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Pesticides and Heavy Metal Distribution in Southern Dead Sea Basin

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Although pesticides are useful for human activities, their presence in the environment poses a threat to mankind when they are misused. Pesticides are harmful when they exist in their non-target sites especially when they become in contact with water resources such as groundwater and surface water. Therefore careful management of pesticide application is desired at the sites of application.

The type of pesticides influences pesticides residue in water bodies. It is known that organochlorine pesticides are more persistent. The availability of pesticide residues in the environment depends on many factors such as solubility in water, volatilization and adsorption on the solid phase during water flow in addition to application frequency. Domagalski and Dubrovsky 1992 showed that fine-grained soils of the unsaturated zone inhibit pesticide leaching into groundwater.

In a developing country such as Jordan, although some of the older persistent and bio-accumulating pesticides banned residue for use, they are still used as they remain the cheapest. For example, some banned pesticides have been reported in untreated wastewater at Karak region indicating that they are still in use in Jordan due to their cheapness and high efficiency (Jiries et al. 2001). Al-Nasir et al.2001 reported elevated levels of organochlorine pesticide in grape and its fermented product wine from various sites in Jordan.

The purpose of this investigation is to determine pesticide residue concentrations in surface and groundwater bodies at the southern edge of the Dead Sea as these sites are agricultural areas with a potential for reuse of water from large industries existing in the area such as potash and other salt extraction from the Dead Sea region.

MATERIALS AND METHODS

Grab water samples were collected from available surface and ground water at the southern basin of the Dead Sea, at the end of summer 2001 for pesticide residues and during summer 2001 for heavy metals, to avoid any dilution or addition of rain water from winter season, also because pesticides are mainly used during the summer season. The site is located at the southern edge of the Dead Sea where an

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intensive agricultural activity exists. The sampling sites were chosen to represent the investigated area.

The surface water in the study area is drainage from agricultural land in the area, drained through canals into collecting ponds where it is exposed to evaporation under prevailing climatic conditions; therefore water of high salinity and pesticide residue content is expected to exist in the area. These ponds are potentially used for large industrial activities existing in the area such as potash and other salts extraction from the Dead Sea region where there is a high demand for water.
Geologically, the study area is a part of the east African rift where the lowest point of the continental crust exists. A large part of the investigated area is covered with quaternary soil of high salinity, as it emerged with Dead Sea regression in the past few decades.

Arid climate conditions prevail in the area, which is characterized by hot dry summers and mild winters seasons. The average rainfall in the area is less than 100 mm, falling during winter season, Oct.-Apr. (NRA, 1978).

The extraction procedure for pesticide residues employed in the present study was based on a previously developed method (Their and Zeumer, 1987). The outline of the procedure is as follows:

1 liter of water sample was mixed with 40g NaCl, 60 ml of dichloromethane and 40 ml of deionized water. The organic phase was separated and used for analysis. It was passed through anhydrous Na_2SO_4 and rotary evaporated to near dryness.

The dissolved residue was purified using activated silica gel, 60-100 mesh, (25g) supplied by Sigma (St. Louis MO, USA) in a 22 mm ID chromatograph column. After prewashing with hexane the sample was added to the column. The column was eluted successively at a rate of 5 ml/min. with 50 ml dichloromethane : acetone : Toluene (5 : 1 : 1 v/v). Fractions were collected and evaporated to near dryness. The pesticide residue was redissolved into 5 ml n-hexane to analysis.

The extracted compounds were analyzed for selected pesticides that are expected to be commonly used in Jordan using Gas Chromatograph (GC), HP 5890 equipped with ECD detector and auto-sampler on HP 608 Capillary column 30 m x 0.53 mm I.D and 0.5 μm film thickness with split ratio of 1: 15 and Ar/CH_4 as a carrier gas and head flow rate of 1.3 ml/min.

1 μL extract samples were injected into splitter injector at 250°C, and separated at a column temperature program of 80 °C for 1 minute, 20°C/minute to 180°C, 4°C/minute to 280°C for 33 minute. Running time was 55 minute and detection was by ECD at temperature of 300°C.

Instrumental operation conditions for pesticides were based on previously developed method (Becker, G.: 1979). The detection limits for the investigated pesticides are 0.003 – 0.06 mg/L.

