cd µg/kg	Pb mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Co mg/kg	Hg µg/kg	As mg/kg
DL*	**0.05**	**0.5**	**0.001**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**1**	**10**	**10**	**2**	**5**	**1**	**2**	**2**	**1**
Reference areas (n=10)																	
Minimum	0.2	<0.5	0.1	260	0.3	89	0.2	30	2.0	<10	<10	<2	<5	3.2	<2	<5	<1
Maximum	0.4	<0.5	0.2	560	2.0	115	0.7	44	5.4	15	<10	4.1	11.3	8.8	3.4	<5	<1
Mean	0.3	<0.5	0.2	346	0.9	107	0.3	37	2.8	<10	<10	2.3	5.0	5.3	1.9	<5	<1
Median	0.2	<0.5	0.1	330	0.7	110	0.2	37	2.4	<10	<10	<2	<5	5.0	<2	<5	<1
St. dev. (s)	0.1	0.0	0.0	82	0.5	9	0.1	5	1.0	6	0.3	1.0	3.4	1.9	0.9	0.0	0.4
Citrus farms (1) (n=12)																	
Minimum	0.9	7.0	0.4	699	1.6	360	0.3	96	17	<10	<10	2	15	3.0	2.0	3.2	1.2
Maximum	2.9	10.0	1.3	11093	7.1	792	2.0	420	130	105	23.0	23	50	67.4	16.9	10.3	4.1
Mean	2.0	8.2	0.8	2273	3.0	524	1.4	319	85	43	18.8	7	35	39.1	7.5	6.4	3.0
Median	2.0	8.0	0.9	1530	2.9	497	1.3	349	97	43	19.5	6	40	40.0	6.3	6.1	3.0
St. dev. (s)	0.6	1.1	0.3	2601	1.4	110	0.6	88	32	23	3.4	5	10	14.5	4.6	2.0	0.7
Citrus farms (2) (n=13)																	
Minimum	0.7	6.0	0.2	1100	1.2	105	0.5	74	12	<10	<10	3	5	18	3.3	<5	<1
Maximum	2.2	11.0	1.2	3128	3.1	473	2.0	393	130	220	22	23	28	72	16.9	10.3	3.9
Mean	1.4	7.7	0.7	1679	2.3	260	1.0	189	66	83	14	11	16	44	7.5	7.2	2.1
Median	1.3	7.0	0.6	1760	2.5	240	0.9	188	65	70	14	7	19	46	5.0	7.0	2.4
St. dev. (s)	0.5	1.5	0.3	634	0.6	133	0.5	94	46	73	4	6	7	17	5.1	1.9	1.3
Greenhouses (1) (n=12)																	
Minimum	2.2	4.0	0.1	677	1.9	119	0.4	165	10	<10	<10	<2	5	7	<2	<5	<1
Maximum	2.5	8.0	2.0	3903	4.4	765	1.3	289	110	432	20	12	25	76	9.4	21	12
Mean	2.4	5.3	0.8	2204	2.9	321	0.9	238	54	119	14	6	17	29	5.2	7	4
Median	2.4	5.0	0.5	2030	3.0	206	1	256	65	49	17	5	19	19	5.7	8	5
St. dev. (s)	0.1	1.2	0.7	1126	0.6	244	0.3	44	29	146	6	3	6	25	3.4	5	4
Greenhouses (2) (n=13)																	
Minimum	1.7	5.0	0.3	324	2.4	222	0.3	132	12	<10	11	6	8	11	<2	8	5
Maximum	2.4	14.0	2.9	4562	4.6	765	1.5	198	72	187	20	12	17	78	9.4	14	12
Mean	2.2	10.8	1.2	1848	3.0	394	0.9	162	49	53	15	9	12	43	3.9	10	8
Median	2.3	12.0	0.8	1800	2.7	366	1.0	160	60	46	15	9	13	47	3.0	10	8
St. dev. (s)	0.2	2.4	0.8	1150	0.6	169	0.4	22	23	52	3	2	2	22	2.4	2	2

Table (2) Continued.

Soil taken from	C %	AOX mg/kg	P g/kg	Mg mg/kg	Ca %	Na mg/kg	Fe %	Mn mg/kg	Cr mg/kg	Cd µg/kg	Pb mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Co mg/kg	Hg µg/kg	As mg/kg
DL*	**0.05**	**0.5**	**0.001**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**1**	**10**	**10**	**2**	**5**	**1**	**2**	**2**	**1**
Greenhouses (3) (n=10)																	
Minimum	1.7	5.0	0.5	422	2.2	156	0.6	309	32	<10	<10	5	8	4	3	4	<1
Maximum	2.9	13.0	2.1	13958	7.0	888	2.9	598	130	227	57	81	23	90	11	12	9
Mean	2.3	8.3	1.1	3434	4.0	580	1.5	474	86	80	25	22	16	50	5	8	3
Median	2.4	9.0	1.1	2211	3.7	588	1.3	518	80	58	21	12	17	52	5	9	3
St. dev. (s)	0.4	2.7	0.5	3271	1.7	204	0.7	90	29	73	14	24	3	27	2	2	3
Strawberry farm (n=15)																	
Minimum	0.5	15	0.3	795	0.1	50	0.2	42	5	<10	<10	2	6	4	<2	6	<1
Maximum	4.0	350	0.9	6771	5.5	351	1.0	210	274	67	200	33	59	60	10	33	14
Mean	2.4	115	0.6	3287	3.8	194	0.6	126	133	26	61	14	25	30	3	15	5
Median	2.3	23	0.6	3225	4.3	189	0.4	106	120	16	14	7	18	18	3	10	4
St. dev. (s)	0.95	126	0.19	2085	1.6	75	0.29	59	102	29	82	12	18	22	3	10	4
Open farms (n=20)																	
Minimum	0.7	4.0	0.3	1633	1.3	156	0.5	140	5	<10	<10	4	5	14	2	5	<1
Maximum	2.9	7.0	1.3	13958	7.0	887	2.9	531	130	177	57	88	23	71	11	14	4
Mean	1.8	5.6	0.9	3118	3.9	404	2.2	430	83	52	30	57	12	50	4	9	1
Median	1.8	5.5	1.1	2075	3.2	347	2.6	505	120	57	29	80	13	60	3	10	1
St. dev. (s)	0.7	0.8	0.3	2710	1.8	225	0.8	136	54	43	17	31	3	17	2	2	1
Fruit farms (n=25)																	
Minimum	0.8	12	0.2	213	0.8	119	0.3	110	5	<10	<10	<2	<5	4	<2	<2	<1
Maximum	21.0	21	1.2	8389	920	920	410	410	472	472	170	170	187	187	28	28	18
Mean	1.9	15	0.6	4470	4.0	537	1.5	307	61	256	82	70	10	111	8	17	10
Median	2.01	15	0.6	5789	3.8	564	1.7	301	84	360	130	16	11	165	10	21	12
St. dev. (s)	0.5	2	0.2	2693	2.1	190	0.6	70	46	212	62	65	5	75	3	9	6
Nearby WWTP (n=20)																	
Minimum	0.2	33	0.1	212	0.1	50	0.2	26	5	<10	<10	<2	5	10	<2	<2	<1
Maximum	4.0	410	1.5	4913	3.4	765	1.7	239	278	1495	210	40	59	300	13	42	15
Mean	2.3	225	0.6	2318	2.0	370	0.7	117	193	236	110	25	36	70	7	24	8
Median	3.0	250	0.6	2108	2.7	350	0.4	106	260	33	114	30	40	31	9	30	11
St. dev. (s)	1.1	110	0.4	1363	1.3	225	0.5	65	112	465	84	11	13	89	3	13	5

Table (2) Continued.

Soil taken from	C %	AOX mg/kg	P g/kg	Mg mg/kg	Ca %	Na mg/kg	Fe %	Mn mg/kg	Cr mg/kg	Cd µg/kg	Pb mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Co mg/kg	Hg µg/kg	As mg/kg
DL*	**0.05**	**0.5**	**0.001**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**1**	**10**	**10**	**2**	**5**	**1**	**2**	**2**	**1**
Nearby SWDS (n=20)																	
Minimum	0.3	33	0.6	213	0.8	50	0.1	26	2	22	146	<2	<5	28	2	27	<1
Maximum	3.2	356	8.0	6914	3.5	765	1.7	239	280	66	210	35	50	190	11	36	19
Mean	2.3	175	1.2	2910	2.7	341	0.5	83	168	41	185	21	38	149	7	31	10
Median	3.0	178	0.9	2395	3.1	372	0.2	41	244	41	186	26	44	172	8	32	12
St. dev. (s)	0.9	105	1.6	1636	0.8	207	0.6	68	119	8	17	9	13	44	2	2	4

*) DL: detection limit

WWTP: Wastewater Treatment Plant

SWDS: Solid Waste Dumping Site

Table (3) Spearman Correlation Coefficient, N= 170.

		C %	AOX mg/kg	P g/Kg	Mg mg/kg	Ca %	Na mg/kg	Fe %	Mn mg/kg	Cr mg/kg	Cd µg/kg	Pb mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	Co mg/kg	Hg µg/kg	As mg/kg
C	Cor. Coef.	1.00	0.29	0.31	0.17	0.31	0.23	-0.02	0.05	0.26	0.00	0.41	0.18	0.31	0.14	0.16	0.31	0.29
	Sig. (2-tailed)		0.00	0.00	0.02	0.00	0.00	0.78	0.47	0.00	0.90	0.00	0.01	0.00	0.06	0.03	0.00	0.00
AOX	Cor. Coef.	0.29	1.00	0.07	0.30	0.11	0.07	-0.25	-0.33	0.41	-0.00	0.42	0.30	0.41	0.32	0.32	0.56	0.50
	Sig. (2-tailed)	0.00		0.34	0.00	0.13	0.30	0.00	0.00	0.00	0.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P	Cor. Coef.	0.31	0.07	1.00	0.06	0.13	0.27	0.11	0.21	0.14	0.11	0.27	0.23	0.18	0.25	0.09	0.25	0.12
	Sig. (2-tailed)	0.00	0.34		0.40	0.07	0.00	0.13	0.00	0.05	0.14	0.00	0.00	0.01	0.00	0.20	0.00	0.12
Mg	Cor. Coef.	0.17	0.30	0.06	1.00	0.33	0.17	0.24	0.18	0.20	0.06	0.17	0.20	0.07	0.18	0.178	0.26	0.13
	Sig. (2-tailed)	0.02	0.00	0.40		0.00	0.02	0.00	0.01	0.00	0.43	0.02	0.00	0.36	0.01	0.02	0.00	0.07
Ca	Cor. Coef.	0.31	0.11	0.13	0.33	1.00	0.19	0.18	0.27	0.18	0.05	0.07	0.19	-0.00	0.05	0.04	0.14	0.11
	Sig. (2-tailed)	0.00	0.13	0.07	0.00		0.01	0.01	0.00	0.01	0.46	0.31	0.01	0.97	0.49	0.54	0.05	0.15
Na	Cor. Coef.	0.23	0.07	0.27	0.17	0.19	1.00	0.50	0.48	0.14	0.23	0.31	0.29	0.07	0.31	0.33	0.22	0.20
	Sig. (2-tailed)	0.00	0.30	0.00	0.02	0.01		0.00	0.00	0.06	0.00	0.00	0.00	0.35	0.00	0.00	0.00	0.00
Fe	Cor. Coef.	-0.02	-0.25	0.11	0.24	0.18	0.50	1.00	0.81	0.03	0.22	0.08	0.22	-0.13	0.10	0.20	0.01	-0.11
	Sig. (2-tailed)	0.78	0.00	0.13	0.00	0.01	0.00		0.00	0.69	0.00	0.27	0.00	0.08	0.16	0.00	0.86	0.15
Mn	Cor. Coef.	0.05	-0.33	0.21	0.18	0.27	0.48	0.81	1.00	0.01	0.29	-0.01	0.19	-0.15	0.09	0.13	-0.09	-0.14
	Sig. (2-tailed)	0.47	0.00	0.00	0.01	0.00	0.00	0.00		0.82	0.00	0.87	0.01	0.04	0.24	0.07	0.24	0.05
Cr	Cor. Coef.	0.26	0.41	0.14	0.20	0.18	0.14	0.03	0.01	1.00	0.11	0.27	0.22	0.32	0.21	0.12	0.26	0.07
	Sig. (2-tailed)	0.00	0.00	0.05	0.00	0.01	0.06	0.69	0.82		0.14	0.00	0.00	0.00	0.00	0.10	0.00	0.35
Cd	Cor. Coef.	0.00	0.00	0.11	0.06	0.05	0.23	0.22	0.29	0.11	1.00	0.10	0.26	-0.08	0.74	0.14	0.07	0.19
	Sig. (2-tailed)	0.90	0.91	0.14	0.43	0.46	0.00	0.00	0.00	0.14		0.17	0.00	0.29	0.00	0.06	0.31	0.01
Pb	Cor. Coef.	0.41	0.42	0.27	0.17	0.07	0.31	0.08	-0.01	0.27	0.10	1.00	0.42	0.30	0.43	0.37	0.53	0.35
	Sig. (2-tailed)	0.00	0.00	0.00	0.02	0.31	0.00	0.27	0.87	0.00	0.17		0.00	0.00	0.00	0.00	0.00	0.00
Ni	Cor. Coef.	0.18	0.30	0.23	0.20	0.19	0.29	0.22	0.19	0.22	0.26	0.42	1.00	0.00	0.50	0.28	0.45	0.28
	Sig. (2-tailed)	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00		0.99	0.00	0.00	0.00	0.00
Cu	Cor. Coef.	0.31	0.41	0.18	0.07	0.00	0.07	-0.13	-0.15	0.32	-0.08	0.30	0.00	1.00	0.11	0.16	0.27	0.22
	Sig. (2-tailed)	0.00	0.00	0.01	0.36	0.97	0.35	0.08	0.04	0.00	0.29	0.00	0.99		0.15	0.03	0.00	0.00
Zn	Cor. Coef.	0.14	0.32	0.25	0.18	0.05	0.31	0.10	0.09	0.21	0.74	0.43	0.50	0.11	1.00	0.28	0.42	0.40
	Sig. (2-tailed)	0.06	0.00	0.00	0.01	0.49	0.00	0.16	0.24	0.00	0.00	0.00	0.00	0.15		0.00	0.00	0.00
Co	Cor. Coef.	0.16	0.32	0.09	0.17	0.04	0.33	0.20	0.13	0.12	0.14	0.37	0.28	0.16	0.28	1.00	0.25	0.28
	Sig. (2-tailed)	0.03	0.00	0.20	0.02	0.54	0.00	0.00	0.07	0.10	0.06	0.00	0.00	0.03	0.00		0.00	0.00
Hg	Cor. Coef.	0.31	0.56	0.25	0.26	0.14	0.22	0.01	-0.09	0.26	0.07	0.53	0.45	0.27	0.42	0.25	1.00	0.49
	Sig. (2-tailed)	0.00	0.00	0.00	0.00	0.05	0.00	0.86	0.24	0.00	0.31	0.00	0.00	0.00	0.00	0.00		0.00
As	Cor. Coef.	0.29	0.50	0.12	0.13	0.11	0.20	-0.11	-0.14	0.07	0.19	0.35	0.28	0.22	0.40	0.28	0.49	1.00
	Sig. (2-tailed)	0.00	0.00	0.12	0.07	0.15	0.00	0.15	0.05	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00	

Table (4) Chemistry of Selected Commercial Fertilizers Used in the Gaza Strip

	K (%)	Ca (%)	Ti (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	Zn (ppm)	Br (ppm)	Rb (ppm)	Sr (ppm)	Pb (ppm)
DL*	**0.05**	**0.05**	**30**	**20**	**10**	**10**	**1.5**	**1**	**0.7**	**0.7**	**0.8**	**0.6**
Gibberellic acid	<0.05	<0.05	<30	<20	13	25	<1.5	11	<0.7	<0.7	<0.8	<0.6
Fe-EDDHA	5	<0.05	<30	<20	<10	58028	4	24	<0.7	8	2	<0.6
NO_2, Fe, Mn	>10%	<0.05	<30	<20	140	360	27	45	19	19	<0.8	<0.6
Thiabendazole	<0.05	1	1142	<20	45	10475	<1.5	<1	45	4	5	<0.6
Clindune	4	<0.05	<30	7794	<10	204	<1.5	<1	38	18	4	<0.6
Cu, Fe fertilizer	<0.05	<0.05	<30	<20	19987	47890	10583	4999	11	<0.7	18	9
$N+P_2O_5+KO$	>10%	3	44	<20	387	949	21	16	6	11	2079	<0.6

*) DL: detection limit

Table (5) Chemistry of Selected Commercial Fungicides Used in the Gaza Strip

	K	Ca	Ti	Mn	Fe	Cu	Zn	Br	Rb	Sr	Pb
Fungicide	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Benony	<0.05	<0.05	<30	23	22	7	<1	<0.7	<0.7	<0.8	<0.6
Fosethyl Aluminum	<0.05	<0.05	388	<10	642	<1.5	7	<0.7	8	3	5
Chlor thalonil	1.0	<0.05	425	76	1327	<1.5	6	3	37	127	18
Propineb	<0.05	<0.05	<30	884	3768	<1.5	>10%	260	18	<0.8	<0.6
Mncozeb	<0.05	<0.05	<30	>10%	<10	<1.5	17500	<0.7	<0.7	<0.8	<0.6
Maneb	<0.05	2.0	10911	19980	11474	23	923	6	20	322	17
Manganes	<0.05	4.0	<30	>10%	<10	<1.5	1875	<0.7	<0.7	56	<0.6
Foscthyl-Aluminum	<0.05	<0.05	440	<10	843	<1.5	8	3	7	4	8
Copper Chloride	<0.05	<0.05	<30	<10	4000	>10%	<1	<0.7	<0.7	<0.8	<0.6
Cyger Sulfate	<0.05	<0.05	<30	<10	5977	>10%	<1	<0.7	<0.7	<0.8	<0.6
Metalaxyl	<0.05	<0.05	<30	>10%	<10	<1.5	20927	73	12	<0.8	<0.6
Simzin	<0.05	>10%	<30	<10	116	<1.5	<1	10	<0.7	70	11
Captan	<0.05	<0.05	2155	16	3072	306	14	72	22	20	30
Mineozab	<0.05	<0.05	<30	>10%	<10	<1.5	10288	<0.7	<0.7	<0.8	<0.6

Adsorbable Organic Halogens (AOX)

The AOX in the soils of Gaza was very low and it ranged between the detection limit (0.5) and 20 mgCl/kg. A few sites showed high AOX values of 250 mgCl/kg due to their location near the sludge disposal areas and solid waste dumping sites.

