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DETERMINATION OF PESTICIDES, NITRATE AND ARSENIC IN GROUND WATER OF SINDH

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ABSTRACT

In the present study Pesticides, Arsenic and Nitrate contents were analyzed in the ground water samples collected from the different districts of Sindh. Endosulfan was found above the MAC level (Maximum Acceptable Concentration 0.1 µg L^{-1} for single pesticide) and chlorpyrifos was found below the MAC level as defined by the Economic European Countries (EEC). Nitrate and arsenic contents were below the National Environmental Quality Standard (NESQS) i.e., 50 mg L^{-1} and 10 µg L^{-1}, respectively. A highly significant correlation of endosulfan with arsenic (r = 0.94) and nitrate (r = 0.95) was recorded followed by moderate correlation of nitrate with arsenic (r = 0.52), chlorpyrifos (r = 0.51). Correlation and between arsenic and chlorpyrifos was also significant (r = 0.50).

Keywords: *Pesticides, Organophosphate, Chlorpyrifos, Endosulfan, Nitrate, Arsenic, Groundwater,*

INTRODUCTION

The ground water contamination is associated with seepage of agrochemicals, sewage and industrial wastewater. (Bashir *et al.,* 2001). The use of shallow ground water sources for drinking and other domestic purposes is common feature of many low income urban communities in developing countries. Pesticide residues in water have been documented (Afzal *et.al*., 2000) and reported from different districts of Pakistan i.e Karachi (Parveen *et al*., 1988), Faisalabad (Jabbar *et al.*, 1993), Mardan, NWEP (Ahad *et al.*, 2000), Bahawalnagar, Punjab (Tariq *et al*., 2004) Bahawalpur, Pujnab (Anwar *et al*. 2005) and Nawabshah, Sindh (Tahir *et al*., 2008). Pesticide residues regulation and its impact on health (Ahmad *et al.,* 2009) and threats of pesticides have recently been discussed by Anwar *et al*. (2006) and Tariq *et al*. (2007).

Nitrate is the most common pollutant found in shallow aquifers. The extensive use of fertilizers is considered a main non-point source of the nitrate that leaches to groundwater (Chowdary *et al*., 2005). Septic tanks and dairy lagoons contribute nitrate contamination of groundwater (Almasri *et al.*, 2007).

Arsenic pollution of drinking water supplies poses a serious health hazard to an estimated 150 million people world-wide and110 million of those people live in ten countries in South and South-east Asia. It has recently been recognized that water and soil pose health hazard to people eating the produce of crops grown on soil and irrigated with arsenic contaminated water (Williams *et al*., 2006). In Pakistan, Farooqi *et al*., (2007) reported high contamination of arsenic in ground water of Kalalanwala areas of Punjab and in drinking water by Malik *et al*., (2009) above the acceptable standards. The geological and anthropogenic sources of arsenic in Sindh were discussed in detail by Baig *et al*. (2009). Moreover, the risk associated with mining activities, combustion of fossil fuels, use of arsenic as pesticides, desiccants and additives to livestock feed have also been highlighted by. Recently, Fatmi *et al*. (2009) studied the skin lesion at low arsenic exposure through ground water in Pakistan.

Due to the great health risk associated with these pollutants the present investigation was initiated to determine the level of contamination of pesticides, nitrate and arsenic in the ground water of Sindh and correlation of occurrence of agricultural and industrial toxicants.

MATERIALS AND METHOD

SAMPLING

Groundwater sample were collected from ten (10) different locations of Sindh i.e Larkana (L), Tando Bhago (TB), Sukkur (S), Hyderabad (H), Tando Adam (TA), Khair Pur (KP), Nawab Shah (NS) and Jackab Abad (JA). Water samples were collected from tube wells or hand pumps at the depth ranging from 40-45 m in polyethylene bottles and glass bottles, respectively. Two ml n-hexane was added to 1.5 L glass bottles to avoid microbial degradation and for nitrate and arsenic analysis I ml Hydrochloric acid was added. Samples were brought to laboratory and refrigerated.

ANALYSIS

Nitrate and arsenic were analyzed by standard methods (Fronson, 1975) and for pesticide analysis water samples were processed by the method of Tahir *et al*. (2008).