The collected water samples were acidified with few drops of HNO_3 after being filtered with Whatman No. 1 filter paper to remove any suspended materials into a 0.5 L tightly capped polyethylene bottles. Lead (II), Cadmium (II), Cobalt (II), Manganese (II) and Iron (III) were determined by flameless atomic absorption spectrophotometery using Varian 800 AA with deuterium lamp background correction (high concentration of Iron (III) and Manganese (II) were determined by flame atomic absorption). Quantification was done for pb^{+2}, Cd^{+2}, Co^{+2}, Mn^{+2} and Fe^{+3} using standard addition method and multiple injection technique for low concentrations. The detection limits for the investigated heavy metals are 0.02-3.00 ppb (flameless) and 0.02 - 0.06 ppm (flame).

RESULTS AND DISCUSSION

Typical chromatograms of standard solutions and one of the analyzed water samples are shown in Figure 1, illustrating a good separation of analytes.

Concentration of pesticide residues in the samples calculated by comparison with external standard peak areas :

$$\text{Conc. of pesticide residues} = \left(\frac{\text{Standard conc.} \times \text{sample peak area}}{\text{Standard peak area}} \right)$$

In all analyzed samples, no organophosphorous pesticides were detected (except Phosalon), although they are widely used in agricultural purposes in the examined area. This can be due to fast rate of degradation of this class of pesticides that was accelerated through the very hot and arid climatic conditions in the area. Statistical summary of the detected pesticides in the investigated area are shown in table 1. Vinclozolin, Tetradifon, bromopropylate, Fenpropathrin op DDT, pp DDT, pp DDE and pp DDD were detected in 72.7% , 72.7% , 18.2% ,18.2% , 18.2% , 18.2% , 18.2% and 27.3 % (with respect to 22 samples) of the surface water samples, respectively. On the other hand, Vinclozolin, Tetradifon, op DDT and pp DDD were detected in 90.9% , 45.5%, 27.3 % and 18.2% (with respect to 22 samples) of the ground water samples, respectively. Vinclozoin and Tetradifon were detected in most of the analysed samples and tetradifon was in the highest concentration in some sites indicating that vinclozoline and tetradifon are still used largely in the investigated area.

Organochlorine insecticides, especially DDT, were used intensively in canals during past years; therefore, it is still detected with its metabolites (DDE and DDD) in Ain younis drainage (irrigation drainage) and in low concentrations in groundwater resources of Safi area but not in other sites of the investigated area. Bastian et al, 1997, reported DDT presence in surface water at detectable levels in USA and it was attributed to its use during the past years.

