

OCCURRENCE OF PESTICIDES IN GROUNDWATER AND TOPSOIL OF THE GAZA STRIP

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Abstract. Agricultural activities in the Gaza Strip have been 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 a 3-year program to monitor types and levels of contamination by 52 pesticides in 94 groundwater wells in Gaza. Two analytical techniques (GC/MS and HPLC/MS) were applied to achieve this objective.

Water from 63 wells showed no detectable levels of pesticides or levels that were much lower than the allowable limit ($0.5 \mu\text{g/L}$) of the German and the European Commission (EC) standards for groundwater. Municipal groundwater wells located in residential areas showed better quality than private wells in agricultural regions. Atrazine, atrazine-desisopropyl, propazine, simazine were detected in 18, 15, 8 and 5 wells with average concentrations of 3.5, 1.2, 1.5 and $2.3 \mu\text{g/L}$, respectively. A linear correlation was found between the chloride concentrations in groundwater and atrazine for the same private wells.

Generally speaking, shallow aquifers in sandy substances in areas of low annual precipitation in the southern areas of Gaza showed detectable concentrations of pesticides. Pesticides were more abundant in clay soils of the northern area. A linear regression analysis showed 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 $39 \mu\text{g/kg}$, respectively. Two soil samples from greenhouses showed maximum contents of 4,4'-DDE and 4,4'-DDT up to 1150 and $823 \mu\text{g/kg}$, respectively.

Groundwater needs to be assessed for pesticide contamination on a routine basis to protect the health of Gaza's residents. Where levels of pesticides are found to exceed levels that protect health, alternative water resources need to be found for drinking and possibly other household uses.

Keywords: gaza, groundwater, pesticides, soil

1. 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. They are often misused by non-professional, inexperienced farmers (Abu Middain, 1994). Overexposure to pesticides can have

both immediate and longterm negative effects on human health (Ribas *et al.*, 1997). As an example, methyl bromide, which is used extensively in Gaza, causes fetal deformations, eye infections and dermatitis (Safi, 2002). Moreover, there is some evidence that organochlorine pesticides of the type used in Gaza cause breast cancer (Aronson *et al.*, 2000).

Pesticides that have been banned or restricted in many countries continue to be marketed and used in Gaza (IARC, 1999). Apparently, misuse of pesticides by the general public increased the level of soil and water contamination across Gaza (Issa, 2000). Leaching of pesticides, a common and growing problem in major agricultural regions including Gaza (DaSilva *et al.*, 2003), from soil can lead to the contamination of the Gaza groundwater.

Groundwater is the most precious natural resource in the Gaza Strip as it is the only source of water. Therefore, groundwater contamination can result in catastrophic consequences to the affected population. The groundwater aquifer of Gaza is extremely susceptible to surface-derived contamination because of the high permeability of sands and gravels that compose the soil profile of Gaza (CAMP, 2000).

The objective of the present study is to identify and quantify the concentration of pesticides in the groundwater and the topsoil of the Gaza Strip. These measurements can be used as baseline levels to monitor future changes and to predict their future impact on the population of the area.

2. Materials and Methods

2.1. THE STUDY AREA

The Gaza Strip (Figure 1), as one of the most densely populated areas in the world (2 638 people/km²; PCBS, 2000), has limited and declining resources and has already started to experience deterioration of environmental quality. Two thirds of the Gaza Strip (total 365 km²) is an agricultural area. 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. Safi *et al.* (2002) detected α and β -endosulfan, chlorpyrifos, carbofuran, chlorfluazuron, triadimenol I and II, penconazole, coptaolmetabolite, pyrimethanil and iprodione in some samples of cucumber, tomatoes and strawberries of Gaza; however, the residue levels were below the maximum residue limits (0.5 mg/Kg).

