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Trace elements in major solid-pesticides used in the Gaza Strip

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Abstract

This study describes the purity of pesticides used in Gaza in terms of trace elements. A semi-quantitative EMMA-XRF technique and quantitative ICP/OES was used to determine 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 50 of the most commonly used solid pesticides collected from the five central shops in the Gaza Strip. The results revealed that the pesticides contain considerable amounts of trace elements and 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 the pesticides were not pure. In some cases they have been mixed in local markets with minor inorganic species without a scientific basis. They may also have been smuggled into Gaza with differing impurities. The results indicate that pesticides should be considered as a source of certain trace metals (particularly Cu, Mn and Zn) and other elements (Br, Sr and Ti), which may affect their mass balances in soil and groundwater as well as their plant uptake. Different scenarios and calculation models of the transport of trace elements in soil and groundwater of the Gaza Strip should include pesticides as an additional source.

Keywords: Gaza Strip; Pesticides; Trace elements

1. Introduction

Research on pesticides primarily focuses on the organic dimension, while the inorganic components receive relatively less attention. This could explain the shortage in the literature about the existence of trace elements in pesticides, as it is assumed that the chemical structure of pesticides is well known, labeled or documented. This is not the case, however, in many countries, particularly in developing countries. Pesticides have greatly improved the agricultural production world-wide and have shown to be very effective in controlling vector-borne diseases. In Gaza their indiscriminate use and improper application are of concern because of the hazards and risks they pose to humans and the environment (Yassin et al., 2002). Pesticides display a variety of chemical characteristics (Stan, 1995); e.g. they can be bound by soil in different ways. Pesticides, including their trace element, constituents have been found in contaminated groundwater and soil (El-Nahhal and Safi, 2004; Shomar et al., in press). Contamination due to leaching of pesticides is a common and growing problem in major agricultural regions (Flury, 1996). Pesticides that have trace metals in their chemical structure (fosetyl-aluminum, propineb, mancozeb, maneb and copper oxychloride) have been detected in groundwater of many regions in the world (Kolpin et al., 2000a,b). A recent study categorized a wide range of pesticides as "leachers" or "non-leachers" for a specific Hawaiian hydrogeological setting (Li et al., 2001). In the United States, there is a considerable body of work demonstrating the occurrence of both parent compound pesticides and their metabolites in groundwater aquifers (Baker et al., 1993; Lawrence et al., 1993).

Ten percent of 170 topsoil samples of the agricultural and non-agricultural areas of the Gaza Strip showed slight contamination, primarily by Zn, Cu, As and Pb, due to anthropogenic inputs. The mean concentrations of these elements were 180, 45, 13 and 190 mg kg^{-1}, respectively. The pollution of several investigated sites was found to

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be most severe for Zn, Pb, Cu, Cd and, to a somewhat lesser extent, for As, whereas anthropogenic input of Hg, Ni and Co seemed to be less important. The application of Cd-containing phosphate fertilizers coupled with Cu containing fungicides may be an important source of Cd and Cu in several soils. High Zn levels (1000 mg kg^{-1}) in several soils may be caused by sewage sludge, which has an average Zn content of 2000 mg kg^{-1} (Shomar et al., 2005).

The main goal of this paper is to introduce a general method for the determination of trace elements in solid pesticides; and to determine their concentrations in 50 pesticides that are intensively used in Gaza.

2. Study area, materials and methods

2.1. Study area

Pesticides are considered priority pollutants in the Gaza Strip and with the growing use of greenhouses Palestinian agriculture is becoming increasingly dependent on chemical pesticides and fertilizers. In the Gaza Strip, several reports have identified misuse of pesticides by shop owners, farmers and agricultural workers (Issa, 2000; Safi et al., 2002; Shomar et al., in press). Similarly, several extremely toxic pesticides that are banned or restricted in many countries are still used in Gaza (Safi, 2002). Poor medical records, absence of health surveillance and monitoring systems, and absence of legislation and control systems for pesticides have resulted in a lack of awareness of potential hazards associated with pesticide handling and use among shop owners, farmers and the public (Safi et al., 2002). 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 are no protocols to monitor pesticide residues in agricultural crops that might endanger the health of the whole population in Gaza (Safi et al., 2002; Shomar et al., in press). More than 250 metric tons of formulated pesticides are used annually in the Gaza Strip, about 90% of which is imported and 10% manufactured locally (Safi, 2002). Since there are no restrictions on the sale and use of pesticides in Gaza, farmers have easy access to all pesticides including banned, highly toxic and restricted species. Additionally, no permit or special training is required before buying pesticides (Issa, 2000; Shomar et al., in press).