Phosphorus, Carbon and Sulfur

The total P concentration in the top soil varies between about 0.4 and 1.2 gP/kg which is suitable for agricultural purposes.

Total C in soils of the Gaza Strip was between 0.5-3%. The lowest percentage of S in the soils of the Gaza Strip was 0.016% while the highest was 0.07%. It is important to mention that the irrigation water in the southern areas of the Gaza Strip has high contents of SO_4 (380 mg/L) and this leads to more soil acidity (Shomar et al., 2004b).

CaCO3, Ca, Mg, Na and K

The results showed great variation (1.6-19%) of $CaCO_3$ contents in soils of Gaza. Calcium in the tested soils was between 0.7 and 5.4%. Several of the residual soils in Gaza are relatively low in Mg (0.03%). Sodium contents in soils were 110-825 mg/kg. The high Na content of household products for laundry, kitchen, bath and cleaning are a primary source of Na in soil. Addition of water softener wastes or the Na content in the local water supply also contributes to the problem. Soils showed suitable amounts of K with respect to agricultural requirements. The lowest and the highest K averages were 330 and 4500 mg/kg, respectively.

Fe and Mn

The contents of Fe in the soils of Gaza ranging between 0.2 and 2% were less than the value listed by Turekian and Wedepohl (1961) of 4.72% in the upper crust. The highest Fe levels were found in the middle area and Khan Yunis. Manganese showed a similar trend to Fe. Generally, Mn levels were low and the range was between 37 to 542 mg/kg. The correlations between Fe and Mn for the same soil types showed that both had the same source and behaviour (r =0.9).

Cu, Zn, Cd, Ni, Pb, Cr, Co, As, and Hg

The median of Cu in soils of the Gaza Strip was 10 mg/kg. The highest (45 mg/kg) was found in the greenhouses and the lowest (2 mg/kg) in the open sandy farms. Zinc seems to be distributed uniformly. The lowest Zn (2 mg/kg) was found in the local reference samples, with the highest (1800 mg/kg) being found in the soils exposed directly to domestic sludge. The Cd unit in µg/kg reflects its low level in soils. More than 75% of the soil samples showed results below the detection limit (10 µg/kg). Several greenhouses had 430 µg/kg of Cd in their soils. One site beside the wastewater treatment plant showed a level of 1500 µgCd/kg. The correlation coefficients between Zn and Cd in the different soils was 0.85 for the soils of the greenhouses of the southern regions, while it was only 0.53 for the northern regions.

Nickel was low with an average of 28 mg/kg and no significant difference was found in the Ni levels of each area. Only one guava farm showed a high level of Pb (145 mg/kg) while the rest of the soils showed an average of 30 mg/kg. The correlation between Pb and organic C was good (r =0.8). This could explain the behavior of Pb in the clay soils as it attaches to the organic matter. An anomalous result for Cr (472 mg/kg) was found in the area of Beit Hanoun. The site was 10 m from the industrial estate. The same soil from Beit Hanoun showed Co to be 29 mg/kg, while the average for all soils was 6 mg/kg. The average of As was 2.2 mg/kg, while the site near the solid waste dumping site reached 19 mg/kg. Finally, the average of Hg in the soils of Gaza was 10 µg/kg with many samples being below the detection limit of the analytical method.

DISCUSSION

The Palestinian environmental strategy (MEnA, 2000) has established that several threats cause the deterioration of soil quality in the Gaza Strip. Accumulation of solid and hazardous wastes, discharge of untreated wastewater, extensive use of fertilizers and fungicides, overgrazing, soil salinization, urbanization, vegetation removal, and soil erosion are examples of these threats. The agricultural areas are exposed to one or more of these threats.

The average contents of AOX in the sludge of Gaza was (550 mgCl/kg), which exceeds the standards of industrial countries (Shomar et al., 2004a). In spite of that the AOX in the tested soils was very low and the highest was 24 mgCl/kg. Moreover, the presence of AOX in soil may be due to the effect of living organisms during natural abiogenic processes (Müller, 2003).

The results revealed that the occurrence of trace metals in the different soils of the Gaza Strip was dependent not only on the soil type but also on the location of the soil, the vegetation cover and the agricultural activities. It showed that the levels of trace metals of the soils planted with the same crop were similar when the soil type, the irrigation water and the fertilizers used were the same. Five soils from open lands in the different geographic regions of the Gaza Strip were almost the same.

Soils covered by wastewater during some of the flooding episodes of the winter season showed high contents of trace elements. The owners used them for agricultural purposes for the rest of the year and insufficient care was taken to avoid contamination. Moreover, these soils were found to have Zn and Cu enrichments and this may be due to recycling by microorganisms (Blaser et al., 2000).

The soils exposed to the solid wastes showed high levels of trace metals. The wastes were disposed to the tested soils for long periods before they were transferred to the central dumping site. During the period of accumulation of the solid wastes, leachates may percolate through soil increasing levels of trace metals.

The greenhouses showed a clear variation in the contents of trace metals. The field surveys indicated that the average age of a greenhouse in Gaza is 5 years. They are used for vegetables such as tomatoes, cucumber, eggplants and others; with some exceptions in the area of Beit Lahia (North) where flowers and strawberries are planted beside the vegetables. The farmers use large amounts of fertilizers and fungicides. More than 200-250 t of formulated fungicides are applied annually in the Gaza Strip (Safi, 2002) and the majority is used in the greenhouses without monitoring. The analyses of trace metals in the most common fertilizers and fungicides revealed that they contain considerable amounts of several metals such as Fe, Mn, Cu, Zn and Cr and as a consequence these elements may increase in the soils of the greenhouses. The greenhouses of the Khan Yunis area showed higher levels of several trace metals and other elements. Fe, Zn, Cu, Ni, Pb, and Cr were higher than those in the greenhouses of the north area of Beit Lahia being 12.4%, 84, 17, 10, 19 and 74 mg/kg, respectively. The reason of variation could be the soil structure where it is sandy in the north and clay in Khan Yunis (South). In addition, the soil of Khan Yunis is affected by traffic contamination. The greenhouses of Khan Yunis were 10 m away from the main highway of Gaza. These results agree with findings from other authors (Manta et al., 2002; Navas and Machin, 2002; Fakayode and Owolabi, 2003).

Variations in the amounts of rainfall strongly influence the crops grown in Gaza. The groundwater quality deteriorates from north (Cl = 40 mg/L) to south (Cl = 3000 mg/L) (Shomar et al., 2004b). Consequently, strawberries and flowers are planted only in Beit Lahia while rain fed agriculture is located in the south eastern parts of Gaza. Presence of considerable amounts of $CaCO_3$ in soils because potential evapo-transpiration exceeds the rainfall in Gaza. On the other hand, in soils with a higher rate of precipitation in the north area, which leads to a higher rate of percolation, carbonates are easily dissolved and leached out. The amount and particle size of $CaCO_3$ minerals can increase the precipitation of calcium phosphate minerals on the surface (Sparks, 1995). This could explain the low levels of P in the north areas of Gaza where soils are sandy and the annual precipitation is higher than in the southern clay soils. In addition, high P levels were found in the greenhouses where P-fertilizers were commonly used. It is assumed that in neutral and calcareous soils of Gaza, inorganic P in the soil solution precipitates as calcium phosphate minerals. The low contents of Ca in several soils of Gaza could be explained as a result of soil erosion, urbanization and vegetation removal (Sparks, 1995).

CONCLUSIONS

1. The soil types, crop patterns, and specific location factors largely control the distribution of trace metals (Pb, Cu, Zn, Cd and Mn) in soils. Linear regression analysis found a correlation coefficient of r =0.85 between Zn and Cd concentrations in soils and the presence of highways nearby.
2. The irrigation water, the applied fertilizers and fungicides, and the sludge and wastewater nearby have played a major role and contributed significantly the enrichment of several soils with Zn, Pb, Cu and Fe. Affected soils by sludge, solid wastes and wastewater showed similar contents of trace metals.
3. With respect to the global comparison, it may be noted that the values for the trace metals in the different soils of the Gaza Strip were well within the worldwide soil average values. These levels were still low and probably harmless to the soil ecosystem. However, the distribution pattern for Zn, Cd, and Cu in several soils clearly indicated that their contamination due to anthropogenic factors were on the rise and may become alarming if mitigation measures are not taken.

CHAPTER SEVEN

Monitoring of pesticides in the groundwater and the topsoil of the Gaza Strip (*)

ABSTRACT

Agricultural activities in the Gaza Strip have associated with excessive and uncontrolled use of dozens of pesticides. Accordingly, groundwater and soil are potentially contaminated causing severe threat to the crowded population. The present study describes in a 3-year monitoring program types and level of contamination by various pesticides used in Gaza. Two analytical instruments (GC/MS and HPLC/MS) were applied to achieve this objective.

More than 92% of targeted pesticides in groundwater were much lower than their allowable limit of the World Health Organization. However, the municipal groundwater wells showed better quality as they are located in the residential areas than the private wells in the agricultural regions. Atrazine, atrazine-desisopropyl, propazine, simazine were detected in water samples with average concentrations of 3.5, 1.2, 1.5 and 2.3 µg/l, respectively. A linear correlation was found between the chloride concentrations in groundwater and atrazine for the same geographic areas. Generally speaking, shallow aquifers of low annual precipitation in the southern areas of Gaza showed detectable concentrations of pesticides. In soil, pesticides presence was found to depend on type of soils. Clay soils for instance, showed 3-4 times more than sandy soils for the same pesticide species.

A linear regression analysis found a correlation coefficient of $r = 0.87$ between the strawberry greenhouses and the occurrence of propazine, sebutylazine, terbutylazine, 4,4’-DDT, 4,4’-DDE, and 4,4’-DDD in soil. The averages of propazine, sebutylazine and terbutylazine were 19, 13 and 39 µg/kg, respectively. One soil sample showed contents of 4,4'-DDE and 4,4'-DDT up to 1104 and 793 µg/kg , respectively.

Key words: Gaza, Groundwater, Pesticides, Soil.

(*) *The study was submitted to an International Journal.*

INTRODUCTION

Pesticides are considered priority pollutants in Gaza and, with the expanding use of greenhouses; Palestinian agriculture is becoming increasingly dependent on chemical pesticides and fertilizers. According to Safi (2002), Gaza Strip consumed more than 393.3 t of pesticides in 1999. Pesticides are often misused by the non-professional, inexperienced farmers, who do not take into consideration the "safe period", which is identified as the period between spraying and gathering of crops, specified according to the type of pesticide (Abu Middain, 1994). Pesticides affect humans, either immediately or in the long run (Carbonell et al., 1995; Bain and LeBlanc, 1996; Ribas et al., 1997; Richer and Safi, 1997). As an example, methyl bromide, which is used extensively in Gaza, causes fetus deformations, eye infections and dermatitis (Safi, 2002). Organochlorine pesticides used in Gaza cause breast cancer (Aronson et al., 2000). Another study conducted by Safi (2002) showed that heavy misuse of pesticides in the Gaza environment correlated with the growing incidence of cancer.

It is ironic that pesticides that are banned or restricted in many countries are being marketed and used in Gaza because of lack proper assessment and monitoring programs (SCF, 1991; Haapala, 1993; UNRWA, 1993; Abu Middain, 1994; Richter and Safi, 1997; IARC, 1999). Also lack of awareness among shop owners, farmers and public increased the level of soil and water contamination across Gaza (Hulshof, 1991; Issa, 2000).

Contamination resulting from leaching of pesticides is a common and growing problem in major agricultural regions (Flury, 1996; DaSilva et al., 2003).
The method and rate of pesticide application, the use of tillage systems that modify soil conditions, and the amount and quality of water can also influence pesticide leaching (Hebb and Wheeler, 1978; Kolpin, 1997; Tomlin, 1997; Kubilius and Bushway, 1998; USGS, 1998).

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. Therefore groundwater contamination will be of catastrophic consequences to the around populated areas. The groundwater aquifer of Gaza is extremely susceptible to surface-derived contamination because of its largely unconfined nature and highly permeable sands and gravels. In the past decade, the aquifer has become the focus of experts and public concern. This concern has resulted from widespread salinity, nitrate and fluoride; from the detection of agricultural pesticides and fertilizers; and from increased pressures for urban development above the aquifer.

The objective of the present baseline study is to identify and quantify the concentration of pesticides in the groundwater and the topsoil of the Gaza Strip.

MATERIALS AND METHODS

The study area

The Gaza Strip, as one of the most densely populated areas in the world (2638 people/km^2; PCBS, 2000), with limited and declining resources, has already started to suffer the outcomes of environmental quality deterioration. The study area is a part of the coastal zone in the transitional area between the temperate Mediterranean climate to the north east and the arid desert climate of the Negav and Sinai deserts to the south east. As a result, the Gaza Strip has a characteristically semi-arid climate and the hydrogeology of the coastal aquifer consists of one sedimentary basin, the post-Eocene marine clay (Saqiya), which fills the bottom of the aquifer.
The quantity and quality of available water varies over space and time, and is influenced by multifaceted natural and man-made factors including climate, hydrogeology, management practices, pollution, etc.

Two thirds of the Gaza Strip (total 365 km^2) is an agricultural area (PCBS, 2000). Approximately 393.3 t of pesticides and more than 900 t of methyl bromide are used annually to protect the major crops, including vegetables, citrus, olives and grapes (Safi, 2002).

Recently, several pesticides were detected in the major vegetables consumed in Gaza. α and β-endosulfan, chlorpyrifos, carbofuran, chlorfluazuron, triadimenol I and II, penconazole, coptafolmetabolite, pyrimethanil and iprodione were detected and confirmed on some samples of cucumber, tomatoes and strawberries (Safi et al., 2002); however, they were low and below the maximum residue limits.

Sampling

The study area (Fig. 1) is divided into five geographic regions, the northern area, Gaza, the middle area, Khan Yunis and Rafah which represent the main five governorates of the Gaza Strip. Three sampling campaigns have been conducted in three years over the periods: 20 November-12 December 2000, 26 June-17 July 2001 and 25 January -17 March 2002. Soil samples were collected in the last sampling campaign.

Under the water quality testing program about 73 municipal wells and 21 private wells in the Gaza Strip were sampled. At the municipal wells, samples were collected from a tap along the water distribution line. Prior to sampling, the injection of chlorine or sodium hypochlorite into the water system was discontinued so the additive would not interfere with the analysis. In addition to the general locations of wells, Table 1 shows the ID of each well. The wells in the table are ordered from north to south where 17, 26, 8, 15, and 7 wells are chosen from the north, Gaza, the middle, Khan Yunis and Rafah regions, respectively.

In order to assure that the sample collected was from groundwater and not water standing in the well, it was originally proposed that the well should be pumped for a minimum of 1-2 h prior to the collection of the sample; however this was not always possible. The third sampling programme occurred at the end of the winter rainy season, and many private well owners were not using their wells extensively. The average private well has a 10-m depth of standing water in a 30-cm diameter pipe representing a volume of approximately 1 m^3. Therefore 1 h of pumping at a rate ranging between 45 and 70 m^3/h was sufficient to purge at least three standing well volumes. Water samples were collected from municipal groundwater wells (Table 1) used for drinking representing all geographic areas: 17 in the north, 26 in Gaza, 8 in the middle, 15 in Khan Yunis and 7 in Rafah.

For general screening of pesticides in the groundwater of Gaza, 4 water samples were collected in the preparation phase of the study and one month before the actual sampling campaigns. One liter of 4 groundwater wells was collected in glass bottles; 2 from municipal wells and 2 from private wells. The wells were selected according to the agricultural activities in the area. The 4 liters were transported and analyzed in Germany by using the high performance liquid chromatography (HPLC/MS).

In the case of soil, sampling was conducted according to the European soil sampling guidelines (Theocharopoulos et al., 2001). Fifty seven sites were selected to represent all soils of Gaza. The depth of sampling varied between 0-10 cm for the open and grass soils; 20 cm for the vegetable soils; and up to 30 cm for the ploughed soils.
Fifteen soil samples from the greenhouses (vegetables) of three different geographic areas, 6 from fruit farms (olive, peach, guava, citrus), 5 from open vegetable farms, 8 from strawberry farms, and 5 from non-agricultural isolated areas representing local reference sites. At each sampling station, a circle of 2-5-m diameter was identified and 10 sub-samples were collected within the perimeter and mixed to form a composite sample. Samples (0.5 kg) were collected and placed into dark polyethylene cups and stored at 4 ^{o}C until extraction and analysis.