2.2. SAMPLING

The Gaza Strip (Figure 1) is divided into five geographic regions, the northern area, Gaza, the middle area, Khan Yunis and Rafah. Water samples were collected at three separate time periods: 20 November–12 December 2000, 26 June–17 July 2001

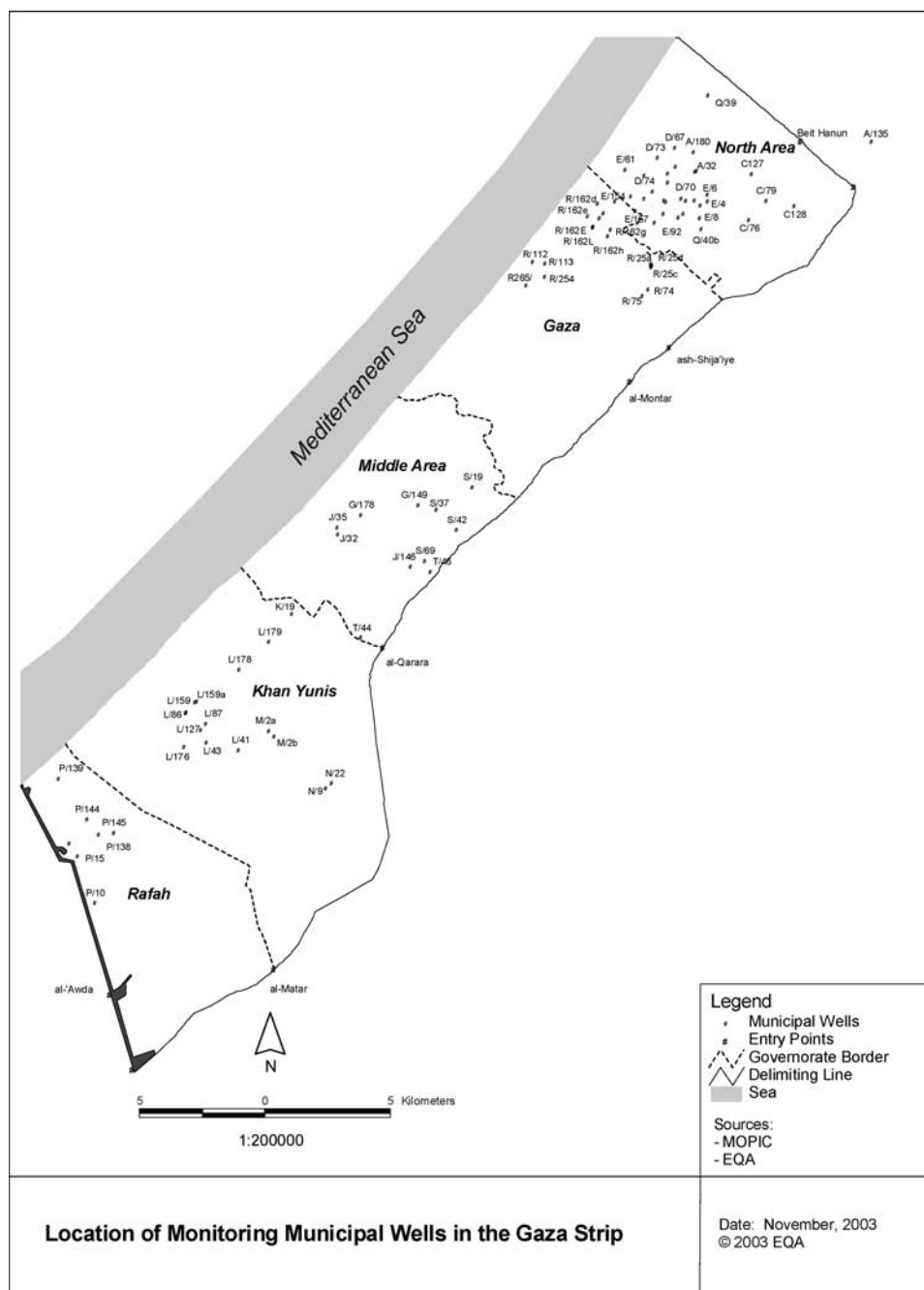


Figure 1. Five regions of the Gaza Strip and location of investigated groundwater wells.