Nitrate: 10 ml water sample was taken in a test tube and the pH was adjusted upto 7.0 with (1:3) diluted acetic acid or 1 N NaOH . Two ml NaCl (30%) was added and mixed content of the tube by swirling. The tubes were placed in cold water bath then 10 ml 13 N H_2SO_4 was added and mixed by swirling. The tubes were again allowed to come to thermal equilibrium in cold water bath. 0.5 ml brucine sulfanilic acid reagent was added and mixed by swirling, then the tubes were placed at 100 C in a water bath for 20 minutes. The tubes were removed and immersed in a cold water bath and allowed to reach thermal equilibrium then absorbance was read at 410 nm against blank using spectrophotometer.

Arsenic: 25 ml of sample was taken in a flask of Gutzeit Arsenic determination apparatus and 5 ml concentrated HCl was added which followed by the addition of 2 ml Kl and 8 drops of $SnCl_2.2H_2O$ then mixed thoroughly. After 15 minutes zinc powder was added and immediately the scrubber was connected to the absorber assembly to the flask. The scrubber contained purified glass wool impregnated with lead acetate solution and absorber contained 4 ml silver diethyl dithiocarbamate solution. The sample was allowed for 30 minutes to complete the reactions and silver diethyl dithiocarbamate solution was directly taken into 1 cm cell then optical density was recorded at 535 nm using a spectrophotometer. In case of arsenic all the samples were analyzed by Kit method and results were confirmed by Gutzeit Arsenic method.

Pesticides: One liter water sample was taken in a separating funnel. 250 ml n-hexane solvent was added and shaken vigorously for 3 minutes and then allowed to settle for 8-15 minutes depending on the impurities in water. The bottom layer was discarded and the upper layer was collected in round bottom flask, passed through sodium sulphate (Na_2SO_4) to absorb the moisture content in the solvent then the solvent was evaporated by Rotatory Evaporator at 37 ^{O}C and concentrated to 1ml and refrigerated in vial for Gas chromatograph (GC) analysis.

RESULTS AND DISCUSSION

The results of samples analyzed for pesticides, nitrate and arsenic are given in Table 1. In all water samples the quantity of nitrate was determined to be less than the Maximum Concentration Limit (MCL) for drinking water set by WHO (50 mg L^{-1}). The average nitrate concentrations for 12 localities (63 samples) were determined by averaging the mean by concentration. In all, the water samples the quantity of nitrate is less than 50 mg/L. Many results that relate pollution by nitrates to the depth of the water table, well characterize, land and land use properties are reported in other regions of the world (Laftouhi *et al*., 2003). Singh *et al.* (2005) reported in Punjab (India) that nitrate content of well water near villages was significantly higher than in the cultivated area. Babiker *et al.* (2004) however, have found in the Kakamigahara Heights (Japan) that nitrate concentration of groundwater under vegetable fields was significantly higher than that of under urban land.

The average arsenic concentration in all the water samples was also found to be less than MCL for drinking water set by WHO (10 µg L^{-1}) and US (50 µg L^{-1}). The average arsenic concentration for 12 localities (63 samples) were determined by averaging the mean by concentration. In the entire water sample the quantity of arsenic is less than 10µg/L. According to WHO (World Health Organization) and guide line value arsenic is 10ug/L is standard for drinking water. According to WHO, 1.0 µg of inorganic As per day may give rise to skin lesions within a few years. Concentrations of naturally occurring arsenic in ground water are varied due to the geological and climatic changes (Smedley *et al.,* 2002). The literature counts various examples, which showed that trace elements including arsenic are more readily mobilized and transported by warm or hot water in the geothermal areas, like Jamshoro (Zaighama *et al.*, 2007).