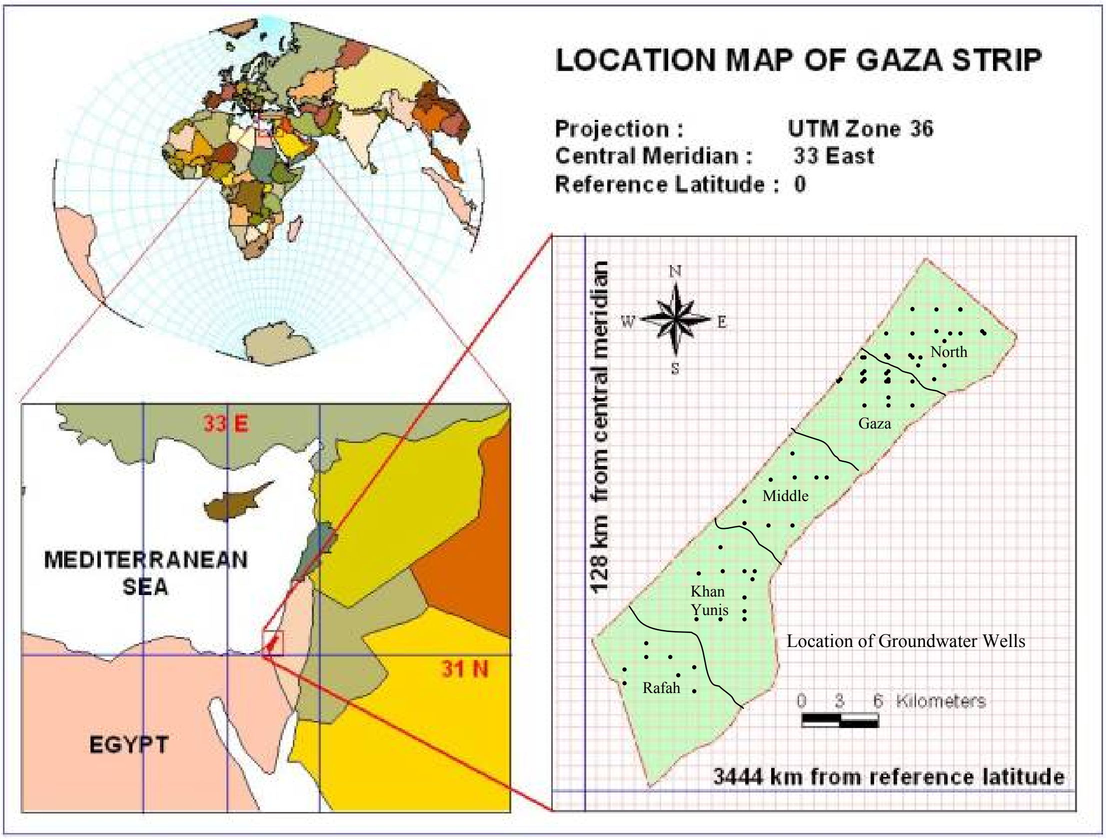

Figure (1) Five regions of the Gaza Strip and location of groundwater wells.

Table (1) Groundwater wells sampled for 3 years.

Region	**Well ID**		**Well ID**		**Well ID**		**Well ID**
North	D/67	Gaza	E/157	Gaza	R/25c	Khan Yunis	L 178A
	D/73		D/68		R/25d		L 179
	D/74		D/69		R/112		L 41
	E/06		D/70		R/254		L 43
	E/10		Q/39		R/265		L 86
	E/11A		R/162L		R/74		L 86A
	E/11B		R/162La		R/75		L 87
	E/11C		R/162Ha	Middle	G1/178		M 2A
	E/138		R/162H		J 146		M 2B
	E/148		R/162G		J 32		N 22
	E/156		R/162F		J 35		N 9
	E/45		R/162E		S 19		T 44
	E/61		R/162C		S 42	Rafah	P 10
	E/8		R/162B		S 69		P 124
	E/90		D/71		T 46		P 138
	E/92		D/72	Khan Yunis	L 127		P 138 old
	Q/40b		R/25a		L 159		P 139
Gaza	E/154		R/25b		L 176		P 144
							P 15

Solvents, chemicals and standards

Aacetone, ethylacetate, methanol, ethanol, acetonitril, n-hexane, cyclohexane, petroleum ether, diethylether, isooctane, toluene, sulfuric acid 95-97% and Phosphoric acid 85% were obtained from Merck (Darmstadt, Germany). Silver nitrate was from Aldrich (Buchs, Switzerland); dodecane and Methyl-t-Butyl-Ether (MTBE) was obtained from Fluka (Buchs, Switzerland). All reagents were tested fusing gas chromatography coupled with mass spectrometer (MS). NaCl, KOH were obtained from Merck and made free of water by heating at 550 °C for 2 h. Silica gel 60 A, 100-200 mesh, was obtained from Merck was activated by previously heating at 300 °C for 12 h, then allowed to cool in a dessicator and later stored in a brown boronsilicate bottle in a dry place.

Pesticide standards: Triclopyr, Picloram, Dicamba, Dichloroprop, 2,4 DB, Mecoprop, Fenoprop, MCPA, MCPB, 2,4-D, 2,4,5-T all from Dr. Ehrensdorfer, Augsburg, Germany and calibration solutions (5 µg/ml) were prepared by dilution of the respective stock solution in methanol; Phenol Kit 27 (standard mix in methanol) is from SUPELCO.INC. Solid reagents were heated at 400 ^{o}C for 5 hours to free them from the interfering organic substances (Stan, 1995). Diazomethane was prepared adapted to de Boer and Baker (1954; see appendices).

Water extraction

Water was collected in 1-liter glass bottle and treated with 5 ml phosphoric acid (85%, analytical grade) followed by 100 µl internal standard solution (5 µg/ml) of 2,4-dichlorophenoxyacetic acid (Ring $^{13}C_6$) in methanol. The bottles were thoroughly shaken and placed in an ice cooling box and later extracted using a solid phase extraction (SPE-cartridge type: Oasis HLB, 200 mg, 6 ccm, 30 µm grain size) technique as described by Stan (1995). The SPE was rinsed with 3 ml ethyl acetate (analytical grade) followed by 3 ml Milli-Q water. The water sample was extracted through the SPE with fixed filtration flow rate of 10 ml/min. At the end of the extraction step, the SPE was washed with 5 ml Milli-Q water and some air was sucked through the cartridge for several seconds. The SPE cartridges were wrapped in aluminum foils in order to protect them from contamination and were kept frozen until they have been sent to Germany for analysis.

For the final preparation of water samples, the solid phase extractors were cleaned by 6 ml methanol/ tert-butyl- methyl ether (TBME), 20:80 (v:v). Then 100 µl of internal standard mix 33 (5 µg/ml) was added. The final volume was reduced to 0.5 ml by a gentle stream of N_2 where it was transferred into measuring vials. 100 µl diazomethane solution were added and the vials were degassed and kept at 4 ^{o}C.

Soil extraction

Soil samples were freeze-dried for 48 h until complete dryness and sieved through a 2-mm sieve. Approximately 10 to 20 g was placed in a Soxhelt extraction-cartridge and extracted over night (12 h) with 75 ml n-hexane/ethylacetate (100:2 v/v). To the extract, 100 µl of the internal standard for the GC/MS (Ehrenstorfer internal standard mix 33, (5µ/ml) was added followed by 1 g anhydrous Na_2SO_4. The samples were evaporated to about 6 ml through a rotary evaporator, then to 1 ml by a gentle stream of N_2. About 0.8 g home made silica gel/$AgNO_3$ (100:5 wt:wt) was poured into the SPE followed by few drops absolute methanol for activation. The SPE cartridges were conditioned by 6 ml n-hexane/ethylacetate. The extract was cleaned by 6 ml n-hexane/ethylacetate where they were received in glass tubes and reduced by a gentle stream of N_2 to 0.5 ml, so an enrichment factor of 20 was reached.

Analytical methods

Table 2 shows the instrument used for the analysis of target pesticides.

GC/MS

Organochlorine pesticides were determined using a gas chromatograph (Agilent GC 6890 N series, Waldbronn, Germany), equipped with cold injection system - CIS (Gerstel, Mülheim, Germany). The detector was mass spectrometer MS-Agilent: 5973 (Waldbronn, Germany). Chromatographic parameters: oven: initial temperature 40 ^{o}C and initial time 1 min; oven ramp level 1: rate 20 ^{o}C/min, final temperature 100 ^{o}C and final time 0.0 min; oven ramp level 2: rate 10 ^{o}C/min, final temperature 310 ^{o}C and final time 3.2 min; oven ramp level 3: rate 100 ^{o}C/min, final temperature 340 ^{o}C and final time 5.0 min; total time 33.5 min. Column parameters: The column was Macherey-Nagel. (30 m x 0.25 mm i.d., 0.25 µm film thickness) mode constant flow; initial flow 1 ml/min; initial pressure 7.04 pound/inch^2 (psi); gas type helium in average velocity 36 cm/sec. MS was in single ion monitoring SIM-Mode.

The application of one internal standard during gas chromatographic analysis is recommended to minimize systematic errors. The internal standard used in this work was 2,4,5-trichlorobiphenyl (TCB), which has physicochemical properties similar to those of the analyzed substances and separated well from all analyzed organochlorine pesticides.

HPLC/MS

HPLC was Agilent System 1100 (Waldbronn, Germany), and the conditions were as follows: PreColumn: Security Guard, SYNERGI Max-RP 4 x 2.0 mm (Phenomenex). Column was SYNERGI Max-RP: 150 mm x 2 mm i.d., 4 µm, 80 Å (Phenomenex), temperature: 30 °C, flow: 0.2 ml/min. Eluents: mobile phase A: 950 ml water, adjusted to pH 2.6 with dropwise addition of formic acid, ad 1000 ml: acetonitrile; degassed. Mobile phase B: methanol, degassed, gradient: linear: 0 until 8 min from 50 to 70% B, 8 until 12 min from 70 to 95% B, 12 until 20 min 95% B.

The detection of the analytes was conducted with MS (Applied Biosystems, API 2000 triple quad system, Langen, Germany). Ionization mode was atmospheric pressure chemical ionization (APCI) and the scan type was multiple reaction monitoring (+MRM). Identification of compounds was performed by comparing their retention times with standards and by their fragment mass ions. Quantification was done using internal quantification. Linearity was identified by using 5 determinations of standard solution in the concentration range of 5 µg/l to 200 µg/l. Software used was Applied Biosystems "Analyst".

Table (2) List of pesticides analyzed and instrument used for analysis.

Pesticide	**Analysis**	**LD[*] (µg/l)**	**Pesticide**	**Analysis**	**LD (µg/l)**
Alachlor	HPLC/MS	0.025	Monolinuron	HPLC/MS	0.05
Atrazine	HPLC/MS	0.025	Monuron	HPLC/MS	0.025
Atrazine-desethyl	HPLC/MS	0.05	Pendimethalin	HPLC/MS	0.025
Atrazine-desisopropyl	HPLC/MS	0.055	Propazine	HPLC/MS	0.025
Azinphos-ethyl	HPLC/MS	0.05	Propiconazol	HPLC/MS	0.05
Benfluralin	HPLC/MS	0.05	Sebutylazine	HPLC/MS	0.025
Bromacil	HPLC/MS	0.025	Simazin	HPLC/MS	0.025
Carbofuran	HPLC/MS	0.05	Terbutryn	HPLC/MS	0.025
Chlorbromuron	HPLC/MS	0.05	Terbutylazin	HPLC/MS	0.025
Chlorfenvinphos	HPLC/MS	0.05	Terbutylazin-desethyl	HPLC/MS	0.05
Chlortoluron	HPLC/MS	0.05	Triadimenol	HPLC/MS	0.05
Cycloat	HPLC/MS	0.05	Triallat	HPLC/MS	0.05
Desmetryn	HPLC/MS	0.035	Trifluralin	HPLC/MS	0.025
Diuron	HPLC/MS	0.03	Aldrin	GC/MS	0.05
Etrimfos	HPLC/MS	0.05	Chlordan	GC/MS	0.05
Fenuron	HPLC/MS	0.025	4,4'-DDD	GC/MS	0.05
Fluometuron	HPLC/MS	0.05	4,4'-DDE	GC/MS	0.05
Hexazinon	HPLC/MS	0.05	4,4'-DDT	GC/MS	0.05
Isoproturon	HPLC/MS	0.05	Dieldrin	GC/MS	0.05
Linuron	HPLC/MS	0.05	Endrin	GC/MS	0.05
Metazachlor	HPLC/MS	0.05	Heptachlor	GC/MS	0.05
Methabenzthiazuron	HPLC/MS	0.025	Heptachlorepoxid	GC/MS	0.05
Metobromuron	HPLC/MS	0.05	Hexachlorbenzol	GC/MS	0.05
Metolachlor	HPLC/MS	0.05	Lindan	GC/MS	0.05
Metoxuron	HPLC/MS	0.025	Methoxychlor	GC/MS	0.05
Metribuzin	HPLC/MS	0.05	Mirex	GC/MS	0.05

LD[*] is limit of detection.

Quality control

Analytical blanks and standards with known concentrations of pesticides were prepared and analyzed using the same procedure and reagents. The extraction efficiencies of pesticides with the SPE cartridges for the target compounds were determined by passing 1000 ml of Milli-Q water spiked with 0.1 µg of each target compound through the cartridges. As a kind of internal quality control, 250-500 µl of same extracted water and soil samples were analyzed in the laboratories of Department of Water Hygiene/Chemistry in the Institute for Hygiene and Public Health at the University of Bonn.

RESULTS

Despite the fact that more than 52 different pesticides were applied across agricultural farmlands in Gaza, only few pesticides were detected in the soils of Gaza and many were found in the groundwater. Generally, no significant difference was observed between the results of same wells for the successive 3 years. The results of same samples analyzed in two laboratories showed ±5% difference. The most important finding of this study was the detection of 12 pesticides in the groundwater (Table 3) and 6 pesticides in the topsoils (Table 4).

Groundwater

The HPLC/MS and GC/MS results showed that 92% of target pesticides in the groundwater were less than the instrumental detection limit.

Also, the results of the analysis indicated low levels of pesticides in 13 of the 94 wells tested. Of the 13 wells, 5 were agricultural wells, and the remaining were municipal wells. The wells are mostly in the areas of Khan Yunis and Rafah.

Bromacil was 0.5 µg/l in Safa 1 and Atrazine-desisopropyl was 0.1 µg/l in Safa 2 (R/25a). Most results of the GC/MS of other target pesticides were generally less than the detection limit. Several private wells in Rafah area showed traces of endrin, heptachlorepoxide, DDT, DDE, and DDD.

Atrazine was detected in 47% of groundwater samples, while atrazine-desisopropyl, propazine, simazine were detected in 40%, 24%, and 13% of water samples, respectively. All showed results above the instrumental detection limit. Two water samples showed 5 µg/l of triadimenol, the wells are private and located in the area of Gaza wastewater treatment plant.

Soil

Several soil samples of strawberry greenhouses in Beit Lahia showed detectable values of propazine, sebutylazine, terbutylazine, 4,4’-DDT, 4,4’-DDE, and 4,4’-DDD. The averages of propazine, sebutylazine and terbutylazine were 19, 13 and 39 µg/kg, respectively. A linear regression $r = 0.87$ was obtained between the occurrence of detected pesticides and soils of strawberry greenhouses.

The results showed that one soil sample had high contents of 4,4'-DDE and 4,4'-DDT which were 1104 and 793 µg/kg, respectively. This sample was collected from the northern area of Beit Lahia in a vegetable farm.

Table (3) Concentration (µg/l, n=3) of various pesticides detected in groundwater wells.

Well ID	Pesticide	Conc.	Well ID	Pesticide	Conc.
E/6	Atrazine	1 ± 0.1	L/43	Terbutryn	1 ± 0.1
E/6	Atrazine-desisopropyl	1 ± 0.1	L/43	Terbutylazin	1 ± 0.3
E/6	Propazine	1 ± 0.2	L/87	Atrazine	1 ± 0.1
E/4	Atrazine	2 ± 0.3	L/47	4,4’DDT	0.008 ± 0.001
E/4	Atrazine-desisopropyl	1 ± 0.1	R/162C	Atrazine	14 ± 2
E/1	Atrazine	2 ± 0.4	R/162L	Atrazine	5 ± 1
E/1	Atrazine-desisopropyl	1 ± 0.2	R/162L	Atrazine-desisopropyl	1 ± 0.2
E/11b	Atrazine	5 ± 0.3	R/162C	Atrazinedesisopropyl	7 ± 2
E/11b	Atrazine-desisopropyl	1 ± 0.1	R/162C	Propazine	8 ± 2
D/20	Atrazine	20 ± 3	R/25	bromacil	0.5 ± 0.02
D/20	Atrazine-desisopropyl	8 ± 0.9	P/101	endrin	6 ± 1
D/20	Simazine	4 ± 0.1	P/101	dieldren	5 ± 1
D/20	Propazine	3 ± 0.1	P/101	4,4’DDT	0.021 ± 0.001
D/72	Atrazine	1 ± 0.1	P/15	Atrazine	6 ± 1
D/68	Atrazine-desisopropyl	1 ± 0.1	P/15	Atrazine-desisopropyl	6 ± 2
D/68	Simazine	1 ± 0.2	P/15	4,4’DDT	0.002 ± 0.001
D/68	Propazine	1 ± 0.2	P/24	Atrazine	8 ± 1
D/74	Atrazine	3 ± 0.3	P/24	Atrazine-desisopropyl	8 ± 1
D/74	Atrazine-desisopropyl	2 ± 0.1	P/139	4,4’DDT	0.002 ± 0.001
D/74	Propazine	1 ± 0.1	P/144	4,4’DDT	0.002 ± 0.001
A/185	Atrazine	4 ± 0.2	P/10	4,4’DDT	0.002 ± 0.001
A/185	Atrazine-desisopropyl	1 ± 0.1	F/191	endrin	0.1 ± 0.01
A/185	Simazine	2 ± 0.2	F/191	4,4’DDT	0.002 ± 0.001
A/185	Propazine	1 ± 0.3	F/191	4,4’DDE	0.006 ± 0.002
A/107	Atrazine	1 ± 0.4	F/191	4,4’DDD	0.006 ± 0.002
A/107	Atrazine-desisopropyl	1 ± 0.2	S/15	4,4’DDT	0.002 ± 0.001
A/180	Atrazine	2 ± 0.5	S/15	heptachlor epoxide	0.003 ± 0.001
A/180	Atrazine-desisopropyl	1 ± 0.3	G/49	Atrazine	1 ± 0.2
A/180	Simazine	1 ± 0.4	K/21	Atrazine	1 ± 0.1
A/180	Propazine	1 ± 0.1	Priv. 1	Simazine	6 ± 1
L/43	Atrazine	5 ± 0.4	Priv. 2	Triadimenol	5 ± 0.7
L/43	Atrazine-desisopropyl	2 ± 0.3	Priv. 3	Triadimenol	5 ± 0.6
L/43	Propazine	1 ± 0.3			

Table (4) Pesticides detected in soil samples.