TABLE I
73 Municipal and 21 private wells sampled for 3 years

Region	No.	Well number	Region	No.	Well number	Region	No.	Well number	Region	No.	Well number
73 Municipal Groundwater Wells											
North	1	D/67	Gaza	19	E/157	Gaza	37	R/25c	Khan	55	L 178A
	2	D/73		20	D/68		38	R/25d	Yunis	56	L 179
	3	D/74		21	D/69		39	R/112		57	L 41
	4	E/06		22	D/70		40	R/254		58	L 43
	5	E/10		23	Q/39		41	R/265		59	L 86
	6	E/11A		24	R/162L		42	R/74		60	L 86A
	7	E/11B		25	R/162La		43	R/75		61	L 87
	8	E/11C		26	R/162Ha	Middle	44	G1/178		62	M 2A
	9	E/138		27	R/162H		45	J 146		63	M 2B
	10	E/148		28	R/162G		46	J 32		64	N 22
	11	E/156		29	R/162F		47	J 35		65	N 9
	12	E/45		30	R/162E		48	S 19		66	T 44
	13	E/61		31	R/162C		49	S 42	Rafah	67	P 10
	14	E/8		32	R/162B		50	S 69		68	P 124
	15	E/90		33	D/71		51	T 46		69	P 138
	16	E/92		34	D/72		52	L 127		70	P 138 old
	17	Q/40b		35	R/25a	Khan	53	L 159		71	P 139
Gaza	18	E/154		36	R/25b	Yunis	54	L 176		72	P 144
										73	P 15
21 Private Groundwater Wells											
North	1	E/4	Khan	7	L/47	Khan	13	Priv. 1	Middle	19	Priv. 7
	2	E/1	Yunis	8	S/15	Yunis	14	Priv. 2		20	Priv. 8
Gaza	3	D/20		9	G/49		15	Priv. 3		21	Priv. 9
	4	A/185		10	K/121	Gaza	16	Priv. 4			
	5	A/107	Rafah	11	P/101		17	Priv. 5			
	6	A/180		12	F/191		18	Priv. 6			

and 25 January–17 March 2002. Soil samples were collected during the last time period. Water samples were from the major 73 municipal wells and 21 private wells selected to represent the 5 geographical areas. At the municipal wells, samples were collected from a tap along the water distribution line. Prior to sampling, chlorine or sodium hypochlorite treatment of water was stopped to minimize interference during analysis. Table I shows the distribution of the investigated wells and their local identification numbers. Some private wells have no identification numbers.

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 h prior to the collection of the sample. However, this was not always possible for 5 private wells during the third sampling period that occurred at the end of the rainy winter season when these wells were not extensively used. The average private well has a standing water of approximately 1 m³. Therefore 1 h of pumping at a rate ranging between 45 and 70 m³/h was sufficient to purge at least 45 standing well volumes.

Methods for determining levels of pesticides in the groundwater of Gaza, were developed using 4 water samples collected one month before the study sampling began. For this preparation phase, one liter of water samples were collected separately in glass bottles from 2 municipal and 2 private wells chosen in areas of intense agricultural production. Samples were transported and analyzed in Germany using high performance liquid chromatography and mass spectrometry (HPLC/MS) according to DIN, 1997.

Soil samples were collected according to the European soil sampling guidelines (Theocharopoulos *et al.*, 2001). Fifty-seven sites were selected to represent all types of soil in Gaza (Shomar *et al.*, 2005). 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 were collected from greenhouses (vegetables) in two different areas, 10 from fruit farms (olive, peach, guava, citrus), 10 from open vegetable farms, 10 from strawberry farms, and 12 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 °C until extraction and analysis.

2.3. WATER EXTRACTION

Sampling and sample preparation was done in Gaza and analysis was done in Germany. Water was collected in 1-L glass bottles and immediately 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 ¹³C₆) in methanol from Dr. Ehrendorfer (Augsburg, Germany). 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 cc, 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 (DIN, 1997). The SPE cartridges were wrapped in aluminum foils in order to protect them from contamination and were kept frozen until they were sent to Germany for analysis.