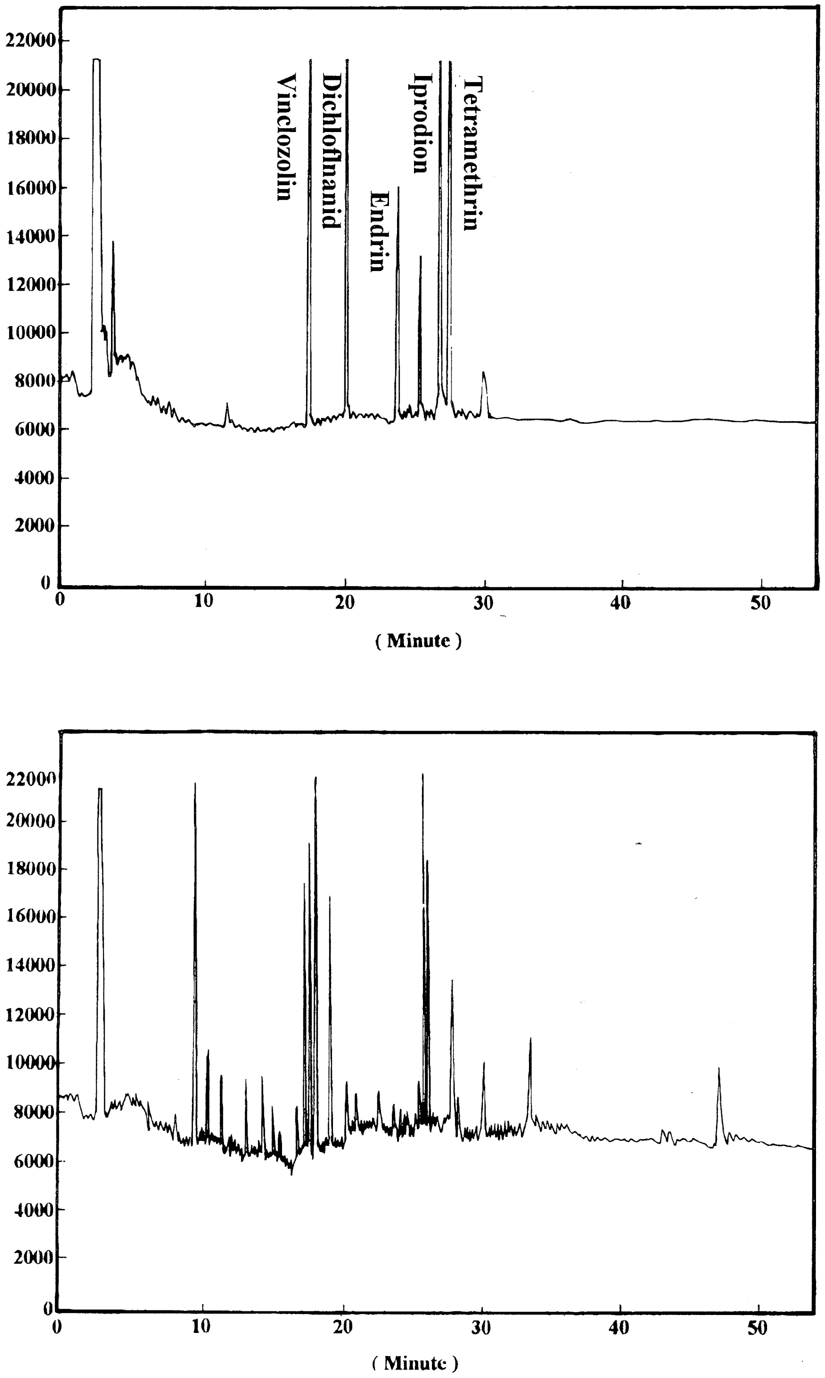

Figure 1. Chromatograms of the standard solutions and water sample

All of the detected pesticides (Table 1) were in low concentrations, except those collected from irrigation drainage sites, with transient peak concentrations reaching 3070 and 3770 ng/L for tetradifon and 1300 ng/L for pp DDT. This could be due to either low rate of application at the source area and attachment to the sediments along their flow as they are associated with solid phase (Mcintrye and Lester, 1984) or due to its low solubility and low photo-oxidation (Dubus et al. 2000), therefore they were found in low concentration under the prevailing hot and dry conditions of the area.

The difference in pesticide type and concentration between the sampling sites could be due to difference in pesticide usage and frequency of pesticide application. An obvious example can be found in DDT and its metabolites (DDE and DDD) where it was detected in the sourthern part of the investigated area but not in its northern part although the two sites are not too far from each other.

The types of pesticide residues in the investigated area are different from those reported in north Jordan Valley, around 100 Km north of the investigated area. This can be due to different application of pesticides at the two sites, although the climatic conditions are similar.

Descriptive statistics of heavy metal concentrations in surface and groundwater of the investigated area is shown in Table 2. In most of the samples heavy metal content (except iron and some samples of managanese) in both surface and groundwater are low and it could be attributed to the high pH value of the water samples enhancing heavy metal precipitation (Revitt et al 1997) in addition to low human activities in the investigated area.

Discernible concentrations of the metals in drainage canals, collection ponds and groundwater were noticed. Heavy metals concentrations, in descending order, were Fe > Mn > Pb > Co > Cd. In general, heavy metals were highest in groundwater, then in the saline canal water and the fresh surface runoff at Safi area, which can be due to contamination from corrosion of casing and steal pipes used for water extraction inside the wells. Although adsorption reduces transfer of heavy metals into the groundwater, Pb concentrations were much higher in groundwater than surface water of the same area which was attributed to corrosion effect of materials inside the wells such as casing, pipes and others. Pb is not highly sorbed by the soil due to association of elevated Fe in the water (Pace et al. 1987).

On the other hand surface runoff showed the lowest concentrations due to the lack of industrialization and urbanized areas close enough to influence surface concentrations of heavy metals, the main source of elevated heavy metals are most probably from natural sources such as Fe which was found in high concentrations in both surface and groundwater and can be attributed to the iron rich sandstone rocks existing in the investigated area.