Soil	Pesticide	Min. (µg/kg)	Max. (µg/kg)	Aver. (µg/kg)	Median (µg/kg)	Stdev.
Strawberry greenhouses farms (n=8)	Propazine	18	20	19	19	0.9
Fruit farms (n=6)	Sebutylazine	13	16	15	15	1.2
Open vegetable farms (n=8)	Terbutylazine	385	410	397	398	10
Strawberry greenhouses farms (n=8)	4,4’DDT	795	823	806	803	10
Vegetable greenhouse farms (n=7)	4,4’DDE	1110	1150	1129	1130	17
Open vegetable farms (n=8)	4,4’DDD	750	795	779	786	16

DISCUSSION

The levels of pesticides found in 92% of the tested wells were below the WHO allowable drinking water standards. Approximately half of the wells, in which pesticides were detected, were below the detection limit for the pesticide in question, and therefore should be used with caution, since at these low levels, the results may not be repeatable; wells P/10 and P/10a are examples of these wells. Some private wells showed a sum of detected pesticides more than the EC standards (1998) and the German legislation (Trinkwasserverordnung, 2001). The later sets a limit of 0.1 µg/l of individual pesticide (for aldrin, dieldrin, heptachlor and heptachlor epoxide the limit is even lower at 0.03 µg/l) and a maximum of 0.5 µg/l for the sum of detected pesticides in drinking water.

The higher detection of pesticides in the groundwater of the southern areas may be due to the presence of large number of greenhouses, which possibly use large quantities of pesticides. The area in the north near well E/45 is also heavily agricultural, with strawberries being a main crop.

The differences in the results of the 3 consecutive years for the same well was insignificant while there was a significant variation in pesticide concentrations for the well depth and location. The deeper the water table, the less likely that pesticides reach groundwater. Most of groundwater wells that showed detectable pesticides have 25-50 m depth. A deep aquifer of municipal wells provides more opportunities and time than does a shallow aquifer of private wells for pesticide adsorption, degradation and other processes to occur. The recharge of rainwater and agricultural activities can carry pesticides down to the aquifer.

There was a correlation between the occurrence of some pesticides in groundwater such as atrazine and water salinity ($r = 0.64$) and this conclusion agrees with Gascon et al. (1998). Most of agricultural wells of the southern area have average Cl concentrations of 1200 mg/l and the highest values of atrazine range between 6-20 µg/l. Wells D20 and E11b in the northern area showed anomalous results as they are old and were used for decades as private wells before they became municipal.

The field surveys revealed that the potential sources of pesticide contamination of private wells include sites used for pesticide storage mainly in the well building, mixing, loading, disposal, or application. Most of private wells are located inside the farm and surrounded by intensive agriculture.

Although many pesticides have been found in the groundwater, few of them were detected in soil samples. They were more abundant in clay soils of the northern area than they were in the southern area where the annual precipitation is lower and the soil is sandy. 4,4'-DDE and 4,4'-DDT, propazine, sebutylazine and terbutylazine were almost the same in the soils of the greenhouses of several areas in the Gaza Strip where they have same vegetables and same loamy soils (sand, silt and clay). These results agree with the findings of Jansma and Linders, 1995; Hatzinger and Alexander, 1997; Chung and Alexander, 1998, 2002; Kolpin, 1998a; Navas and Machin, 2002; Worrall et al., 2002.

Detected pesticides were found in clay soils while none of them was detected in sandy soils. Clay soils -which have higher organic matter- have both a low leaching potential and a high sorption potential. Mobility is always correlated with soil organic carbon content where higher organic carbon contents in the upper soil layer slow down dislocation of pesticides to deeper layers (Burnside et al. 1969; Huang and Frink 1989).

Triazine (atrazine, atrazine-desisopropyl, propazine, simazine and terbutylazine)

Some of the triazine derivatives including atrazine, atrazine-desisopropyl, propazine, and simazine were detected in some wells. Triazines are known to be somewhat persistent in water and mobile in soil (Tchounwou, et al., 2000). In many agricultural areas, triazine metabolites and transformation products such as desethylatrazine and deisopropylatrazine are also commonly found in groundwater, together with their parent compounds (Kolpin et al., 1998b). It has been found that metabolite concentrations in groundwater often exceed parent compound concentrations for triazine herbicides (Kolpin et al., 2000). None of atrazine, atrazine-desisopropyl, propazine and simazine was detected in soil samples; however results of water samples showed that 47%, 40%, 24% and 13%, respectively of these pesticides were >1µg/l in the monitored groundwater wells. The USEPA maximum contaminant level (MCL) drinking water standard for atrazine is 3.0 µg/l (USEPA, 1994).

Atrazine was the only herbicide found in 90% of groundwater samples; however it was not detected in soil samples. Katz et al. (2000) reported that atrazine in soil could be degraded by denitrifying bacteria. Atrazine has the potential to move rapidly in sandy soils with low organic matter content, especially when these soils are irrigated (Chung and Alexander, 2002). This agrees with the findings of atrazine in the southern areas of Gaza where the soil is sandy with very low contents of organic matter (0.5%).

Until its prohibition in many countries including Gaza in 1991, atrazine was substituted mainly by terbutylazine in Germany. Nevertheless, atrazine and its metabolite desethylatrazine are by far the most abundant herbicides detected in shallow groundwater (Tappe et al., 2002). Atrazine is applied with water, liquid fertilizer, or impregnated on dry bulk fertilizer to the soil either as a preplant on the soil surface, pre-plant incorporated, or as a pre-emergence treatment. Atrazine is not approved for fall application but may be applied up to 45 days before planting. It can also be applied after crop emergence.

It is found that farmers of Gaza use atrazine more than any other pesticide because it is highly effective and less expensive compared to other herbicide options currently available. One of the reasons why all atrazine containing products are classified as restricted use pesticides is that atrazine is relatively mobile and can move with water or sediment, through runoff or leaching (USNRCS, 2004).
Although atrazine desisopropyl is a biotic degradation product of atrazine and it was detected in several wells where atrazine was not detected. Bromacil is mainly used on citrus of Gaza and it is easily lost from soil by leaching. However bromacil uptake is mainly via the roots of the plants, it was not detected in any soil sample.

Farmers of Gaza use simazine on many crops especially citrus. However, high amounts of simazine are applied in Gaza; it was not detected in any soil sample but only in groundwater. Several articles (Snedeker and Clark, 1998; DaSilva et al., 2003) indicated that simazine is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution. Furthermore, it is expected that the half-life of simazine in soil of Gaza is short and has been expected to be in the range of few days. This is based on several studies showed that the half-life of simazine is short when: soil in general is sandy to loamy, low organic matter content, pH is neutral to basic, high temperature, low moisture content (Chen et al., 1983; Rahman and Holland, 1985; USEPA, 1994; Redondo, 1997). Consequently, simazine was not detected in any of soil samples. Use of an efficient irrigation management technique could have enhanced simazine’s performance through a decreased leaching of residues.

Terbutylazine belongs to triazines where they are intensively applied in the agriculture of Gaza over the past decades. Terbutylazine was detected in several soil samples of fruit trees, citrus and open vegetable farms. However, atrazine was substituted mainly by terbutylazine in many countries; the later was not detected in groundwater but only in soil samples.

Propazine was found in 24% of groundwater wells and was the major detected pesticide in several soil sites. Propazine has a high potential to leach into groundwater. It was detected in 90% of soils of greenhouses. Propazine is moderately persistent to degradation under aerobic soil conditions, degrading with half-lives of 12 to 24 weeks in nonsterile loamy sand and 8-12 weeks in sterile loamy sand soils.

DDT, DDE and DDD

DDT was banned in several countries, but is still used in Gaza. Traces of DDT and its breakdown products DDE and DDD were detected in several soils of Gaza as well as in several groundwater wells of Khan Yunis and Rafah areas.

DDT adsorbs strongly to soil (Fischer et al., 1993; Thompson et al., 1999; Bacchetta et al., 2001; Binelli and Provini, 2003); breaks down slowly to DDE and DDD by light and microorganisms (Spencer et al., 1996; Morrison et al., 2000). Half life of the DDT in soil is 2-15 years, depending on the type of soil (Wiberg et al., 2001). Due to strong adsorption to soil, only a small amount of DDT migrates through the soil into groundwater (Hung and Thiemann, 2002). Consequently, few wells in Rafah area, where the soil is sandy; showed some DDT and its breakdown products.

CONCLUSIONS

1. Several pesticides were detected in the groundwater of Gaza and the minority has concentrations exceeded their respective WHO maximum contaminant levels or health advisory levels for drinking water.
2. Private groundwater wells showed higher contents of pesticides than the municipal wells. The levels of pesticides found in the municipal wells were at levels well below the water quality guidelines, and many were at levels close to the detection limit for the method and should therefore be used with caution.
3. Several factors affecting the occurrence of pesticides in the groundwater of Gaza; soil type, aquifer characteristics and meteorological conditions, well location, well depth and groundwater quality.

CHAPTER EIGHT

Heavy Metals in Major Solid-Pesticides Used in the Gaza Strip (*)

ABSTRACT

Two different techniques were used to determine different elements in pesticides; a semi-quantitative EMMA-XRF technique followed by ICP/OES were used to test the concentrations of Al, As, Ba, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sc, Se, Sr Ti and Zn in the most used 53 different species of solid pesticides collected from many markets of the Gaza Strip. The results revealed that the tested pesticides contain considerable amounts of heavy metals and they do not comply with the expected-theoretical structure of each species; moreover, they don't reflect the actual constituents mentioned in the trade labels. Interviews with market owners and field surveys confirmed that pesticides were not pure and they have been mixed in local markets with minor inorganic species without a scientific basis; or they have been smuggled to Gaza with different impurities. The results propose that pesticides should be considered as a source of certain heavy metals (Cu, Mn, and Zn) and other elements (Br, Sr and Ti) that may affect their mass balances in soil and groundwater as well as plant uptake; and different scenarios and calculation models of heavy metal transport in soil and groundwater of the Gaza Strip should include pesticides as an additional source of certain heavy metals.

Key words: Gaza Strip, Heavy metals, Pesticides.

(*) *The study was submitted to an International Journal.*

INTRODUCTION

Researchers on pesticides focus on the organic dimension while the inorganic field has been neglected or has been less investigated. This could explain the shortage in the literature about the existence of heavy metals in pesticides as it is assumed that the chemical structure of pesticides is well known, labeled or documented. But this is not the case in many countries, especially in the developing countries. Pesticides have greatly improved the agricultural production world-wide and have shown to be very effective to control vector-borne diseases. However, their indiscriminate use and improper application raise great concern because of the hazards and risks they pose to human beings and the environment (Abu Middain, 1994). They represent a variety of different chemical characteristics (Stan, 1995); they can be bound in different ways such as metal complexes.

Pesticides including their heavy metal constituents have been found in contaminated groundwater and soil. Contamination resulting from leaching of pesticides is a common and growing problem in major agricultural regions (Flury, 1996; Roberts, 1996). For example, bromacil and hexazinone are often detected in groundwater in the areas that they are used (Hebb and Wheeler, 1978; Kubilius and Bushway, 1998; USGS, 1998). Pesticides that have heavy metals in their chemical structure (fosetyl-aluminum, propineb, mancozeb, maneb and copper oxychloride) were detected in groundwater of many regions in the world. A recent study categorized a wide range of pesticides as ‘‘leachers’’ or ‘‘non-leachers’’ for a specific Hawaii hydrogeological setting (Li et al., 2001b). In the United States, a considerable body of work exists relating to the occurrence of both parent compound pesticides and their metabolites in groundwater aquifers (Baker et al., 1993; Lawrence et al., 1993; Kolpin et al., 2000a,b). The US Geological Survey (USGS) has conducted extensive sampling of groundwater for pesticides throughout the Midwestern United States. The findings of this work have been reported extensively. The study used results from 100 monitoring wells sampled by the USGS. These wells were a subset of a study of 303 wells originally sampled in 1991, the subset being chosen by a stratified random design based on geography and aquifer class. The data from this subset were chosen for this study rather than that from the larger initial survey because they were analysed over a period of 2 years. The compounds analyzed were: alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine and terbutryn (Kolpin, 1997; Kolpin et al., 1995, 1998a,b; Kolpin et al., 2000a,b). Moreover, occurrence of pesticides in soil was reported in many locations of the USA and Canada (Wiberg et al., 2001).

The main goal of this paper is to introduce a general method for determination of heavy metals in solid pesticides; and to reveal the heavy metal contents and some elements in 53 pesticides which are intensively being used in Gaza. A secondary objective is to prove that even pesticides originally with no heavy metals in their chemical structure have impurities of such metals that have been added by local markets.

MATERIALS AND METHODS

Study area

Pesticides are considered priority pollutants in Gaza and, with the expanding use of greenhouses; Palestinian agriculture is becoming increasingly dependent on chemical pesticides and fertilizers. In the Gaza Strip, a few reports have identified some of malpractices of pesticides use by shop owners, farmers and agricultural workers. Similarly, the use of extremely toxic pesticides that are banned or restricted in many countries are being used in Gaza (Haapala, 1993). Nevertheless, poor medical records, absence of health surveillance and monitoring systems and absence of legislation and control systems, have resulted in a lack of awareness among shop owners, farmers and the public (Hulshof, 1991). Consequently, farmers continue to use pesticides excessively without being aware of the hazards they cause to their own health, that of the consumers, and the environment (Issa, 2000). Moreover, there is no monitoring of pesticide residues in agricultural crops that endanger the health of the whole population (UNRWA, 1993). More than 200-250 metric tons of formulated pesticides are used annually in the Gaza Strip, and about 90% is imported from Israel while the other 10% is manufactured locally. Since there is no restriction on the sale and use of pesticides, farmers have easy access to all of them including the banned, the highly toxic and the restricted species, and they do not have to show a special permit or require special training before buying them (Happala, 1993; Hulshof, 1991; Issa, 2000). There are around 55 pesticide shops in the Gaza Strip and there are no wholesalers; all pesticides come from Israel through Israeli Arab wholesalers, who usually get most of their products from Israeli pesticide companies and sometimes from agents for imported chemicals (UNRWA, 1993; SCF, 1991). Since there is no monitoring either on the sale of pesticides, or on their chemical composition (there are neither laboratories nor facilities for this purpose), adulteration and fraudulent sale of pesticides are common practices (Abu Middain, 1994; Hulshof, 1991).

There are about 400 officially registered pesticides in Israel, some of which are banned for use in industrialized countries due to their high toxicity, low biodegradability, and mutagenic or carcinogenic potential. In addition there are pesticides registered in Israel that have not been registered in the countries of origin.

Sampling and analysis

Fifty-three solid samples of pesticides were collected between March and May 2002. Samples were collected from 5 private stores in Gaza, and they were bought in the same storage containers, the majority of which are commercial plastic, some other are made of polyethylene and few are metallic containers. Table 1 shows the pesticide samples and the chemical formula of each one as well as its use. It was found that same pesticides have different names not only in different shops but also sometimes in the same shop; they were treated independently in the analysis procedure. Table 1 also shows the similarities between numbers 3, 31; 9, 30; 12, 13; 20, 52 and 35, 50.

Samples were freeze-dried until complete dryness then the non-powder species were ground until they were very soft.

EMMA-XRF

As a rough estimating technique, pesticide samples were measured using the Energy-dispersive Miniprobe Multielement Analyzer-X Ray Fluorescence (EMMA-XRF) (Cheburkin, and Shotyk, 1996). Direct analyses were conducted for K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr and Pb. The EMMA-XRF analyzer was designed for trace element analysis of plant soil and rock samples. The analyzer used monochromatic excitation with the energy of 19.6 keV. The software includes a possibility to normalize the peak area of each element by intensity of incoherent scattering radiation. This feature allows the elimination of the matrix effect for samples with a different matrix. However, with the extremely wide range of matrices for pesticide samples even such normalizing does not work well. Some of pesticide samples have a very heavy matrix due to the presence of high concentration of Mn, Cu, Zn and Br.

The EMMA-XRF analyzer has been calibrated using different Standard Reference Materials (SRM) like: NIST 1575 (Pine needles); 1632b (Coal); 1635 (Coal); G-2 (Granite); BCR60 (Olive leaves); BCR62 (Aquatic plants); MAG-1(Marine mud); W-1 (Diabase). The SRMs are made by the National Institute of Standards & Technology, NIST USA. The CRB Standards have been produced by Community Bureau of Reference, Commission of the European Communities. One of the problems is that these SRMs have very different matrices from those of many pesticide samples and this means that it was not easy to make a precise calculation of trace elements in some pesticide samples. Generally, the analytical data for trace elements in such pesticides are semi-quantitative and may have a relative error up to 30%.