TABLE II

Recovery rates of standard compounds enrichment through solid phase extraction ($n = 6$)

Compound	Recovery Rate in %	Standard Deviation in %
Ticlopyr	87	10.2
Picloram	89	8.8
Dicamba	92	9.1
Dichloroprop	94	7.9
2,4 DB	88	8.7
Mecoprop	86	9.0
Fenoprop	83	11
MCPA	88	9.9
MCPB	90	7.6
2,4-D	82	8.4
2,4,5-T	84	9.5

In Germany, the solid phase extractors were cleaned by 6 mL methanol/tert-butyl-methyl ether (TBME) (Fluka, Switzerland), 20:80 (v:v). Then 100 μ L of internal standard mix 33 (5 μ g/mL) was added. The final volume was reduced to 0.5 mL by a gentle stream of N₂ where it was transferred into measuring vials. Diazomethane of 100 μ L were added and the vials were degassed and kept at 4 °C. Diazomethane is an ideal derivatization reaction of analytes for the GC/MS analysis (King, 1977; Knapp, 1979; Cohen, 1984; Blau and Halket, 1993).

The recovery rates and standard deviations of the enrichment step by the SPE (Water Oasis) for water samples are given in Table II. The volume of water samples influenced the recovery rate. For this work, the recovery rate was determined for five and ten liters of water samples. The water samples were dosed with the standard compounds pro analysis at a concentration of 100 ng/L. The specified values were calculated in each case via six measurements. The calculate recovery rates were stable and corresponded to the guidelines of the supplier Waters Oasis.

2.4. SOIL EXTRACTION

Soil samples were freeze-dried for 48 h, and then passed through a 2-mm sieve. Approximately 10 to 20 g of the dry soil were Soxhelt extracted for 12 h with 75 mL *n*-hexane/ethylacetate (100:2 v/v). One hundred μ L of the internal standard for the GC/MS (Ehrenstorfer internal standard mix 33 (5 μ g/mL) was added to the extract followed by 1 g anhydrous Na₂SO₄. The samples were evaporated to about 6 mL through a rotary evaporator, then to 1 mL by a gentle stream of N₂. About 0.8 g homemade silica gel/AgNO₃ (100:5 wt:wt) was poured into the SPE followed by few drops absolute methanol for activation. The SPE cartridges

TABLE III
Recovery rates of the Soxhelt extraction step ($n = 6$)

Compound	Recovery rate in %	Standard deviation in %
Aldrin	85	7.7
α -HCH	87	7.4
β -HCH	86	8.2
δ -HCH	89	9.1
γ -HCH	90	9.0
4,4'-DDD	91	10.1
4,4'-DDE	78	8.6
4,4'-DDT	76	8.7
Dieldrin	80	9.4
Endosulfan I (isomers II, sulphate)	82	9.3
Endrin (isomers aldehyde, ketone)	84	7.7
Heptachlor (isomer epoxide)	87	8.5
<i>p,p'</i> -Methoxychlor	86	8.4

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 N₂ to 0.5 mL, so an enrichment factor of 20 was reached. The recovery rates and standard deviations of the Soxhelt extraction step for soil samples are given in Table III.

2.5. ANALYTICAL METHODS

Table IV shows the analytical technique used for the analysis of target pesticides.

2.5.1. 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). Macherey-Nagel capillary column (30 m $\times$ 0.25 mm i.d., 0.25 μ m film thickness) was used. The column temperature started at 40 °C and raised at 10 °C/min to a final temperature of 340 °C.

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 separates well from all analyzed organochlorine pesticides.

2.5.2. HPLC/MS

The collected samples were separated by HPLC-MS. Liquid chromatography was carried out with an Agilent System 1100 (Waldbronn, Germany) connected to a triple quad MS detector (Applied Biosystems, API 2000, Langen, Germany).