Five major pesticide shops distribute pesticides and other agricultural needs to about 55 smaller shops scattered in all areas of the Gaza Strip. All pesticides enter Gaza through Israeli Arab wholesalers, who usually get their products from Israeli pesticide companies and sometimes from agents for imported chemicals (Safi et al., 2002). Since there is no monitoring of either the sale of pesticides or their chemical composition (there are neither laboratories nor facilities for this purpose), alteration and fraudulent sale of pesticides are common practices (Shomar et al., in press).

2.2. Sampling and analysis

In a full coordination with the Palestinian Ministry of Agriculture, pesticide shops were identified and samples were collected between March and May 2005. A meeting interview was used for filling in the questionnaire. All interviews were conducted face to face by the author and the staff of the ministry. General guidelines of the United States Environmental Protection Agency (USEPA, 1995) were followed. The target population was the five major pesticide distributors who normally give the instructions for the use of pesticides to the small shops. Pesticides were bought in the same storage containers generally used by the stores, the majority of which are commercial plastic, with some polyethylene and few are metallic containers. Samples were freeze-dried and then the non-powder samples were subsequently ground into powder.

Table 1 shows the pesticide samples and the chemical formula of each, as well as its intended use. It was found that identical pesticides have different names not only in different shops, but sometimes in the same shop. Pesticides with different names were treated independently in the analysis procedure. Table 1 also shows similarities between numbers 3 and 26, 11 and 50, 16 and 43, 30 and 41.

2.3. EMMA-XRF

Pesticide samples were firstly screened for trace elements using a energy-dispersive miniprobe multielement analyzer-X ray fluorescence (EMMA-XRF) (Cheburkin and Shotyk, 1996). The EMMA-XRF analyzer was designed for trace element analysis of plant, soil and rock samples. The analyzer used monochromatic excitation with an energy of 19.6 keV. The software allows for normalizing 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 is not always satisfactory. For example, some pesticide samples have a very heavy matrix due to high concentrations of Mn, Cu, Zn and Br.

The EMMA-XRF analyzer was calibrated using different standard reference materials (SRMs) such as: NIST 1575 (Pine needles); 1632b (Coal); 1635 (Coal); G-2 (Granite); BCR60 (Olive leaves); BCR62 (Aquatic plants); MAG-1 (Marine mud); W-1 (Diabase). These SRMs have very different matrices from those of many pesticide samples, making it difficult to calculate precisely the 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%.

2.4. ICP/OES

Because the results from the EMMA-XRF were not precise, the author conducted a full digestion procedure and

Table 1
List of 50 collected samples of solid pesticides used in the Gaza Strip

No.	Common name	Chemical formula[a]	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	$C_8C_{14}N_2$	Fungicide
5	Propineb	$(C_5H_8N_2S_4Zn)_x$	Fungicide
6	Mancozeb	$[–SCSNHCH_2CH_2\ NHCSSMn–]_x(Zn)_y$	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	Fosetyl-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

[a] From the Pesticide Manual (BCPC), 1997.

used an inductively coupled plasma–optical emission spectrometer, ICP/OES (VISTA-MPX, VARIAN) instrument for more precise determination of trace elements in the pesticides. The samples were handled with great care, under a hood. About 0.5–1.0 g of the homogenized sample was dissolved with 10 ml of concentrated nitric acid (Merck 65%) in 50 ml retorts. The samples were degassed (24 h), then heated on a sand bath to 50 °C for 30 min then to 160 °C for 3 h. 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 the ICP/OES (VISTA-MPX, VARIAN). The detection limit of the ICP/OES was estimated 10% less than the lowest standard used for calibration.