ICP/OES

As the results of the EMMA-XRF are semi-quantitative and showed a signal to go for detailed quantitative determination, full digestion procedure and ICP instrument was used. The samples were handled with great care, under a hood, and about 0.5 to 1.0 grams of the homogenized sample were dissolved with 10 ml of concentrated nitric acid (Merck 65% p.a.) in 50 ml retorts. The samples were allowed to degas (24 h), and then they were heated on a sand bath to 50 ^{o}C for 30 minutes then to 160 °C for 3 hours. After cooling, the solutions were diluted with Milli-Q water in 50 ml volumetric flasks, then filtered through 0.45 µm pore size membrane filters and transferred in 100 ml polyethylene bottles for analysis. Elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sc, Sr and Zn) were analyzed by ICP/OES (VISTA-MPX, VARIAN). The detection limit of the ICP/OES was estimated 10% less than the lowest standard used for calibration.

Quality control

For quality control, analytical blanks and 2 reference materials with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents. The reference materials were pine needles (American National Bureau of Standards, Washington, D.C. 20234, 1976). Precision was estimated evaluating the reproducibility between the duplicates and a coefficient variation of lower than 5%.

Table (1) List of 53 collected samples of solid pesticides used in the Gaza Strip.

No.	Common Name	Chemical Formula*	Type
1	Methomyl	$C_5H_{10}N_2O_2S$	Insecticide
2	Benomyl	$C_{14}H_{18}N_4O_3$	Fungicide
3	Fosetyl-aluminum	$C_6H_{18}AlO_9P_3$	Fungicide
4	Chlorothalonil	$C_8C_{l4}N_2$	Fungicide
5	Propineb	$(C_5H_8N_2S_4Zn)_x$	Fungicide
6	Mancozeb	$[-SCSNHCH_2CH_2NHCSSMn-]_x\ (Zn)_y$	Fungicide
7	Aluminum Phosphide	AlP	Pesticide
8	Carbaryl	$C_{12}H_{11}NO_2$	Insecticide
9	Sulphur 704	S_x	Insecticide
10	Sulphur 904	S_x	Insecticide
11	Chinomethionat	$C_{10}H_6N_2OS_2$	Insecticide
12	Maneb	$C_4H_6MnN_2S_4$	Fungicide
13	Aldicarb	$C_7H_{14}N_2O_2S$	Insecticide
14	Permethrin	$C_{21}H_{20}Cl_2O_3$	Insecticide
15	Warfarin	$C_{19}H_{16}O_4$	Rodenticide
16	Bromacil	$C_9H_{13}BrN_2O_2$	Herbicide
17	Bromadiolone	$C_{30}H_{23}BrO_4$	Herbicide
18	Dicofol	$C_{14}H_9Cl_5O$	Acaricide
19	Pyrethroid	$C_{21}H_{20}Cl_2O_3$	Insecticide
20	Manage-imibenconazole	$C_{17}H_{13}Cl_3N_4S$	Fungicide
21	Aminotriazole	$C_2H_4N_4$	Herbicide
22	Chlorobenzilate	$C_{16}H_{14}Cl_2O_3$	Acaricide
23	Trichlorfon	$C_4H_8Cl_3O_4P$	Insecticide
24	Azinphos-methyl	$C_{10}H_{12}N_3O_3PS_2$	Insecticide
25	Carbaryl	$C_{12}H_{11}NO_2$	Insecticide
26	Foscthyl-Aluminum	$C_6H_{18}AlO_9P_3$	Fungicide
27	Copper Oxychloride	$ClCu_2H_3O_3$	Fungicide
28	Copper Sulfate	$CuH_{10}O_9S$	Fungicide
29	Metalaxyl	$C_{15}H_{21}NO_4$	Fungicide
30	Simazine	$C_7H_{12}ClN_5$	Fungicide
31	Metaldehyde	$C_8H_{16}O_4$	Molluscicide
32	DDT	$C_{14}H_9Cl_5$	Insecticide
33	Fenbuconazole	$C_{19}H_{17}ClN_4$	Fungicide
34	Terbutryne	$C_{10}H_{19}N_5S$	Herbicide
35	Etaconazole	$C_{14}H_{15}Cl_2N_3O_2$	Fungicide
36	Amitrole	$C_2H_4N_4$	Herbicide
37	Bromadialone	$C_{30}H_{23}BrO_4$	Rodenticide
38	Trifluralin	$C_{13}H_{16}F_3N_3O_4$	Herbicide
39	Metiram	$(C_{16}H_{33}N_{11}S_{16}Zn_3)_x$	Fungicide
40	Dichlofluanild	$C_9H_{11}Cl_2FN_2O_2S_2$	Herbicide
41	Simazin	$C_7H_{12}ClN_5$	Herbicide
42	Terbutryne Ametryne	$C_{10}H_{19}N_5S$	Herbicide
43	Bromacil	$C_9H_{13}BrN_2O_2$	Herbicide
44	Linuron	$C_9H_{10}Cl_2N_2O_2$	Herbicide
45	Triazine	$C_7H_{12}ClN_5$	Herbicide
46	Zineb	$C_4H_6N_2S_4Zn$	Fungicide
47	Dimethoate	$C_5H_{12}NO_3PS_2$	Insecticide
48	Baycor	$C_{20}H_{23}N_3O_3$	Fungicide
49	Captan	$C_9H_8Cl_3NO_2S$	Fungicide
50	Chinomethionet	$C_{10}H_6N_2OS_2$	Fungicide

*) *From the Pesticide Manual (PCPC), 1997.*

RESULTS AND DISCUSSION

General reading of the results

Tables 2 and 3 show the results of EMMA-XRF and ICP/OES keeping in mind that the final calculations (Table 4) are obtained from the ICP/OES results except for Br. Generally, tested elements were not only found in the corresponding first 14 pesticides shown in table 4, but some heavy metals were also found with high amounts in other pesticides which do not have these metals in their structure table 1 and 3. Based on the results, the collected samples can be classified into two categories: the ones that have one or more of the tested elements in their structures and showed positive results; and the ones that have none of the collected elements in the structure but showed them in the analysis. Fourteen samples only have one or more of the tested elements in their structures and the concentration of the corresponding element is measured and calculated to compare the measured and the calculated values (Table 4). The calculated value of each element was obtained from the percentage it represents in the chemical formula of the relevant pesticide. Ten samples also showed the highest concentrations of the tested elements, and although they have none of the tested elements in their chemical structure they showed anomalous contents of corresponding element (Table 4). For the first category of the tested pesticides, the calculated value of each element is much higher than the measured value (Table 4). Al, for example, in fosetyl-aluminum was 4 times higher than the measured value and it was 3 times higher in the second sample of the same pesticide; Zn was 11, 6, 1 and 12 in propineb, mancozeb, metiram, and zineb respectively; Mn was 4 and 9 times higher than the measured value in mancozeb and maneb respectively; Br 3 times higher in the two samples of bromacil; while it is 6895 and 9480 times higher in the two samples of bromadiolone; and finally Cu was 2 times higher in both copper oxychloride and copper sulfate.

The second category of pesticides represents the species that have none of the tested elements in their structure but they showed high amounts of them. The last 10 pesticides in table 4 clearly showed the amounts in mg/kg dry weight.

Some pesticides of the first category showed high amounts not only of the metal present in their structure but also other metals not present in their structure; a good example is copper oxychloride which has high amounts of Pb; copper sulfate showed high amounts of Ni; and maneb showed high amounts of Fe beside the Mn as well.

Table (2) Heavy metals and some elements in 54 pesticide samples collected from Gaza, results of the EMMA-XRF.

LD	**0.05**	**0.05**	**30**	**20**	**20**	**10**	**2.5**	**1.5**	**1**	**1.5**	**0.6**	**0.7**	**0.7**	**0.8**	**0.6**
Element	**K**	**Ca**	**Ti**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Br**	**Rb**	**Sr**	**Pb**
Unit	**%**	**%**	**ppm**	**ppm**	**Ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
1	0.0	0.0	0	0	10	**33**	0	0	0	0	0	0	0	0	7
2	0.0	0.0	0	0	23	**22**	0	7	0	0	0	0	0	0	0
3	0.0	0.0	388	0	0	**642**	0	0	7	0	0	0	8	3	5
4	1.0	0.0	425	0	76	**1327**	0	0	6	0	0	3	37	127	18
5	0.0	0.0	0	0	884	**3768**	0	0	>10.0%	0	0	260	18	0	0
6	0.0	0.0	0	0	>10.0%	0	0	0	17500	0	0	0	0	0	0
7	0.0	0.0	0	0	0	**1211**	0	6	6	50	0	7	0	8	0
8	0.0	0.0	0	0	15	**304**	0	22	9	0	0	0	23	0	0
9	0.0	0.0	4072	0	0	**4295**	0	7	9	0	0	4	2	96	11
10	0.0	0.0	118	0	28	**229**	0	10	7	0	0	0	0	6	0
11	0.0	0.0	184	0	560	**373**	0	0	14	0	2	2	0	7	0
12	0.0	2.0	10012	0	19011	**10939**	36	32	940	4	0	5	19	303	18
13	0.0	2.0	10911	0	19980	**11474**	0	23	923	0	0	6	20	322	17
14	0.0	6.0	456	0	110	**4514**	0	0	12	0	0	9	0	452	4
15	1.0	0.0	1052	0	67	**5639**	45	10	63	0	0	81	21	45	3
16	0.0	3.0	19	0	22	**103**	0	0	7	0	0	3	9	12	0
17	0.0	0.0	0	0	0	0	0	0	0	0	0	>10.0%	0	0	0
18	0.0	0.0	189	0	0	**164**	0	0	0	0	0	22	0	0	0
19	0.0	1.0	831	0	72	**4513**	23	8	540	11	0	473	73	54	0
20	0.0	0.0	12025	0	20	**9623**	21	18	13	0	0	9	6	173	31
21	0.0	4.0	0	0	>10.0%	0		0	1875	0	0	0	0	56	0
22	0.0	0.0	0	0	179	**214**		0	12	0	0	195	0	0	0
23	0.0	>10.0%	5853	81	81	**7790**	42	17	210	13	3	32	9	1261	7
24	0.0	5.0	8126	57	32	**8901**	22	10	102	3	0	18	6	723	14

Table (2) continued

Element	**K**	**Ca**	**Ti**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Br**	**Rb**	**Sr**	**Pb**
Unit	**%**	**%**	**ppm**	**ppm**	**Ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
25	0.0	4.0	5833	48	31	**7444**	14	36	83	0	0	48	13	188	13
26	0.0	0.0	5063	26	187	**8029**	17	2318	3748	3	0	26	13	105	20
27	0.0	0.0	440	0	0	**843**	0	0	8	0	0	3	7	4	8
28	0.0	0.0	0	0	0	**4000**	0	>10.0%	0	0	0	0	0	0	0
29	0.0	0.0	0	0	0	**5977**	0	>10.0%	0	0	0	0	0	0	0
30	0.0	0.0	0	0	>10.0%	0	0	0	20927	0	0	73	12	0	0
31	0.0	>10.0%	0	0	0	**116**	0	0	0	0	0	10	0	70	11
32	1.0	2.0	0	0	208	**126**	0	178	69	0	0	9	5	9	0
33	0.0	>10.0%	4032	35	41	**5153**	32	29	245	3	0	21	0	1323	16
34	2.0	0.0	1205	0	0	**7463**	0	7	25	4	0	5	133	57	9
35	0.0	9.0	532	0	313	**4550**	0	8	46	0	0	23	16	57	4
36	0.0	0.0	1991	0	62	**2748**	0	0	16	0	0	70	23	15	0
37	0.0	4.0	7694	49	38	**7959**	0	15	95	0	1	0	8	647	18
38	0.0	0.0	0	0	47	**72**	0	19	33	0	0	16	3	4	0
39	0.0	0.0	0	0	121	**512**	0	7	18	0	0	28	24	15	12
40	0.0	0.0	0	0	6885	**553**	0	0	>10.0%	0	0	32	11	21	0
41	0.0	0.0	0	0	0	**419**	0	41	7	0	0	13	25	11	0
42	0.0	>10.0%	0	0	97	**83**	0	0	10	0	0	11	0	72	9
43	0.0	0.0	0	0	64	**3014**	0	6	44	0	0	151	15	10	0
44	0.0	0.0	0	0	0	0	0	0	0	0	0	>10.0%	0	0	0
45	5.0	7.0	974	0	0	**6143**	0	445	37	14	0	6	171	1359	0
46	0.0	>10.0%	66	0	42	**1318**	0	18	13	0	0	3	4	446	7
47	0.0	0.0	158	0	589	**2684**	0	37	92	5	0	6	176	51	8
48	0.0	0.0	0	0	>10.0%	0	0	0	17819	0	0	0	0	0	0
49	0.0	0.0	0	0	106	**315**	0	0	8	0	0	0	0	8	0
50	2.0	0.0	1116	0	49	**7004**	0	0	22	4	0	5	126	50	10
51	0.0	0.0	871	0	0	**3747**	0	28	0	4	0	3	16	21	12
52	0.0	0.0	2155	0	16	**3072**	0	306	14	0	0	72	22	20	30
53	0.0	0.0	0	0	>10.0%	0	0	0	10288	0	0	0	0	0	0
54	0.0	0.0	0	0	219	**3697**	0	16	89	13	0	15	176	124	16

Table (3) Heavy metals and some elements in 50 pesticide samples collected from Gaza, results of the ICP/OES.

	Mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Sample	**Al**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sc**	**Sr**	**Zn**
1	47	5.5	0.1	BDL	0.4	0.4	17	2	7.3	BDL	28	2	1
2	1	0.8	0.1	BDL	BDL	1.4	BDL	5	5.1	BDL	43	2	3
3	65140	8.0	0.3	BDL	1.6	4.0	250	3	5.6	1.4	36	4	7
4	4428	193.0	4.3	42.0	1.1	1.7	802	56	8.5	5.5	55	12	9
5	1255	2.6	0.5	BDL	1.7	2.4	584	102	4.0	0.3	29	3	20277
6	381	2.2	0.1	BDL	BDL	9.4	414	4634	58.6	15.5	28	5	10913
7	233475	8.3	0.1	0.2	3.5	8.8	1398	284	8.7	BDL	29	6	63
8	1269	9.4	0.1	BDL	0.0	42.4	171	24	4.9	1.4	35	10	18
9	2542	4.5	1.3	4.8	9.9	16.0	3275	6	3.9	2.6	28	22	5
10	5	1.5	2.7	10.4	BDL	11.1	248	5	6.0	0.2	50	17	7
11	23364	33.8	0.1	0.3	40.7	40.2	5123	22536	20.5	10.5	48	150	1224
12	25560	35.1	2.9	0.8	42.7	28.0	5183	23339	21.2	10.5	48	156	1316
13	2509	28.2	0.5	BDL	5.8	2.8	2386	106	11.8	0.6	55	482	12
14	3927	40.0	0.2	BDL	17.9	8.4	2657	24	28.3	0.2	44	20	66
15	6074	27.5	0.1	BDL	BDL	1.1	159	38	6.0	1.0	49	12	35
16	1038	5.2	2.0	0.6	2.4	1.4	374	28	9.2	BDL	60	11	125
17	256	15.5	0.5	BDL	BDL	1.8	27	3	16.8	BDL	137	8	8
18	8475	44.1	1.8	8.0	19.8	14.6	2389	77	35.1	3.9	91	33	713
19	6881	32.6	0.1	BDL	33.5	19.3	4671	5	9.5	5.4	71	47	5
20	4465	3.0	27.8	0.1	BDL	2.0	323	14059	26.9	14.3	78	49	2997
21	60	1.9	5.0	BDL	BDL	0.8	46	208	8.0	BDL	61	3	34
22	28670	80.3	0.3	BDL	125.0	26.9	5891	15	33.1	7.1	49	823	316
23	32785	71.0	0.4	BDL	74.8	22.7	5543	15	24.5	9.3	82	457	152

Table (3) continued

	Mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Sample	**Al**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Sc**	**Sr**	**Zn**
24	11661	30.7	0.4	BDL	23.9	37.7	4239	30	26.8	1.5	139	76	95
25	6838	26.9	0.3	BDL	13.0	2471.5	2897	97	21.6	10.6	154	44	3603
26	74735	11.9	0.4	BDL	0.5	5.0	280	6	15.2	1.9	110	7	8
27	1395	23.5	0.3	BDL	12.9	169791.7	1822	19	88.5	2790.9	101	19	1149
28	81	2.6	17.2	28.7	BDL	135129.7	108	11	1742.8	BDL	120	4	338
29	33	2.0	1.7	BDL	BDL	104.1	280	21021	21.3	15.7	116	4	20852
30	708	56.1	0.3	BDL	4.3	28.7	99	46	16.0	7.8	113	42	9
31	33	23.8	0.4	BDL	BDL	284.5	88	280	24.3	BDL	149	16	95
32	66897	216.6	0.7	BDL	252.1	102.7	9150	25	70.6	16.1	139	1958	870
33	2345	46.6	0.2	BDL	0.8	5.9	958	15	10.3	0.9	68	8	10
34	4479	86.5	7.9	BDL	12.0	3.2	1804	431	17.9	BDL	116	35	68
35	5432	12.5	0.3	BDL	2.7	3.0	273	73	18.0	3.9	137	11	16
36	37451	83.1	0.2	BDL	80.8	35.2	5663	36	26.4	10.6	92	473	144
37	8	2.4	11.7	BDL	43.0	16.2	56	35	12.1	BDL	77	7	31
38	1276	19.3	0.3	BDL	BDL	6.4	111	141	13.3	11.2	106	13	23
39	606	11.1	0.3	BDL	BDL	5.3	174	2996	13.8	40.7	94	18	52715
40	1669	14.8	0.8	BDL	BDL	66.4	171	15	15.6	0.5	119	16	62
41	566	57.4	0.5	BDL	0.5	1.1	79	82	11.0	8.3	83	40	20
42	5281	13.2	0.2	BDL	19.5	17.3	2765	123	18.9	BDL	100	10	193
43	328	5.1	0.3	BDL	BDL	2.6	295	208	14.3	1.8	99	19	36
44	4256	56.4	2.9	26.6	BDL	622.0	159	15	14.3	0.9	117	1119	7
45	594	225.4	0.3	BDL	2.9	29.6	725	95	20.7	5.0	125	396	24
46	208	3.8	0.4	BDL	BDL	13.3	423	22760	82.4	16.7	128	8	20114
47	42	6.3	0.6	BDL	BDL	1.5	191	15	13.5	BDL	101	11	5
48	5510	12.6	0.4	BDL	10.8	19.2	1618	23	17.7	4.2	129	8	6
49	6923	18.2	0.4	BDL	4.1	335.7	373	19	19.0	9.2	141	20	129
50	8132	146.2	0.5	BDL	0.1	16.9	1039	190	20.0	9.1	155	66	99

Comments on the field surveys

A very serious situation exists with respect to pesticide use, due to the exceedingly large volumes used and the lack of information available in Arabic, to wholesalers, farmers and others dealing with pesticides. Gaza is suffering of absence of legislations, limited experience, shortage in the qualified individuals, in addition to the key point that pesticides are present in unspecialized shops and they are handled and sold by low or uneducated persons. The absence of governmental monitoring and inspection systems coupled with limited awareness among pesticide users allow the later group to store pesticides under bad conditions. Because pesticides are very expensive, some shop owners mix different pesticides without scientific rules and the field visits revealed some of this practice. During the application of pesticides, farmers spray, eat and smoke at the same time, disregarding the general instructions of spraying. Around 24 chemical pesticides that have been prohibited or restricted worldwide are still being used in the Gaza Strip; examples of such pesticides are Lindane, Dorspan, DDT, Tamaron and others.