TABLE IV
List of pesticides analyzed and instrument used for analysis

Pesticide	Analysis	LD* (ng/L)	Pesticide	Analysis	LD (ng/L)
Alachlor	HPLC/MS	25	Monolinuron	HPLC/MS	50
Atrazine	HPLC/MS	25	Monuron	HPLC/MS	25
Atrazine-desethyl	HPLC/MS	50	Pendimethalin	HPLC/MS	25
Atrazine-desisopropyl	HPLC/MS	55	Propazine	HPLC/MS	25
Azinphos-ethyl	HPLC/MS	50	Propiconazol	HPLC/MS	50
Benfluralin	HPLC/MS	50	Sebutylazine	HPLC/MS	25
Bromacil	HPLC/MS	25	Simazin	HPLC/MS	25
Carbofuran	HPLC/MS	50	Terbutryn	HPLC/MS	25
Chlorbromuron	HPLC/MS	50	Terbutylazin	HPLC/MS	25
Chlorfenvinphos	HPLC/MS	50	Terbutylazin-desethyl	HPLC/MS	50
Chlortoluron	HPLC/MS	50	Triadimenol	HPLC/MS	50
Cycloat	HPLC/MS	50	Triallat	HPLC/MS	50
Desmetryn	HPLC/MS	35	Trifluralin	HPLC/MS	25
Diuron	HPLC/MS	30	Aldrin	GC/MS	20
Etrifos	HPLC/MS	50	Chlordan	GC/MS	20
Fenuron	HPLC/MS	25	4,4'-DDD	GC/MS	20
Fluometuron	HPLC/MS	50	4,4'-DDE	GC/MS	20
Hexazinon	HPLC/MS	50	4,4'-DDT	GC/MS	20
Isoproturon	HPLC/MS	50	Dieldrin	GC/MS	20
Linuron	HPLC/MS	50	Endrin	GC/MS	20
Metazachlor	HPLC/MS	50	Heptachlor	GC/MS	20
Methabenzthiazuron	HPLC/MS	25	Heptachlorepoxyd	GC/MS	20
Metobromuron	HPLC/MS	50	Hexachlorbenzol	GC/MS	20
Metolachlor	HPLC/MS	50	Lindan	GC/MS	20
Metoxuron	HPLC/MS	25	Methoxychlor	GC/MS	20
Metribuzin	HPLC/MS	50	Mirex	GC/MS	20

*LD : limit of detection.

Ionization was conducted using positive atmospheric pressure ionization (API). Separation was performed on a SYNERGI Max-RP column (150 mm $\times$ 2 mm i.d., 4 μ m, 80 Å) (Phenomenex, USA) at 30 °C and pH 2.6. Separation was performed by a gradient of degassed formic acid and acetonitrile (mobile phase A) and methanol (mobile phase B). The initial composition of 50–70% B and 50–30% A was held for 0 to 8 min and switched linearly in 20 min to 5% A and 95% B. The identity of the analyte was confirmed by comparing the mass spectrum obtained with that obtained with a reference standard material. Linearity was identified by using 6 determinations of standard solution in the concentration range of 20 to 100 ng/L. The mass-spectrometer was operated in a positive mode for neutral

pesticides and in negative mode for the acidic ones by applying a voltage of +5 kV or -5 kV; respectively to the sprayer needle. The source temperature was kept at 300 K. Linearity was identified by using 6 determinations of standard solution in the concentration range of 20 to 100 ng/L. Software used was Applied Biosystems "Analyst".

2.6. QUALITY CONTROL

Analytical blanks and standards with known concentrations of pesticides were prepared and analyzed using the same procedures and reagents. Dr. Ehrendorfer (Augsburg, Germany) supplied standards for triclopyr, picloram, dicamba, dichloroprop, 2,4 DB, mecoprop, fenoprop, MCPA, MCPB, 2,4-D, 2,4,5-T. The lead author prepared calibration solutions (5 µg/mL) by dilution of the respective stock solution in methanol; Phenol Kit 27 (standard mix in methanol) is from SUPELCO.INC. 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 20 ng of each target compound through the cartridges. Additionally, 250–500 µL of same extracted water and soil extracts were analyzed in the laboratories of Department of Water Hygiene/Chemistry in the Institute for Hygiene and Public Health at the University of Bonn.