Table 2
Trace elements and other parameters in 50 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	%	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
1	BDL	BDL	BDL	BDL	10	33	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	7
2	BDL	BDL	BDL	BDL	23	22	BDL	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	388	BDL	BDL	642	BDL	BDL	7	BDL	BDL	BDL	8	3	5
4	1.0	BDL	425	BDL	76	1327	BDL	BDL	6	BDL	BDL	3	37	127	18
5	BDL	BDL	BDL	BDL	884	3768	BDL	BDL	>10.0%	BDL	BDL	260	18	BDL	BDL
6	BDL	BDL	BDL	BDL	>10.0%	BDL	BDL	BDL	17500	BDL	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	1211	BDL	6	6	50	BDL	7	BDL	8	BDL
8	BDL	BDL	BDL	BDL	15	304	BDL	22	9	BDL	BDL	BDL	23	BDL	BDL
9	BDL	BDL	4072	BDL	BDL	4295	BDL	7	9	BDL	BDL	4	2	96	11
10	BDL	BDL	118	BDL	28	229	BDL	10	7	BDL	BDL	BDL	BDL	6	BDL
11	BDL	BDL	184	BDL	560	373	BDL	BDL	14	BDL	2	2	BDL	7	BDL
12	BDL	2.0	10012	BDL	19011	10939	36	32	940	4	BDL	5	19	303	18
13	BDL	2.0	10911	BDL	19980	11474	BDL	23	923	BDL	BDL	6	20	322	17
14	BDL	6.0	456	BDL	110	4514	BDL	BDL	12	BDL	BDL	9	BDL	452	4
15	1.0	0.0	1052	BDL	67	5639	45	10	63	BDL	BDL	81	21	45	3
16	BDL	3.0	19	BDL	22	103	BDL	BDL	7	BDL	BDL	3	9	12	BDL
17	BDL	0.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	>10.0%	BDL	BDL	BDL
18	BDL	0.0	189	BDL	BDL	164	BDL	BDL	BDL	BDL	BDL	22	BDL	BDL	BDL
19	BDL	1.0	831	BDL	72	4513	23	8	540	11	BDL	473	73	54	BDL
20	BDL	0.0	12025	BDL	20	9623	21	18	13	BDL	BDL	9	6	173	31
21	BDL	4.0	BDL	BDL	>10.0%	BDL	BDL	BDL	1875	BDL	BDL	BDL	BDL	56	BDL
22	BDL	0.0	BDL	BDL	179	214	BDL	BDL	12	BDL	BDL	195	BDL	BDL	BDL
23	BDL	>10.0%	5853	81	81	7790	42	17	210	13	3	32	9	1261	7
24	BDL	5.0	8126	57	32	8901	22	10	102	3	BDL	18	6	723	14
25	BDL	4.0	5833	48	31	7444	14	36	83	BDL	BDL	48	13	188	13
26	BDL	BDL	5063	26	187	8029	17	2318	3748	3	BDL	26	13	105	20
27	BDL	BDL	440	BDL	BDL	843	BDL	BDL	8	BDL	BDL	3	7	4	8
28	BDL	BDL	BDL	BDL	BDL	4000	BDL	>10.0%	BDL	BDL	BDL	BDL	BDL	BDL	BDL
29	BDL	BDL	BDL	BDL	BDL	5977	BDL	>10.0%	BDL	BDL	BDL	BDL	BDL	BDL	BDL
30	BDL	BDL	BDL	BDL	>10.0%	BDL	BDL	BDL	20927	BDL	BDL	73	12	BDL	BDL
31	BDL	>10.0%	BDL	BDL	BDL	116	BDL	BDL	BDL	BDL	BDL	10	0	70	11
32	1.0	2.0	BDL	BDL	208	126	BDL	178	69	BDL	BDL	9	5	9	BDL
33	BDL	>10.0%	4032	35	41	5153	32	29	245	3	BDL	21	BDL	1323	16
34	2.0	BDL	1205	BDL	0	7463	BDL	7	25	4	BDL	5	133	57	9
35	BDL	9.0	532	BDL	313	4550	BDL	8	46	BDL	BDL	23	16	57	4
36	BDL	BDL	1991	BDL	62	2748	BDL	BDL	16	BDL	BDL	70	23	15	BDL
37	BDL	4.0	7694	49	38	7959	BDL	15	95	BDL	1	BDL	8	647	18
38	BDL	BDL	BDL	BDL	47	72	BDL	19	33	BDL	BDL	16	3	4	BDL
39	BDL	BDL	BDL	BDL	121	512	BDL	7	18	BDL	BDL	28	24	15	12
40	BDL	BDL	BDL	BDL	6885	553	BDL	BDL	>10.0%	BDL	BDL	32	11	21	BDL
41	BDL	BDL	BDL	BDL	BDL	419	BDL	41	7	BDL	BDL	13	25	11	BDL

(*continued on next page*)

Table 2 (*continued*)

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	%	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
42	BDL	>10.0%	BDL	BDL	97	83	BDL	BDL	10	BDL	BDL	11	BDL	72	9
43	BDL	BDL	BDL	BDL	64	3014	BDL	6	44	BDL	BDL	151	15	10	BDL
44	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	>10.0%	BDL	BDL	BDL
45	5.0	7.0	974	BDL	BDL	6143	BDL	445	37	14	BDL	6	171	1359	BDL
46	BDL	>10.0%	66	BDL	42	1318	BDL	18	13	BDL	BDL	3	4	446	7
47	BDL	BDL	158	BDL	589	2684	BDL	37	92	5	BDL	6	176	51	8
48	BDL	BDL	BDL	BDL	>10.0%	BDL	BDL	BDL	17819	BDL	BDL	BDL	BDL	BDL	BDL
49	BDL	BDL	BDL	BDL	106	315	BDL	BDL	8	BDL	BDL	BDL	BDL	8	BDL
50	2.0	BDL	1116	BDL	49	7004	BDL	BDL	22	4	BDL	5	126	50	10

LD: instrumental limit of detection; BDL: below detection limit of EMMA-XRF.