Leniency in laws against irresponsible use of pesticides and lack of government and social awareness programs allow toxic and dangerous pesticides to easily reach the hands of the people.

Malpractices include sales of pesticides that have passed their expiration date; internationally wrong labeling containers to sell cheap products at high prices; and sale of organic and inorganic chemicals instead of pesticides. Another dangerous problem is the labels of the pesticide's containers. As the wholesalers import pesticides in big containers, they divide big size containers into small ones (mostly made of plastic) as the final containers have the commercial name in the best cases and only numbers in the majority. Although farmers of Gaza are very professional, they do not have the access either to information on pesticide application, safety and storage measure or to pesticides adverse effects on human health and environment.

Table (4) Calculated and measured values of some elements.

Pesticide	**Chemical Structure**	**Tested Element**	**Calculated value (mg/kg)**	**Measured value (mg/kg)**
Fosetyl-aluminum	$C_6H_{18}AlO_9P_3$	Al	245455	65140
Propineb	$(C_5H_8N_2S_4Zn)_x$*	Zn	224293	20277
Mancozeb	$[-SCSNHCH_2CH_2NHCSSMn-]_x (Zn)_y$	Mn, Zn	25500, 200000	4634, 10913
Maneb	$C_4H_6MnN_2S_4$	Mn	207312	23339
Aluminum phosphide	AlP	Al	224000	233475
Bromacil	$C_9H_{13}BrN_2O_2$	Br	>30%	>10%
Bromadiolone	$C_{30}H_{23}BrO_4$	Br	151688	22
Foscthyl-Aluminum	$C_6H_{18}AlO_9P_3$	Al	245455	74735
Copper Oxychloride	$ClCu_2H_3O_3$	Cu	299625	169792
Copper Sulfate	$CuH_{10}O_9S$**	Cu	256308	135130
Bromadialone	$C_{30}H_{23}BrO_4$	Br	151688	16
Metiram	$(C_{16}H_{33}N_{11}S_{16}Zn_3)_x$	Zn	59704	52715
Bromacil	$C_9H_{13}BrN_2O_2$	Br	306396	>10%
Zineb	$C_4H_6N_2S_4Zn$	Zn	235678	20114
Triazine	$C_7H_{12}ClN_5$	Ba	0	225
Manage-imibenconazole	$C_{17}H_{13}Cl_3N_4S$	Cd	0	28
Terbutryne	$C_{10}H_{19}N_5S$	Co	0	42
Amitrole	$C_2H_4N_4$	Cr	0	125
Linuron	$C_9H_{10}Cl_2N_2O_2$	Cu	0	622
Maneb	$C_4H_6MnN_2S_4$	Fe	0	5183
Chinomethionat	$C_{10}H_6N_2OS_2$	Mn	0	22536
Copper Sulfate	$CuH_{10}O_9S$	Ni	0	59
Copper Oxychloride	$ClCu_2H_3O_3$	Pb	0	2791
Carbaryl	$C_{12}H_{11}NO_2$	Sc	0	154
DDT	$C_{14}H_9Cl_5$	Sr	0	1958
Manage-imibenconazole	$C_{17}H_{13}Cl_3N_4S$	Zn	0	2997

*) Theoretical monomer
**) Pentahydrate

CONCLUSIONS

1. Tested pesticides have considerable amounts of heavy metals and there is no agreement between measured and calculated values; the calculated values are much higher.
2. The same pesticides have different names in the same shop and in different shops, as well as different amounts of the same heavy metals.
3. Many tested pesticides have no heavy metals in their chemical structure in the pure form but they have them in the marketed forms in Gaza.
4. The field surveys revealed that the contamination of pesticides by heavy metals may occur due to bad procedures of storage and preservation; mixing of some pesticides in the market itself without scientific rules; and finally the absence of legislations and governmental inspection programs.
5. Pesticides should be considered as a source of some heavy metals in soil and groundwater of the Gaza Strip and they should be included in mass balance and geochemical cycle of some heavy metals.

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APPENDICES

Preparation and digestion of soil, sediment and sludge samples

Soil, sediment and sludge samples could be found as:
* Dry samples or
* Wet samples.

Collection and preparation:

- Open and grass soils: 0-10 cm deep.
- Vegetable soils: 20 cm deep.
- Ploughed soils: 30 cm deep.

At each sampling station, a circle of 2-5-m diameter to be identified and 10 sub-samples to be collected within the perimeter and mixed to form a composite sample. Remove all plant tissues and large stones. Samples (0.5 kg) to be collected using a stainless steel dredge, placed into polyethylene cups and stored at 4 ^oC. Approximately 0.5 kg of soil was put in polyethylene cups and stored at 4 ^oC during transport to laboratories where soil was dried in an oven at 50 ^oC until constant weight. Then they were shipped to Germany in plastic sampling bags. The samples were sieved through a 20-µm sieve and ground to a very soft powder. The sample could be used for all cations including heavy metals, C, N, S, B, F and P. For organic parameters samples should be dry-frozen for 48 hours.

Preservation:

Keep the samples in dark and dry conditions or in the refrigerator at 4 ^oC.

Digestion of soil, sediment and sludge samples for heavy metal and P analysis

1. In glass beakers, weight 0.5 or 1 to 2 g of each sample in duplicates (depending on the expected range of heavy metals and phosphate; for sludge samples 0.5 g is enough, for soil 1-2 g).
2. Under a hood, add 3.3 ml HNO_3 (65%), shake gently. Add 9.9 ml HCl (37%), shake gently by using a glass rod. The ratio is 1 conc. HNO_3: 3 conc. HCl.
3. Use acids only as blanks, and known Standard Reference Materials (SRM) as a reference. Blanks and SRF should be treated as samples and digested together.
3. Cover the beakers by glass-watches.
4. Leave at room temperature for 1 to 2 days for dissolving and degassing.
5. Place the samples in a sand bath at 160 ^oC for 3 to 4 hours, increase the temperature gradually and avoid boiling by shaking the beakers from time to time.
6. Transfer beaker contents to a 50-ml volumetric flask including all sample residues, mix well and complete the total volume up to 50 ml by dH_2O.
7. Filter the samples by using normal filter paper into plastic containers 100 ml.
8. Keep at room temperature until analysis.

Determination of soil pH

1. Take about 10 g of dry soft soil.
2. Add 20 ml of $CaCl_2$ (0.01 N).
3. Wait for about 1 hour.
4. Measure by the pH electrode.

Determination of total fluorides in soil samples

Sample preparation:

1. Take about 50 mg dry-sieved sample in a nickel crucible.
2. Add 2 g 1:1 Na_2CO_3-K_2CO_3 (anhydrous dried at 110 ^{o}C overnight).
3. Place in the oven (a muffle furnace) at 800 ^{o}C for 15 minutes.
4. After cooling, add 15 ml of 1 M citric acid to the crucible and allow the mixture to digest until CO_2 evolution is no longer detected (3-4 hours, or preferably overnight). (1M citric acid prepared by dissolving 210.15 g citric acid monohydrate in 1 liter dH_2O).
5. Add 25 ml of sodium citrate buffer (1M) to the contents of the crucible. (Prepared by dissolving 294 g Sodium citrate dihydrate in about 800 ml dH_2O, adjust the pH to 6 with 6N HCl and finally dilute the solution up to 1 liter).
6. Transfer the mixture to a 100-ml polypropylene beaker.
7. Carefully rinse the crucible with dH_2O.
8. Dilute the sample solution to 100 ml by dH2O.

Reagents:

Stock fluoride solution:
- Dissolve 2.21 g anhydrous (dried at 110 ^{o}C overnight) sodium fluoride (NaF) in distilled water and dilute to 1 liter, **1000 mg/l is produced**. (or use the MERCK stock 1000 ppm).

Sodium hydroxide (NaOH) 6 N:
- Dissolve 60 g NaOH in 250 ml dH_2O.

Fluoride buffer solution:
- Place about 500 ml dH_2O in a 1-liter beaker.
- Add 57 ml glacial acetic acid.
- Add 58 g NaCl.
- Add 4 g 1,2 cyclohexylenediamineteteraacetic acid (CDTA = trans-1,2-Diaminocyclohexane-N,N,N,N-tetraacetic acid.).

<u>Note:</u> CDTA can be replaced by EDTA.
- Stir to dissolve, place beaker in a cold water bath and add slowly 6 *N* NaOH (about 125 ml) with stirring until pH is between 5.3 and 5.5.
- Transfer to a 1-L volumetric flask and complete the volume up to 1 liter by dH_2O.

Determination of inorganic carbon in soil samples using a carbonate bomb to measure total inorganic carbon as % $CaCO_3$

Procedure:

1. Weight exactly 0.74 g of dry-sieved soil sample.
2. Place the wt. in the measuring bottle.
3. Add 25% HCl (6N) into the internal chamber of the bomb head, up to the mark.
4. Close the bottle vertically very tight.
5. Let the acid flow to the sample in the bottle, shake very well (don't touch the bottle but only the head).
6. Wait until you have constant reading which represents % $CaCO_3$.

NOTES:

a) When the sample has high amounts of $CaCO_3$, the reading will appear very fast, but when it has high $MgCO_3$ then you have to wait up to 15 minutes.
b) Use a reference material (Calcite $CaCO_3$ which gives 99.2% $CaCO_3$) each 15-20 samples. When the reference material gives less than 99.2% then include a correction factor in the final results.
c) The meter can minimally read 5% and more, when the sample gives less than 5% then you can use (X) 0.74 g sample.
E.g. 2*0.74 = 1.48 g or even 3*0.74 = 2.22 g.
The final reading should be divided by X
e.g. 1.48 g sample gives 8% CaCO3, so the final $CaCO_3$ is 8/2 = 4%

How to prepare 6N of HCl?

1. When you have a concentrated acid of 12 N (in the label), take acid to water v/v (1:1).
2. When the normality or the molarity is not labeled:
    Density = 1.19 g/ml.
    Purity = 37%.
    M.wt. = 36.5 g.
    Needed volume to be prepared = 1000 ml (1liter).

Molarity = No. moles/liter
No. moles = weight (g)/M.wt(g)

$$\text{Weight} = \frac{\text{Density} * \text{volume (ml)} * \text{purity \%}}{100}$$

$$\text{Molarity} = \frac{1.19 * 1000 * 37}{36.5 * 100} = 12.06 \text{ M (or N).}$$

Note: Molarity of HCl 35% = 11.4 M

Preparation of Diazomethane

Important:

Diazomethane was prepared using the method of de Boer and Baker (1954). Every step of this reaction has to be performed under a hood with a security glass pane. Diazomethane is poisonous, carcinogenic and mutagenic.

Preparation:

- Dissolve 8 g KOH in 20 ml ethanol/water (90:10 v/v) in a 250 ml double-necked round bottom flask.
- The flask is equipped with a magnetic stirrer and mounted on a heating bath (filled with water or glycerol).
- Dissolve in a separate vessel 5 g N-methyl-N-nitroso-p-toluenesulfonamide in 50 ml diethylether under stirring or shaking.
- Place a dropping funnel containing the ethereal solution on top of the two-necked flask.
- Connect a distillation bridge with a Vigreux coloumn to the flask. The receiving flask for the distillate is cooled in an ice bath.
- Heat the reaction flask to about 50-60 °C.
- Now add slowly under stirring the ethereal solution drop by drop.
- Collect about 30 ml of the distilled yellow diazomethane solution in ether.
- Pipette it into three 10 ml tubes (screw cap with Teflon liners).
- Store them at -18 °C.

Finally neutralize the alkaline reaction mixture with HCl. Decontaminate all glassware, which has been in contact with diazomethane which dilute acetic acid.

Caution! Diazomethane is highly volatile, toxic and carcinogenic. Work under a hood and apply the usual precaution measures carefully! A suitable destroying agent against spilled Diazomethane solution is acetic acid.

Reference:

de Boer T J, Baker H J. (1954) A new method for the preparation of Diazomethane. *Recl. Trav. Chim.* Pay-Bas **73**, 229-234.

Extraction procedure and sample preparation for the combined GC/MS Analysis of PAHs, PCBs, Chlorobenzenes and non-polar chloropesticides in soil and similar materials

Chemicals and reagents:

1. Extraction solvent of cyclohexane/ethylacetate (100:2) **(only if present)**
   - mix 1000 ml cyclohexane + 20 ml ethylacetate.

2. Extraction solvent of n-hexane/ethylacetate (100:2)
   - mix 1000 ml n-hexane + 20 ml ethylacetate.

3. Silica gel/ $AgNO_3$ (100:5 wt:wt): to adsorb all polar groups during the extraction process:
   - Dissolve 50 g $AgNO_3$ in about 30 to 50 ml dH_2O.
   - Weight 1 kg of commercial silica gel.
   - Mix the $AgNO_3$ and the silica gel very well, divide the mixture into 3 glass bottles (each 1 l volume) about 2/3 of each.
   - Place in the rotating shaker for about 24 hours.
   - Dry and mix all bottles to form homogenous mixture.
4. Anhydrous sodium sulfate (Na_2SO_4) as a dehydrating agent.
5. Internal standard: (Ehrenstorfer internal standard mix 33, diluted by cyclohexane to a concentration of 5µg/ml.

Sample preservation and preparation for the Extraction:

1. Freeze-dry the samples for 48-72 hours depending on the water content.
2. Sieve the samples through < 2 mm.
3. Store in cool and dark (about -18 ^oC stand for years).

Extraction procedure:

First: Soxhlet Extraction (12 hours)

1. In a beaker, take about 10-15 g dry soil sample.
2. Transfer to the filter thimble by a plastic funnel.
3. Place the filter thimble in the Soxhlet extraction assembly.
4. Take 75 ml of **n-hexane/ethylacetate** (100:2) in a 100 ml spherical flask.
5. Connect the upper end of the Soxhlet extraction assembly to the cooler by using a Teflon ring seal, be sure the system is tight.
6. Connect the lower end of the Soxhlet extraction assembly to the spherical flask.
7. Adjust the water current of the cooler.
8. Adjust the temperature to the boiling point of the solvent (about 50 ^oC), level 2.
9. Leave it overnight (about 12 hours).

Notes:

*The filter thimbles may be reused by drying them under the hood and emptying them.

* Do not use grease for the glassware, but use Teflon rings only.

Second: Rotating Evaporation:

1. After the extraction, remove the filter thimble and leave to dry under the hood.
2. To the extraction, add 100 µl of internal standard for the GC/MS (Ehrenstorfer internal standard mix 33, (5µ/ml).
3. Add 1 spatula (1-2 g) anhydrous Na_2SO_4, shake and leave to settle down.
4. Transfer all contents **(without Na_2SO_4 ppt.)** to a pear-shaped (special spherical) flask with graduated centrifuge tube at the bottom.
5. Use a Teflon ring and connect the pear-shaped flask to a rotating evaporator and use a plastic ligament to connect the upper part of the flask to the cooling system.
6. Keeping the following conditions: the pressure is adjusted at **260** mbar, the speed is between 3-4 rpm, and the water temperature is between 40-50 ^{o}C. Close the cooling glass helix upper valve during evaporation.
7. Reduce the total volume into 2-3 ml.

Switch the system off (the thermostat, the pressure and the instrument, open the helix valve gently).