3. Results

This study detected one or more of 14 types of pesticides in the groundwater supplying 31 of 94 wells sampled in Gaza (Table V). Generally, there was no significant difference between the results of same wells for the successive three years. At least one of six pesticides was detected in the 45 soil samples taken from agricultural lands through Gaza (Table VI). The results of same water and soil samples analyzed in two laboratories showed a difference of $\pm 5\%$.

3.1. GROUNDWATER

Thirty one wells of the 94 sampled wells showed detectable levels of pesticides while the remaining 63 had pesticides less than the instrumental detection limit. Of the 31 wells, 16 were municipal and the other 15 were private wells. The 15 private wells included all of the wells sampled in the Khan Yunis, Rafah and North areas.

Atrazine was detected most frequently and were detected in all areas. Atrazine was detected in 18 wells, while atrazine-desisopropyl, propazine, simazine were detected in 15, 8 and 5 wells, respectively. DDT was detected in eight wells, six in Rafah area and two in Khan Yunis. One of these wells also had measurable levels of DDE and DDD. Two private wells showed 5 µg/L of triadimenol, the wells are located in the area of Rafah wastewater treatment plant.

TABLE V
Concentration ($\mu\text{g/L}$, $n = 3$ triplicates) of various pesticides detected in groundwater wells

No.	Well ID	Pesticide	Conc.	No.	Well ID	Pesticide	Conc.
1	E/6	Atrazine	1 ± 0.1	12	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	13	L/87	Atrazine	1 ± 0.1
2	E/4	Atrazine	2 ± 0.3	14	L/47	4,4'-DDT	1 ± 0.2
	E/4	Atrazine	1 ± 0.1	15	R/162C	Atrazine	14 ± 2
3	E/1	Atrazine	2 ± 0.4	16	R/162L	Atrazine	5 ± 1
	E/1	Atrazine-desisopropyl	1 ± 0.2		R/162L	Atrazine-desisopropyl	1 ± 0.2
4	E/11b	Atrazine	5 ± 0.3	17	R/162C	Atrazine-desisopropyl	7 ± 2
	E/11b	Atrazine-desisopropyl	1 ± 0.1		R/162C	Propazine	8 ± 2
5	D/20	Atrazine	20 ± 3	18	R/25a	Bromacil	1 ± 0.02
	D/20	Atrazine-desisopropyl	8 ± 1	19	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	0.3 ± 0.01
6	D/72	Atrazine	1 ± 0.1	20	P/15	Atrazine	6 ± 1
7	D/68	Atrazine-desisopropyl	1 ± 0.1		P/15	Atrazine-desisopropyl	6 ± 2
	D/68	Simazine	1 ± 0.2		P/15	4,4'-DDT	0.3 ± 0.01
	D/68	Propazine	1 ± 0.2	21	P/124	Atrazine	8 ± 1
8	D/74	Atrazine	3 ± 0.3		P/124	Atrazine-desisopropyl	8 ± 1
	D/74	Atrazine-desisopropyl	2 ± 0.1	22	P/139	4,4'-DDT	0.3 ± 0.01
	D/74	Propazine	1 ± 0.1	23	P/144	4,4'-DDT	0.3 ± 0.01
9	A/185	Atrazine	4 ± 0.2	24	P/10	4,4'-DDT	0.3 ± 0.01
	A/185	Atrazine-desisopropyl	1 ± 0.1	25	F/191	Endrin	0.1 ± 0.01
	A/185	Simazine	2 ± 0.2		F/191	4,4'-DDT	0.3 ± 0.01
	A/185	Propazine	1 ± 0.3		F/191	4,4'-DDE	0.7 ± 0.01
10	A/107	Atrazine	1 ± 0.4		F/191	4,4'-DDD	0.7 ± 0.01
	A/107	Atrazine-desisopropyl	1 ± 0.2	26	S/15	4,4'-DDT	0.3 ± 0.01
11	A/180	Atrazine	2 ± 0.5		S/15	Heptachlor epoxide	0.4 ± 0.01
	A/180	Atrazine-desisopropyl	1 ± 0.3	27	G/49	Atrazine	1 ± 0.2
	A/180	Simazine	1 ± 0.4	28	K/21	Atrazine	1 ± 0.1
	A/180	Propazine	1 ± 0.1	29	Priv. 1	Simazine	6 ± 1
12	L/43	Atrazine	5 ± 0.4	30	Priv. 2	Triadimenol	5 ± 0.7
	L/43	Atrazine-desisopropyl	2 ± 0.3	31	Priv. 3	Triadimenol	5 ± 0.6
	L/43	Propazine	1 ± 0.3				