The cotton growing areas in Pakistan receives heavy amount of pesticides that can find their way into ground water through leaching, channeling (downward percolation), direct spillage and wind drift (Tahir *et al.,* 2008). In the present investigation endosulfan was found above the Maximum Acceptable Concentration (MAC) i.e. 0.1µg L^{-1} for a single pesticide. In the present investigation the detected concentration of endosulfan is in agreement by the earlier investigations (Ghadiri *et al.*, 2001). Ahad *et al*., (2001) reported 0.13 µg L^{-1} in ground water collected from Multan, Punjab. The frequency of detection of endosulfan was reported to be 8% as compared to other pesticides detected in the range of 5.4-59.0 % in the ground water samples colleted from cotton growing areas of Punjab. Chlorpyrifos was not found above the MAC for single pesticides in samples collected form eight locations in the range from 0.006 to 0.003 µg L^{-1}, whereas no water sample was recorded above the MAC for multiple pesticide residues (0.5ug/L) as set by EEC (Economic European Union Countries). The multiple pesticides residues are very less which is below 0.5ug/L in drinking water as set by EEC (Economic European Union Countries). The pesticide in groundwater may threaten the human health because the shallow water is used for drinking purposes. Although the concentration of endosulfan was above the 0.1ug/L as regard to the drinking water standard, chlorpyrifos is below the health risk levels. Persistent pesticides move through air, soil, and water finding their way into living tissues where they can biologically accumulate up the food chain into human diets. Roughly 85–90% of pesticides applied agriculturally never reach target organisms, but disperse through air, soil and water (Moses *et al*., 1993).

Table 1 Pesticide residues, Nitrate (mg L-$^{-1}$) Arsenic (µg L^{-1}) in ground water of Sindh.

S.NO	**Locations**	**Pesticides**			**Fertilizer**	**Metal**
	Code	Endosulfan	Chlorpyrifos	Total	Nitrate (MAC 50 mg L^{-1})	Arsenic (MAC 10 µg L^{-1})
1	HD	0.126	0.0008	0.127	0.354	0
2	TA	0.124	0.0007	0.125	0.133	0
3	NS	0.2	0.0008	0.201	0.337	0.005
4	LR	0.14	0.002	0.142	0.372	0.005
5	KP1	0.184	0.0016	0.185	0.266	0
6	KP2	0.21	0.0009	0.211	0.239	0.005
7	TB	0.137	0.0022	0.139	0.306	0.005
8	KP3	0.119	0.0029	0.122	3.2	0.005
9	JA	0.148	0	0.148	0.53	0
10	SK	0.203	0	0.203	0.306	0.005
	Mean ± S.E	0.159± 0.0114	0.0015 ± 0.0003	0.160± 0.0112	0.604± 0.290	0.005± 0.00

Note: Ground water samples codes stand for HD: Hyderabad, TA: Tando Adam, NS: Nawab Shah, LR: Larkana, KP: Khair Pur, TB: Tando Bhago, JA: Jacab Abad and SK: Sukkur . 0, pesticides and Arsenic not detectable.

Table 2 Correlation coefficients matrix for ground water sample of Sindh.

Xenobiotics	Nitrate	Endosulfon	Chlorpyrifos	Arsenic
Nitrate	1			
Endosufon	0.95 (8.29)**	1		
Chlorpyrifos	0.51(1.67)*		1	
Arsenic	0.52 (1.74)*	0.94 (8.31)**	0.5 (1.6)*	1
	The values in the parenthesis are the t-values, (**) strong (*) moderate , df = 8			

Numerous studies have reported contamination of water resources by these chemicals (El Bakouri *et al*., 2008). Environmental pesticide contamination is frequently found at considerable distances from the original point of application of these compounds (Siddique *et al*., 2003). Even when used adequately, pesticides entail major risks. Their persistence, mobility and tendency to accumulate in living organisms when ascending the food chain can aggravate their toxic effects and have negative impacts on the health and well-being of humans (Sudaryanto *et al*., 2006).

A significant strong correlation of endosulfan with arsenic (r = 0.94) and nitrate (r = 0.95) was recorded followed by the moderate correlation of nitrate with arsenic (r = 0.52), chlorpyrifos (r = 0.51) and between arsenic and chlorpyrifos (r = 0.50) (Table 2). In contrast to the present finding, Tariq *et al. (2004) has* shown no correlation among these pollutants including nitrate. Such studies should be performed so that if really such relationship exits it would help predict the presence or absence of the other.

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