Third: Volume Reduction and SPE System:

1. Under a gentle current of N_2 gas, reduce the volume into 1-2 ml only. The probe inside the flask bottom should not touch the extract.
2. Use a **6-ml SPE florisil cartridge** (a magnesium silicate), (filled with a combination of several absorbents). Fix it to the extraction beaker. Inside the beaker, place a plastic centrifuge-tube in the corresponding position to the cartridge.
3. Add few drops (about 1 ml) of absolute methanol to the SPE to activate its content.
4. Fill the cartridge with about 2 ml solvent (n-hexane/ethylacetate).
5. By using a dry funnel, pour in SPE ca. 0.8 g home made silica gel/$AgNO_3$.
6. Condition and clean with 4 ml solvent.
7. As soon as the liquid level has reached the solid phase surface, close the small tap and discard the 5-6 ml solvent of the tube (from the beaker) into the wastes.
8. During this step the column should remain wet, transfer the concentrated extract (about 1 ml) gently to the column.
9. Add 6 ml solvent above the sample extract, open the small tap and leave to percolate to the surface of solid phase. (Add 2 ml solvent in 3 steps).
10. The collected liquid is about 5-6 ml (in the centrifuge tube inside the beaker).
11. Reduce the extract into 1 ml under a gentle current of nitrogen gas.
12. Transfer to the autosampler vials (glass cells), close well, label and keep in the refrigerator (4 ^{o}C) for analysis (can stand for few years).

Notes:

1. If there are impurities in the column, you can use a vacuum to achieve flow rate of filtrate (1-2 ml/minute).
2. Clean the extraction **SPE**-system (small taps you used), by fixing an empty cartridge, then add about few mls acetone (**or** ethylacetate) for rinsing (allow to leave then close the tap), followed by 4 ml solvent.
3. The empty cartridge are dried under the hood and been used again.
4. Used cartridge: let them dry under the hood and collect the silver-containing upper phase in a special container of wastes for recycling.

Fourth: Preparation of Blank

Use only an empty filter thimble and do the exact procedure of extraction.

Fifth: Preparation of Reference Standard (identify extraction procedure)

1. Use a clean sample (soil or sediment), after 12 hours Soxhlet extraction, dry the filter thimble under the hood. Take the clean sample and weigh few grams (or take the entire amount available).
2. Use 75 ml Cyclohexane, and connect the flask to the Soxhlet extractor.
3. Place the filter thimble inside the Soxhlet and by a long pipette:
4. Add **1 ml** of PAHs standard (500 ng/ml).
5. Add **1 ml** of PCBs and Pesticides standard (500 ng/ml).
6. Do the rest as usual.

Sixth: Efficiency of Cleaning Procedure

1. In a centrifuge tube, place **1 ml** of PAHs standard (500 ng/ml) and **1 ml** of PCBs and Pesticides standard (500 ng/ml).
2. Add **100 µl** of the internal standard for the GC/MS (Ehrenstorfer internal standard mix 33, (5µ/ml).
3. Reduce the volume by $\mathbf{N_2}$ gas into 1 ml.
4. Continue the SPE procedure as usual.

Important:

Determination of PAHs, PCBs, Chlorobenzenes and non-polar chloropesticides in groundwater by Using HPLC/MS.

The prepared vials could be used for HPLC by minor modifications in the solvent used.

Modification Procedure:

- Transfer 500 µl of the old vials to new clean vials (Keep the rest for the GC/MS analyses later).
- Under N_2 gentle current, dry the contents of the vials to complete dryness or to very minute droplet.
- Add 1 ml (absolute methanol: dH_2O) 1:1 v/v. to each vial.
- Shake, leave for few minutes and close well.
- Label the new vials of water and soil samples.

Water extraction for polar and medium-polar compounds

Reagents and solvents:

1) Absolute methanol.
2) 1,3,5-trimethoxybenzene (ready in the refrigerator).

Internal Standard Solution:

1) 2,4-D (Ring **$^{13}C_6$**) with concentration of 5 µg/ml. Store the standard solution cool, if possible, and in the dark. Tightly close the bottle immediately after every use.
2) Ethyl acetate (analytical grade).
3) Acetonitril (analytical grade).
4) Phosphoric acid (85 %, analytical grade).
5) Internal standard: (Ehrenstorfer internal standard mix 33, diluted by cyclohexane to a concentration of 5µg/ml.
6) PAHs standard (500 ng/ml).
7) PCBs and Pesticides standard (500 ng/ml).
8) Explosives standard (2000 ng/ml = 2µg/ml).
9) Diazomethane solution (in deep freezer).
10) Major Pesticides:
- *Triclopyr (5 µg/ml) = (5 mg/l).*
- *Picloram (5 µg/ml).*
- *Dicamba (5 µg/ml).*
- *Dichloroprop (5 µg/ml).*
- *2,4 DB (5 µg/ml).*
- *Mecoprop (5 µg/ml).*
- *MCPA (5 µg/ml).*
- *MCPB (5 µg/ml).*
- *2,4-D (5 µg/ml).*
- *2,4,5-T (5 µg/ml)*

11) Methanol/ Tert-Butyl- Methyl Ether (TBME), 20:80 (v:v).
(take 20 ml Methanol and 80 ml MTBE and mix).

Extraction procedure:

1. In a glass-container cleaned and dried in an oven over night at 120 °C, and later on washed many times by methanol, collect 1 liter of the groundwater sample.
2. Add 5 ml phosphoric acid (85 %, analytical grade)
3. Add 100 µ l internal Standard solution 2,4-D (Ring $^{13}C_6$).
4. Add 100 µl of 1,3,5-trimethoxybenzene.
5. Add 100 ml absolute methanol.
6. Shake thoroughly
7. **As standard sample, add 100 µl of each of the following standards:**
    - *Triclopyr (5 µg/ml).*
    - *Picloram (5 µg/ml).*
    - *Dicamba (5 µg/ml).*
    - *Dichloroprop (5 µg/ml).*
    - *2,4 DB (5 µg/ml).*
    - *Mecoprop (5 µg/ml).*

- Fenoprop (5 µg/ml) ***(if present).***
- MCPA (5 µg/ml).
- MCPB (5 µg/ml).
- 2,4-D (5 µg/ml).
- 2,4,5-T (5 µg/ml)
Add 1 ml of PAHs standard (500 ng/ml) and1 ml of PCBs and Pesticides standard (500 ng/ml) and 100 µl of Explosives standard (2000 ng/ml = 2µg/ml).

8. Shake very well.
9. As Blank sample, use 1 liter of Milli-Q dH2O (add every thing except the standards).
10. Use a fresh SPE-cartridge type: Oasis HLB, 200 mg, 6 ccm, 30 µm grain size.
11. Condition the SPE as shown in the figure.
12. Rinse the SPE with 3 ml Ethyl acetate (analytical grade), then rinse again with 3 ml d-water.
13. Discard the received 6 ml as waste.
14. Connect the assembly as shown in step (3) extraction and adjust the flow rate at ca. 10-20 ml/min
15. At the end of the extraction step, suck some air through the cartridge for several seconds. Freeze or - if possible - freeze-dry the cartridge. Wrap it in aluminum foil in order to protect it from contamination. Keep frozen or - if freeze-dried - store cool in the dark in a closed container. In this state it can be maintained virtually for an unlimited duration.
16. For final preparation and for measurements, rinse the SPE by 6 ml methanol/TBME solvent.
17. Add 100 µl of internal standard mix 33 (5 µg/ml).
18. Reduce the final volume into ca. 500 µl by a gentle current of N_2.
19. Transfer to measuring vials, add 100 µl Diazomethane solution, N_2 gas is librated from the vials, cover them and leave for one hour at room temperature to allow all N_2 to liberate and finally, close the vials very well, keep in the refrigerator at 4 ^oC.

IMPORTANT:

a) One standard is used to chick the accuracy and the performance of the enrichment step, **do not do steps 3 and 4** and add 100 µ l internal Standard solution 2,4-D (Ring $^{13}C_6$) then 100 µl of 1,3,5-trimethoxybenzene to the extract after step 16 above .

b) For Comparison, you can try 6 ml ethylacetate, or 6 ml acetonitril in new SPEs). Use another two solvents, **do not use methanol in step 16** and to the first standard add 6 ml ethylacetate, and to the second add 6 ml acetonitril.

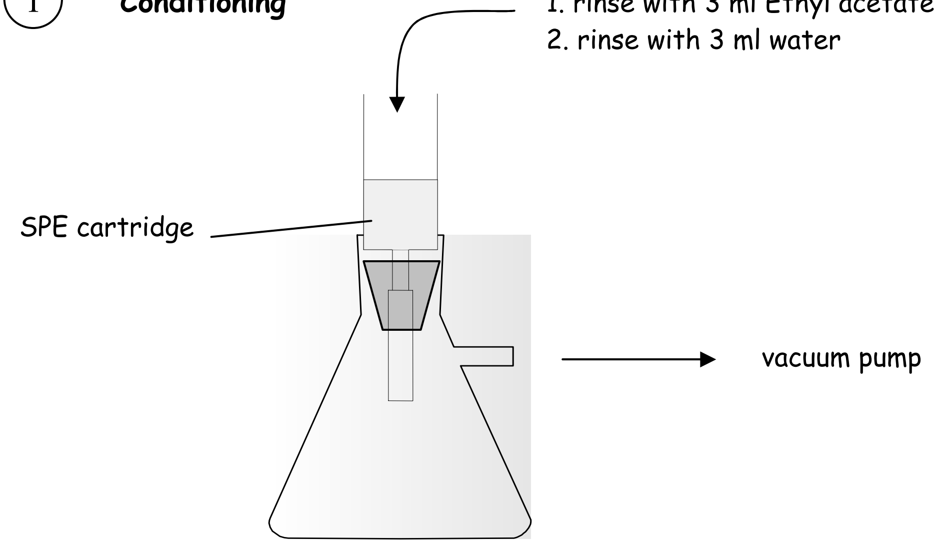
Solid phase extraction (SPE) procedure for water samples using commercial SPE Cartridges

Used SPE-cartridge type: Oasis HLB, 200 mg, 6 ccm, 30 µm grain size.

Steps

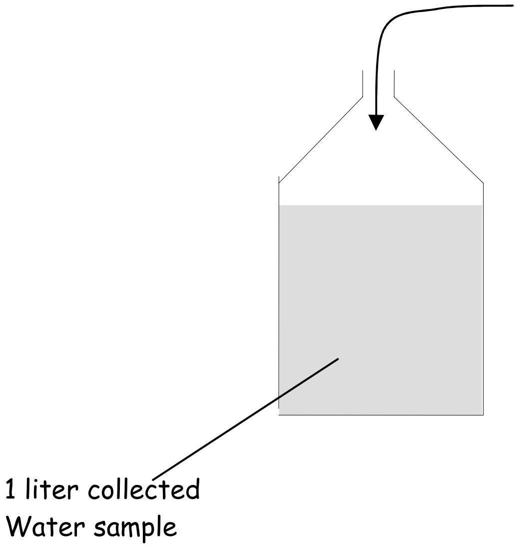
① Conditioning

1. rinse with 3 ml Ethyl acetate (analytical grade)
2. rinse with 3 ml water



② Sample preparation

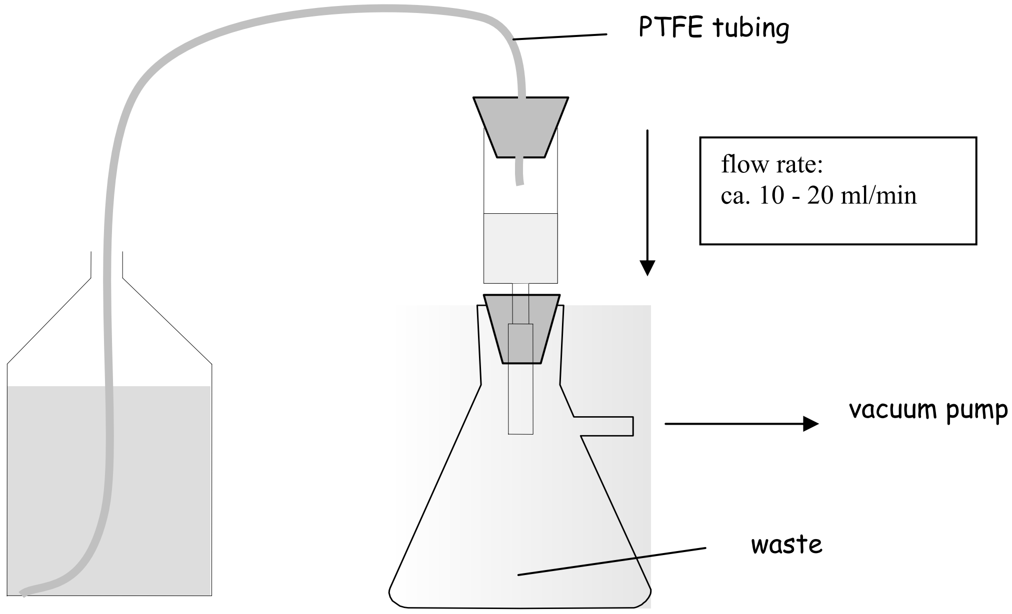
1. add 5 ml phosphoric acid (85 %, analytical grade)
2. add 100 µl internal standard solution (ring $^{13}C_6$) (*)
3. shake thoroughly



(*) contains 500 ng 2,4-D (ring $^{13}C_6$).
This step may be omitted, if the standard is not available at the sampling site. In this case the internal standard must be added in the laboratory later during SPE re-extraction.

Note: Function of phosphoric acid (H_3PO_4) is to donate protons.

③ Extraction



④ Storing conditions

At the end of the extraction step, wash with 5 ml distilled water (analytical grade) and suck some air through the cartridge for several seconds. Freeze or - if possible - freeze-dry the cartridge. Wrap it in aluminium foil in order to protect it from contamination. Keep frozen or - if freeze-dried - store cool in the dark in a closed container. In this state it can be maintained virtually for an unlimited duration.

Internal Standard Solution

The internal standard is:
2,4-dichlorophenoxyacetic acid (ring $^{13}C_6$) in Methanol.
Conc. = 5 µg/ml.

⑤ Re-extraction and final preparation

1. Place the SPEs in the freeze-dryer for 48 hours (open the Al-foil but don't remove).
2. **Add 100 µl internal standard solution (ring $^{13}C_6$) directly to SPE.**
3. Re-extract the SPE with 6 ml TBME (Tert. Butyl methylether) solvent.
4. To the receiving tube, add 0.4 g anhydrous Na_2SO_4. (to adsorb water and moisture).
5. Stir and leave the tubes for about 30 minutes.
6. Transfer the solvent (avoid the ppt of Na_2SO_4) to new tubes.
7. Reduce the final volume into ca. 500 µl by a gentle current of N_2.
8. Transfer to measuring vials, **add 100 µl Diazomethane solution**, N_2 gas is librated from the vials, cover them and leave for one hour at room temperature to allow all N_2 to liberate and finally, close the vials very well, keep in the refrigerator at 4 °C.

Preparation of standards used for determination of polar and medium-polar compounds in water samples

We are searching for three groups of compounds:
1) Phenoxy acetic acid (e.g. 11 standards herbicides).
2) PAHs and PCBs (including chloropesticides).
3) Phenols. (Phenol kit 27. (Standard mix in Methanol) is from SUPELCO.INC under Cat. No. 4-4570).

Standards are prepared in the same procedure of water samples

1. In **3** clean- dry 1000 ml sampling bottles (in an oven over night at 120 °C, and later on washed many times by methanol), collect 1000 ml Elga-water (Milli-Q Water).
2. Add 5 ml phosphoric acid (85 %, analytical grade)
3. Add 100 μ l internal Standard solution 2,4-D (Ring $^{13}C_6$).
4. Add 5 ml absolute methanol. Shake thoroughly.

5. Bottle (a) Standards of Phenoxy acetic acid:
Add 100 μl of each of the following standards:

1) Triclopyr (5 μg/ml).
2) Picloram (5 μg/ml).
3) Dicamba (5 μg/ml).
4) Dichloroprop (5 μg/ml).
5) 2,4 DB (5 μg/ml).
6) Mecoprop (5 μg/ml).
7) Fenoprop (5 μg/ml) ***(if present).***
8) MCPA (5 μg/ml).
9) MCPB (5 μg/ml).
10) 2,4-D (5 μg/ml).
11) 2,4,5-T (5 μg/ml.

6. Bottle (b) Standards of PAHs and PCBs:
Add the mixture of following standards:
- In a centrifuge tube, Mix **1 ml** PAHs standard (500 ng/ml) and **1 ml** of PCBs and Pesticides standard (500 ng/ml) and **also: 100 μl** Internal standard: (Ehrenstorfer internal standard mix 33 diluted by cyclohexane to a concentration of 5μg/ml) **in a tube**.
- Reduce the volume under **N_2** gas to dryness (leave only one small drop).
- Add 3 ml acetonitril.
- For complete dissolution, put into ultrasonicator (u.s bath) for about 5 minutes.
- Add the mixture to the sampling bottle.

(**Note**: the mixing step and the complete dissolution of the standards with this solvent is important to water samples. The solvent changes cyclohexane into water miscible Acetonitril).

7. Bottle (c) Standards of Phenols:
Add 0.5 ml of phenol kit 27 (1-50, conc. = 10mg/100ml).

8. Shake the three bottles very well.
9. Use a fresh SPE-cartridge type: Oasis HLB, 200 mg, 6 ccm, 30 μm grain size. Condition the SPE (Step 3) as shown in the figure and extract (Step 5 from point 3 to 8).