3.2. SOIL

Seven soil samples of strawberry greenhouses in Beit Lahia (north) showed detectable levels of propazine, sebutylazine, terbutylazine, 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD. The averages of propazine, sebutylazine and terbutylazine were 19, 15 and $397 \mu\text{g/kg}$, respectively. 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. Two soil samples had maximum concentrations of 4,4'-DDE and 4,4'-DDT which

TABLE VI
Pesticides detected in soil samples

Soil	Pesticide	Min. ($\mu\text{g/kg}$)	Max. ($\mu\text{g/kg}$)	Aver. ($\mu\text{g/kg}$)	Median ($\mu\text{g/kg}$)	Stdev.
Vegetable greenhouse farms ($n = 15$)	4,4'-DDE	1110	1150	1129	1130	17
Fruit farms ($n = 10$)	Sebutylazine	13	16	15	15	1.2
	Terbutylazine	250	390	320	320	70
Open vegetable farms ($n = 10$)	4,4'-DDD	750	795	779	786	16
Strawberry greenhouses farms ($n = 10$)	Propazine	18	20	19	19	0.9
	4,4'-DDT	795	823	806	803	10
	Terbutylazine	385	410	397	398	10
Non-agricultural soils ($n = 12$)	None					

were 1,150 and 823 $\mu\text{g/kg}$, respectively. These samples were collected from two greenhouses of vegetables and strawberry in the northern area of Beit Lahia.

4. Discussion

The levels of pesticides found in 57 of the 73 municipal wells were below the German allowable drinking water standards. Four wells in which pesticides were detected were at detection limit, and therefore should be used with caution, e.g. wells P/10 and P/139 (Rafah). Five private wells showed a sum of detected pesticides exceeding the European Commission (EC) standards (1998) and the German legislation (Trinkwasserverordnung, 2001). The latter sets a limit of 0.1 $\mu\text{g/L}$ for aldrin, dieldrin, heptachlor and heptachlor epoxide measured individually and a maximum of 0.5 $\mu\text{g/L}$ for the sum of detected pesticides in drinking water.

The relatively frequent detection of pesticides in the groundwater of the southern areas is due to the concentration of greenhouses, which use large quantities of pesticides.

The difference in the results of the three consecutive years for the same well was insignificant while a significant variation in pesticide concentrations was noted among different wells vary in depth and location. The deeper the water table, the less likely the occurrence of pesticides at detectable concentrations. Most groundwater wells that showed detectable pesticides are 25–50 m deep. Deeper aquifers that feed municipal wells provide more opportunities and time for pesticide adsorption and transformation to occur than the shallow aquifer feeding private wells.

There was a correlation between the occurrence of atrazine in groundwater and water salinity ($r = 0.85$) consistent with the finding of Gascon *et al.* (1998). Most

of agricultural wells of the southern area have average chloride concentrations of 1200 mg/L associated with high values of atrazine (6–20 $\mu\text{g/L}$). Wells D/20 and E/11b (north), which have low concentrations of chloride (<500 mg/L), showed high atrazine concentrations. These wells are old and were used for decades as private wells before they became municipal.