2.5. Quality control

For quality control of the ICP/OES, analytical blanks and two standard reference materials with known concentrations of trace elements were prepared and analyzed using the same procedures and reagents. The reference materials were pine needles 20234 from the American National Bureau of Standards (1976). Precision was estimated by evaluating the reproducibility between duplicates and a coefficient variation of lower than 5% was found.

3. Results and discussion

3.1. Laboratory results

The results of EMMA-XRF and ICP/OES are shown in Tables 2 and 3. Generally, trace elements were not only found in the first 14 pesticides shown in Table 4, but some were also found at high level in other pesticides which do not have these elements in their chemical formulae (Table 1). Based on the results, the sampled pesticides can be classified into two categories: (1) the samples that have one or more of the tested elements in their structures and showed positive results; and (2) pesticides that have none of the tested elements in their chemical formulae, but yet showed significant concentrations in the analysis. The upper 14 pesticides in Table 4 belong to the first category while the following 12 belong to the second one. The calculated value of each element was obtained from the percentage it represents in the chemical formula of the relevant pesticide.

For the first category of pesticides, the calculated value of each element is much higher than the observed value (Table 4). The calculated aluminum concentration in fosetyl-aluminum, for example, was four times higher than the analyzed value and three times higher in a second replicate collected from another shop. Calculated Zn was 11, 6, 1 and 12 times higher than the analyzed values in propineb, mancozeb, metiram and zineb, respectively. Calculated Mn was four and nine times higher than the analyzed value in mancozeb and maneb, respectively. Bromide was three times higher than the analyzed value in the two samples of bromacil, while it was 6895 and 9480 times higher in the two samples of bromadiolone. Finally, calculated Cu was two times higher than the analyzed value in both copper oxychloride and copper sulfate.

Some pesticides from category (1), also showed high amounts of other elements theoretically not present in their structure; for example, copper oxychloride which has high levels of Pb; copper sulfate showed high concentrations of Ni; and maneb showed high amounts of Fe and Mn.

The second category, represented by the last 12 pesticides in Table 4, have none of the tested elements in their chemical structure but still showed high concentrations in the analyzed samples.

Table 3
Trace elements and other parameters in 50 pesticide samples collected from Gaza, results of the ICP/OES

	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
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
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

BDL: below detection limit of the ICP/OES.

3.2. Field survey results

A very serious situation exists with respect to pesticide use due to the exceedingly large volumes used and the lack of information available to Arabic to wholesalers, farmers and others dealing with pesticides. The field surveys revealed that several known and unknown pesticides have been smuggled to Gaza from Israel under the absence of governmental and non-governmental control. Gaza is suffering of absence of pesticide regulation and a shortage of experienced, qualified pesticide retailers and users. Pesticides are sold in general retail, non-specialty shops and are handled and sold by persons with little or no education. The absence of governmental monitoring and inspection systems coupled with limited awareness among pesticide users allow the latter group to store pesticides

Table 4
Calculated and measured values of some elements

Pesticide	Chemical structure	Tested element	Calculated value (mg kg^{-1})	Measured value (mg kg^{-1})
Category (1) Pesticides with tested elements in their formulae				
Fosetyl-aluminum	$C_6H_{18}AlO_9P_3$	Al	245455	65140
Propineb	$(C_5H_8N_2S_4Zn)_x$ [a]	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	$CuH_{10}O_9S$ [b]	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
Category (2) Pesticides with no tested elements in their formulae				
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

[a] Theoretical monomer.
[b] Pentahydrate.

under potentially dangerous conditions. Because pesticides are expensive, some shop owners mix different pesticides without a scientific background. During the application of pesticides, farmers spray, eat and smoke, disregarding the general spraying instructions. An estimated 24 chemical pesticides that have been prohibited or restricted world-wide are still being used in the Gaza Strip; examples of such pesticides are Lindane, Dorspan, DDT and Tamaron.

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 farmers and the general public.

Malpractices include sales of pesticides that have passed their expiration date; intentional incorrect labeling of containers to sell cheap products at high prices; and sale of organic and inorganic chemicals instead of pesticides. Shop owners import pesticides in large containers. They distribute the pesticides into small containers (mostly made of plastic). At best, these small containers show the commercial name, but generally the labeling only provides a pesticide number. Although farmers of Gaza are very professional, they do not have the access to information on safe application and storage methods or to information on potential adverse effects on human health and environment.

4. Conclusions

Tested pesticides have considerable amounts of trace elements and there is no agreement between analyzed and calculated values; the calculated values are much higher for samples that should contain the respective trace element. Contamination of pesticides by trace elements 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. Pesticides should be considered as a source of some trace elements in soil and groundwater of the Gaza Strip and they should be included in mass balance and geochemical cycles.

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