Coordinates of municipal wells in the Gaza Strip used in this study

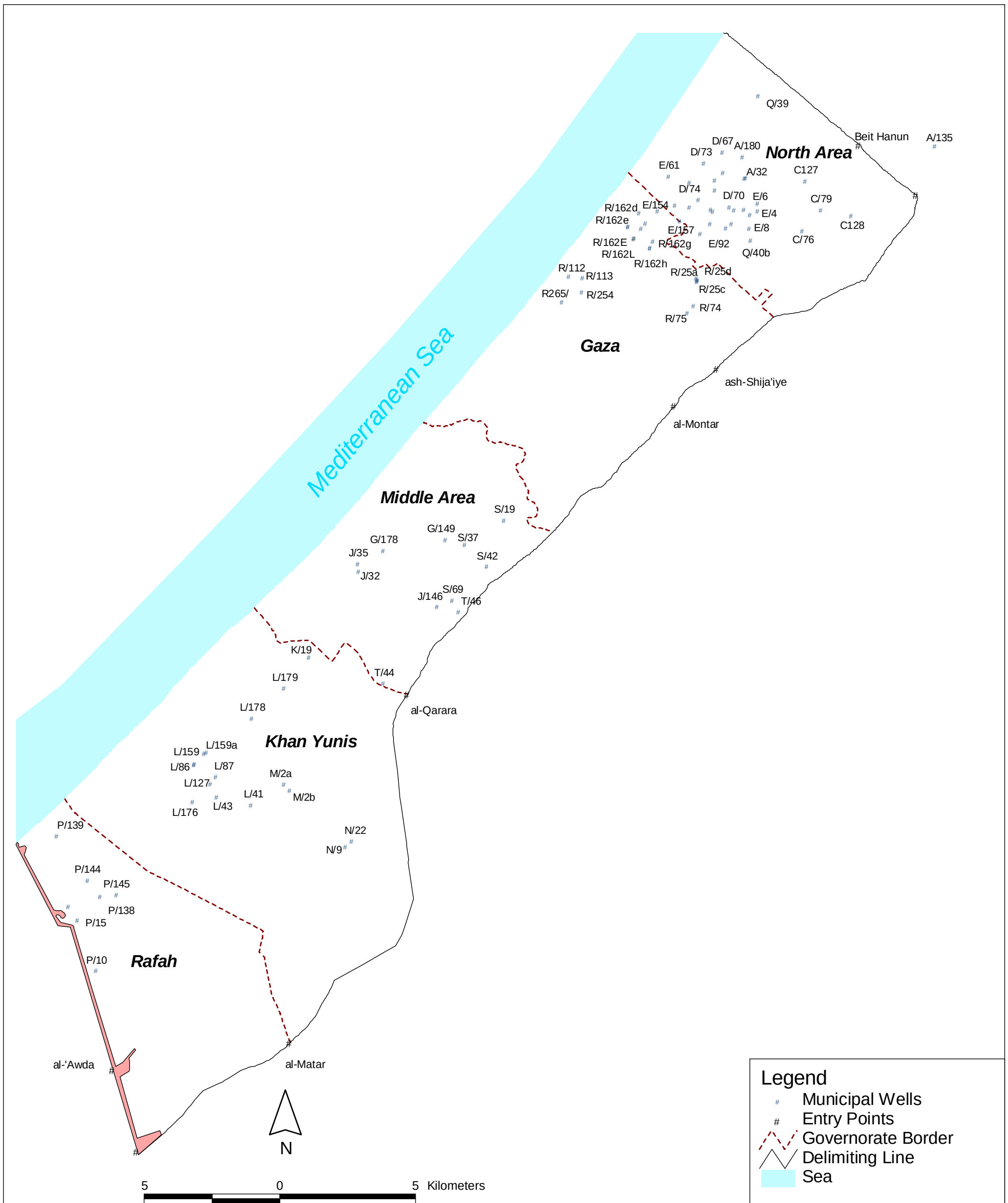
Name	ID	(X)	(Y)	(Z)
Indus. Area Iriz	A/135	109560	107460	40
Ghabn	A/180	102458.9	107032.7	24.071
Al Mashrooa'	A/185	102530	106252.3	40.629
Al Majlis	A/32	102583.8	106270.5	40.015
Assalatin-old	D/67	101715.9	107217.9	22.902
Assalatin-new	D/73	101036.5	106827.4	22.902
Al Izba	C127	104777.6	106153.9	57.238
Abu Ghazala	C128	106476.9	104891.2	66.019
Industrial estate	C/76	104667.1	104337.1	41.098
Awqaf	C/79	105349.3	105095.3	42.45
Abu Sharkh-East	D/2	101379.3	105027.6	40.23
Abu Sharkh-West	D/60	101286	105111.8	35.978
Aamer	D/74	100503.7	106104.1	39.986
Ashshwa	E/6	103013.3	105334.3	35.165
Al Alami	E/10	102522.5	105106	38.162
UNRWA-1	E/11a	101845.1	104418.8	35.8161
UNRWA-2	E/11b	102164.8	105095	28.4091
UNRWA-3	E/11c	101970.5	105190.4	33.8914
Abu Rashid	E/138	102719.8	104398.4	41.34
Ashanti	E/142	99980	105260	
Abu Talal	E/156	102066.9	104589.4	27.207
Al Bahtimi	E/4	103034	105064.1	37.885
Murad	E/61	99737.38	106339.3	44.753
Atturk	E/8	102740	104910	40
Al Khazzan	E/90	101277.9	104582.7	46.205
Al Majlis	E/92	100910	104230	
Nammar	Q/40b	102769	103963.3	55.001
Abu Haseera	E1			

Coordinates of municipal wells in the Gaza Strip…..*continued*

Name	**ID**	**(X)**	**(Y)**	**(Z)**
Sheikh Radwan 8	E/154	99330.04	105052.3	43.634
Sheikh Radwan 9	E/157	100155.9	104669.8	26.235
Sheikh Radwan 10	D/68	100513.6	105179.3	22.848
Sheikh Radwan 7	R/162h	99054.74	103698.8	33.049
Sheikh Radwan 7a	R/162ha	99049.88	103698.8	34.45
Sheikh Radwan 1a	R/162La	98480.54	104045.3	57.796
Sheikh Radwan 1	R/162L	98441.98	104037.2	56.88
Sheikh Radwan 11	D/69	100834.7	105466	27.499
Asalia	Q/39	103040	109300	53.5
Sheikh Radwan 12	D/70	101439.9	105833.2	24.894
Sheikh Radwan 12	D/72	101739.3	106462.4	21.591
Sheikh Radwan 3	R/162b	98725.4	104402.2	53.504
Sheikh Radwan 4	R/162c	98866.31	104595.4	50.544
Sheikh Radwan 5	R/162d	98638.31	104989.9	39.853
Sheikh Radwan 2	R/162e	98247.77	104479.3	40.033
Sheikh Radwan 6	R/162f	98480.54	104045.3	
Sheikh Radwan 13	R/162g	99165.91	103952.4	35.715
Ashija'ea 4	R/66b			
Ashija'ea 2	R/75	100417.2	101298.9	42.053
Ashija'ea 3	R/74	100661.2	101542.9	44.657
Sheikh Ejleen 3	R265/	95809.39	101707.6	39.099
Sheikh Ejleen 4	R/113	96558.03	102588.6	40.96
Sheikh Ejleen 2	R/254	96542.39	102055.5	36.055
Sheikh Ejleen 1	R/112	96061.2	102650.2	20.712
Assafa 4	R/25d	100819.9	102495.9	34.456
Assafa 3	R/25c	100774.7	102456	34.44
Assafa 1	R/25b	100778.7	102527.2	33.108
Assafa 2	R/25a	100758.5	102581.4	32.269
Sheikh Radwan 15	D/71	101458	106192.9	27.969
Sheikh Radwan 2	R/162E	98247.77	104479.3	40.033
Deir Balah-East	T/46	91983.82	90272.48	78.541
Deir Balah-2	S/69	91767.68	90702.94	67.685
Deir. B. Abu Bashir	G/178	89227.91	92534.58	24.01
Al Maghazi-Bin Said	S/42	93032.33	91934.48	74.81
Al Maghazi-Municipality	S/37	92220.31	92755.94	42.871
Al Bureij	S/19	93660	93660	94910
Deir Balah-3	J/35	88270	92040	13.79
Desalination Plant	J/32	88304.06	91767.2	28.257
Deir Balah-1	J/146	91200.34	90460.38	60.98
Al Maghazi	G/149	91516.8	92948.4	26.536

Coordinates of municipal wells in the Gaza Strip…..*continued*

Name	ID	(X)	(Y)	(Z)
Assa'da	L/87	83040.16	84200.69	52.698
UNRWA-new	L/86a	82235.27	84662.68	47.982
UNRWA-new	L/86	82244.33	84658.55	47.72
Ayya	L/43	83062.92	83461.37	59.907
Municiaplity-East	L/41	84345.8	83160.51	61.624
Qarara-new	L/179	85570.28	87462.72	28.545
Assatar	L/178	84366.49	86366.49	22.835
Municiaplity-South	L/176	82186.59	83276.65	38.386
Al Amal-new	L/159a	82677.99	85081.92	45.12
Al Amal-old	L/159	82604.9	85047.02	42.815
Al Ahrash	L/127	82850.87	83935.06	52.96
Qarara	K/19	86461.66	88591.6	24.09
Tawfeek Al Kurd	T/44	89230.79	87641.99	86.542
Abasan Kabeera	N/9	87833.14	81623.57	76.42
Abasan Kabeera	N/22	88050	81820	79.967
Bani Suhail-East	M/2b	85766.62	83686.87	87.369
Bani Suhail	M/2a	85554.73	83908.8	67.447
Rafah-East	P/124	77598.02	79413.99	24.152
UNRWA	P/10	78612.96	77038.7	81.72
Zo'rob	P/153			
Canada	P/144	78301.93	80376.27	32.159
Al Hashash	P/145	79368.62	79856.37	48.206
Municipality-new	P/138	78772.7	79764.8	47.8
Municipality	P/139	77166.57	82010.52	9.815
Municipality	P/15	77926.76	78904.24	21.967



Sources:
- MOPIC
- EQA

Location of Monitoring Municipal Wells in the Gaza Strip

Date: November, 2003
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Curriculum Vitae

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basemshomarphd@hotmail.com
Nationality: Palestinian.
Date of Birth: February 6th, 1968.
Place of Birth: Gaza, Palestine.
Marital Status: Married.

Education:

1983 – 1986 General Secondary School, Scientific Branch, Gaza Strip-Palestine.
Grade: Excellent, 91%

1986 – 1994 BSc. Biology and Biochemistry, Birzeit University, West Bank-Palestine.
Grade: Excellent, 88%.

1997 – 1999 MSc. Environmental and Water Quality, UNESCO-IHE - Institute for Water Education, Delft, The Netherlands.

2001-2005 PhD. Environmental Geochemistry, University of Heidelberg, Germany.
(Expected: February 2005).

Research Experience:

1992–1993 Research Assistant, Chemical composition of snail's saliva, Department of Biology and Biochemistry, Birzeit Uiversity, Ramaalah, West Bank. (Dr. Adimar Zogheier).
1993-1994 Research Assistant, Male fertility in relation to Glycogen contents of rat testes, Biology & Biochemistry Department, Birzeit University, Ramaalah, West Bank. (Prof. Nabeel Nahhas).
1993-1994 Advanced research in Genetics, Modes of heredity in Dorosophilla, Biology & Biochemistry Department, Birzeit University, Ramaalah, West Bank. (Dr. Ahed Abdulkhaliq)
1993-1994 Research on the Health Aspects of Black Yeasts, Mycology, Biology & Biochemistry Department, Birzeit University, Ramaalah, West Bank. (Dr. Mo'nes Abou Asab).
1993-1994 Graduation Project, Regulation of Inflammation by Lipocortin 1, Immunology, Biology & Biochemistry Department, Birzeit University, Ramaalah, West Bank. (Dr. Tamer Issawi).
1993-1995 Teacher Assistant, Biology & Biochemistry Department, Birzeit University, Ramaalah, West Bank.
1994-1997 Researcher, Environmental sciences, Center for Environmental and Occupational Health Sciences, Birzeit University, Ramaalah, West Bank.
1995-1997 Teacher Assistant, Biology & Biochemistry Department, Al Azhar University, Gaza Strip (Part-Time Job).

Job Experience:

1994 – 1997 ***Director*** of Birzeit University- Center for Environmental & Occupational Health Sciences-Branch Gaza.

Coordinator of four projects concerning water and wastewater management in the Gaza Strip:

- **Dutch Project**: Monitoring of groundwater quality surrounding the solid waste dumping site of Gaza. April 95 to October 1996. My mandates were: the ***evaluation*** of the project in terms of selection of the monitoring wells, management of groundwater quality in the area, ***coordination*** with municipalities and ***reporting*** to the Dutch team leader.
- **Italian Project:** Desalination Plants in Khan Yunis area. My mandates were: Project management, assessment of water quality in the area, evaluation of desalination plants performance, and reporting. July to November 1995.
- **Japanese Project:** Wastewater treatment plant in Khan Yunis area. My mandates were: Evaluation of wastewater situation, communication with different stakeholders and policymakers also public representatives. Monitoring of groundwater quality of five wells surrounding the proposed plant. Reporting to the Japanese Team. September to November 1996 and August to October 1997.
- **USAID project:** Wastewater Treatment Plant of Gaza area. My mandates were: Implementation of sampling schemes, sample analysis, adopting financial issues, and reporting to the team leader. July 96 to October 1997.

1999- 2001 UNDP Consultant for the Ministry of the Environmental Affairs (MEnA), Gaza, Palestine (Participation in Environmental Strategy, Action Plan and several Environmental reports).

- Focal Point of UNDP project- Institutional Capacity Building of MEnA, communication, reporting and planning to Environmental Inspection and Monitoring Program (with Mr. T. Rothermyl, UNDP Director General).
- Focal Point of Sensitivity mapping project. Coordination, communication and arrangement for training courses in MEnA and USA.
- Organizer and Facilitator of UNDP-GEF Project. Rehabilitation and Protection of Wadi Gaza as a natural Reserve.
- Focal Point for the Gaza Marine and coastal zone Environmental management Plan. EU Project, LIFE Third countries.
- Member of Coastal Aquifer Management Plan (CAMP). Monitoring of groundwater in the Gaza Strip. USAID Project.
- Member of Groundwater protection Plan (Dutch project).
- Organizer and Facilitator of Sector Working Group on the Environment.
- Member of International Water Association (IWA).

Training Courses:

August -November 1994	Water and Environmental Research, CEOHS, Birzeit University, Ramallah, West Bank.
October - November 1995	Food Quality Control, Al Azhar University, Gaza, Gaza Strip.
November – December 1995	Water and Wastewater Management, CDG (Germany)
August– September 1996	Water and Wastewater Treatment Technologies, JICA, Japan.

September 1999	Protection of sea and sea shore from oil spills organized by The American National Oceanic and Atmospheric Administration (NOAA).
February 2003	Short Course, Chemical Reactions at Mineral and Bacteria Surfaces, Institute of Environmental Geochemistry, Heidelberg, Germany.
October 2003	Presenting and Publishing of Scientific Work, Springer Verlag, Heidelberg, Germany.

TV Programs:

1. Deterioration of water quality in Palestine, an inventory studies (Arabic Language Articles in Al Quds Newspaper) March 1996.
2. Impacts of Solid Waste leachate on the groundwater quality of selected Groundwater wells surrounding the solid waste dumping site of Gaza Governorate. June 1996
3. Heavy metals in the groundwater of Gaza Strip, MSc Thesis - March 1999.
4. Three TV programs for the Palestinian TV about Environmental Health in Palestine (1999-2000).

International Conferences:

1. Impacts of Climate change on ecosystems, organized by the UNDP-GEF, Amman Jordan, February 2000.
2. Renewable sources of Energy, Organized by the Middle East Desalination Center, Oman, Utilization of Passive Solar Energy for water desalination. May 2000.
3. Performance of Wastewater Treatment Plants in the Gaza Strip, Current situation and future approach. Proceedings of the International Water Association (IWA) Specialist Conference, BIOSOLIDS 2003, Wastewater Sludge as a Resource, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, June 23-25, 2003. pp. 429-437.
4. Environmental Aspects of the Gaza Strip, Case Studies: Soil Geochemistry and Fluoride Geochemistry. Bilateral Meeting, Environmental research and Wildlife Development Agency, Abu Dhabi, United Arab Emirates, 25-30 February 2004.
5. Fluorides in groundwater, soil and infused-black tea and the occurrence of dental fluorosis among school children of the Gaza Strip. Third International Conference on Children's Health and the Environment, London, UK, 31 March-2 April 2004.
6. Deterioration of Groundwater Quality in the Gaza Strip: Alarm for Actions. Proceedings of 2nd International IWA Conference on Automation in Water Quality Monitoring, AutMoNet 2004, Vienna, Austria, April 19-20, 2004. pp. 373-378.
7. Gaza Streifen: eine brisante Umweltsituation auf heißem Terrain, Umweltbörse, institut für Umwelt Geochemie, University of Heidelberg, 1 July 2004.
8. Seasonal variations of chemical composition of water and bottom sediments in the wetland of Wadi Gaza, Gaza Strip. The 7th INTECOL International Wetlands Conference, Utrecht, the Netherlands, 25 - 30 July 2004.
9. Wastewater of Gaza, Chemistry and Management Approach. Second Internatuional Conference: Water for Life in the Middle East, Turkey, Antalya, 10-14 October 2004.

Languages:

Arabic: Mother language
English: Very Good
German: Fair

<u>Things I love:</u>

- Literature (Arabic and English).
- Virgin Nature.
- Children songs.
- Classic Music (Beethoven, Handel, Bach, Mozart,...).
- All human beings.

<u>Referees:</u>

1. Dr. Yuosef Abu Safieh
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Hiermit erkläre ich an Eidesstatt, dass ich die vorliegende Arbeit selbständig und ohne unerlaubte Hilfsmittel durchgeführt habe.

Heidelberg,

20/01/2005

Basem Hasan Shomar