Field surveys revealed that the potential source of pesticide contamination of private wells is caused by their proximity to storage, mixing, loading, disposal, or application of pesticides.

Although pesticides were detected frequently in about one-third of the groundwater wells, only seven of the 45 soil samples from the agricultural areas contained detectable levels of pesticides. All of these pesticides were detected in clay soils of the northern area. Pesticides were not detected in the 12 non-agricultural soils and also 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 the pesticides most frequently found in soils of greenhouses in areas in Gaza characterized by their vegetation 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, 1998; Navas and Machin, 2002; Worrall *et al.*, 2002). Pesticides were detected in clay soils but not 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 the dislocation of pesticides to deeper layers (Huang and Frink, 1989).

4.1. TRIAZINE (ATRAZINE, ATRAZINE-DESIISOPROPYL, SIMAZINE, TERBUTYLAZINE AND PROPAZINE)

Triazines are known to be somewhat persistent in water and mobile in soil (Tchounwou *et al.*, 2000). Atrazine, atrazine-desisopropyl, and simazine were not detected in soil samples; however, water samples showed that 18, 15, and 5 wells contained these pesticides, respectively. These pesticides were >1.0 $\mu\text{g/L}$ in the sampled wells, while the USEPA maximum contaminant level (MCL) of drinking water standard for atrazine is 3.0 $\mu\text{g/L}$ (USEPA, 1994). It has been found that metabolite concentrations in groundwater often exceed parent compound concentrations for triazine herbicides (Kolpin *et al.*, 2000).

Atrazine was the only herbicide found in 18 of the investigated wells; 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 of the southern areas (organic matter 0.5%), especially when these soils are irrigated (Chung and Alexander, 2002).

Since 1991, atrazine has been banned in many countries, including Gaza and substituted mainly by terbutylazine. Nevertheless, atrazine and its degradation product

desethylatrazine are by far the most abundant herbicides detected in shallow groundwater (Tappe *et al.*, 2002). In spite of being banned, farmers of Gaza use atrazine more than any other pesticide because it is highly effective and less expensive compared to other herbicide currently available (USNRCS, 2004).

Although atrazine desisopropyl is a degradation product of atrazine, it was detected in 2 wells (D/68 and R/162c) where atrazine was not detected. Bromacil, simazine, terbutylazine are mainly used on citrus of Gaza but because of the physical and chemical characteristics of the soils of Gaza (Redondo, 1997), none of these pesticides was detected in any of the soil samples.

Terbutylazine was detected in several soil samples of fruit trees, citrus and open vegetable farms but not in groundwater samples. Propazine was found in 7 wells and was the major detected pesticide in soil samples of greenhouses.

4.2. DDT, DDE AND DDD

Although DDT was banned in several countries, it is still used in Gaza. Traces of DDT and its breakdown products DDE and DDD were detected in several soils of Gaza. Due to strong adsorption to soil, only a small amount of DDT migrates through the soil into groundwater (Hung and Thiemann, 2002). Nonetheless, eight wells in Rafah area, where the soil is sandy showed the presence of DDT and its breakdown products.

5. Conclusions

1. Fourteen pesticides were detected in the groundwater of Gaza with some concentrations exceeding their respective German maximum contaminant levels or health advisory levels for drinking water. There was no significant difference between the results of same wells for the successive three years.
2. Private groundwater wells showed higher concentrations of pesticides than the municipal wells. The levels of pesticides found in the municipal wells were below the water quality guidelines, and many were at levels close to the detection limit for the method.
3. At least one of six pesticides was detected in the 45 soil samples taken from agricultural lands through Gaza. No pesticides were detected in the 12 samples taken from non-agricultural lands.
4. Until there is a substantive decrease in the amount of pesticides applied annually on agricultural lands in Gaza, well water needs to be assessed for pesticide contamination on a routine basis to protect the health of Gaza's residents. Where levels of pesticides are found to exceed levels that protect health, alternative water resources need to be found for drinking and possibly other household uses.

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