Table 1. Pesticides residue concentration (ppb) in surface and groundwater in the investigated area.

Pesticides			Concentration							
Common name	Chemical name	Formula	Surface water				Groundwater			
			min.	max.	av.	n	min.	max.	av.	n
Vinclozolin	(RS)-3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione	$C_{12}H_{19}Cl_{12}NO_3$	128	390	239	16	60	220	160.5	20
Tetradifon	4-chlorophenyl-2,4,5-trichlorophenyl sulfone	$C_{12}H_6Cl_4O_2S$	42	3770	1341	16	38	415	155.4	10
Bromopropylate	Isopropyl 4,4-dibromobenzilate	$C_{17}H_{16}Br_2O_3$	54	70	62.5	4	ND	ND	ND	0
Fenpropathrin	(RS)-a-cyano-3-phenoxybenzyl 2,2,3,3-tetra-methylcyclopropanecarboxylate	$C_{22}H_{23}NO_3$	308	580	443	4	ND	ND	ND	0
opDDT	1,1,1-trichloro-2,2-bis(2,4-dichlorophenyl)-ethane	$C_{14}H_9Cl_5$	550	700	630	4	460	570	469	6
ooDDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane	$C_{14}H_9Cl_5$	1010	1300	1160	4*	ND	ND	ND	0
ppDDE	1,1-dichloro-2,2-bis(p-chlorophenyl)-ethylene	$C_{14}H_8Cl_5$	48	70	57.5	4	ND	ND	ND	0
ppDDD	1,1-dichloro-2,2-bis(p-chlorophenyl)-ethane	$C_{14}H_{10}Cl_5$	90	121	104	6	86	115	99.3	4

n : No. of samples detected out of 22 analyse samples
ND: Not detected
* At high temperature more than 40°C (effect of temperature on the solubility)

Table 2. Heavy metals concentration (ppb) in surface and ground water in the investigated area.

Heavy metals	Surface water				Groundwater			
	min	max	mean	n	min	max	mean	n
Pb	0.30	7.00	3.16	39	6.56	10.57	8.84	78
Cd	0.16	0.79	0.46	39	0.12	1.96	0.79	78
Co	0.10	5.20	1.69	39	0.73	2.61	1.70	78
Mn	2.50	269.40*	63.21	39	3.17	570.67**	72.42	78
Fe	50	1850	630	39	10	10900	901.9	72

n : No. of samples detected out of 39 analyzed samples (Surface water) and 78 (Groundwater)
* Nine samples out of 39 samples.
** Nine samples out of 78 samples

Table 3. Statistical difference between heavy metals concentration with sites.

Ionic species	Sum of squares between groups	df	Mean square between groups	Sum of squares within groups	df	Mean square between groups	F	$\alpha_{Obs.}$
Cd	69.670	63	1.106	54.792	40	1.370	0.807	0.780
Co	120.7	80	1.509	9.3	23	0.404	3.731	0.001*
Fe	122.462	98	1.250	2.0	5	0.4	3.124	0.10
Mn	425292.43	3	141764.143	473855.02	100	4738.550	29.917	0.001*
Pb	120.5	94	1.282	9.5	9	1.056	1.214	0.404

* Significant Difference between variables

The results of one way ANOVA at $\alpha = 0.05$ (Statistical Program) calculated for surface water only is presented in Table 3. The data suggest that there are no significant differences for Cd, Fe and Pb between the sites whereas significant variation exists for Co and Mn within sites. This can be attributed to differences in salinities between the sites as higher metal contents are associated with higher salinity and not from a point source pollution where the area is lacking of metallic industrial activities.

The overall results, for surface and groundwater resources at southern Dead Sea basin, showed that these resources are not highly contaminated with heavy metals. Except for those of iron and manganese, concentrations of other heavy metals in most samples were relatively low due to the high pH value (about 7-8) of water enhancing precipitation of these ions. Casing and steal pipes used in wells in addition to water salinity had an effect on the contents of heavy metals (especially of iron and manganese) of the extracted water; oraganohalogenated and Fenpropathrin pesticide residues were detected in most of the samples (except irrigation drainage) of the investigated area at low concentrations; all organophosphorous pesticide residues were below the detection limit that was attributed to low persistence under hot and dry climatic conditions of the investigated area.

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