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Liability for Groundwater contamination by Organochlorine and Organophosphorus pesticide residues in Parbhani District

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ABSTRACT
Ground water samples in Parbhani district have had a designated Maximum Contaminant Limit (MCL) of pesticides in drinking water set by the U.S. Environmental Protection Agency (EPA) and WHO guideline for drinking water. Residues of several organochlorine and organophosphorus pesticide residues were monitored in the ground water from villages of Parbhani district for two years (2012-14). Most of the samples were found to be contaminated with residues of endosulfan, HCH and Dichloro-diphenyl-trichloroethane (DDT), Phosphamidon, dimethoate, malathion, chlorpyrifos. Heptachlor was absent in all samples. Migration of pollutants through ground water recharge with polluted Godavari River and monsoon rains carrying undegraded residues downwards from the soil surface are thought to be important sources of insecticide contamination of ground water in the region. The impact of agricultural chemicals on groundwater quality has become an issue of national importance.

Key Words: Groundwater, Godavari Plain of Parbhani, Pesticides analysis.

1. INTRODUCTION

Groundwater contamination by pesticides is serious issue because ground water is used for drinking purposes by most of the Parbhani people. This especially concerns people living in the agricultural areas where pesticides are most often used, as about all of that population relies upon ground water for drinking water. There is a common misconception among people that groundwater is generally safe for human consumption. However, it is not correct to presume that ground water is generally safe owing to qualitative changes in ground water (Bhattacharya et al., 2012), especially in the high-density residential areas where sewage and industrial disposal practices are not proper (Koul Nishtha et al., 2012). Our ancestors believe that soil acted as a protective filter that stopped pesticides from reaching ground water. But now studies have now shown that this is not the case. Pesticides can reach water-bearing aquifers (Doughton, 2004) below ground from applications onto crop fields, seepage of contaminated surface water, accidental spills and leaks, improper disposal, and even through injection waste material into wells. (Ronen 1996; Campos 1998)

Pesticides are bio-accumulative and relatively stable, and, therefore, require close monitoring. Lack of proper amenities in many housing societies and apartments has rendered the water unsafe for drinking as well as for domestic purpose (Shivashranappa et al., 2012). That leads us to ask just how concerned we should be about their presence in our drinking water (BIS, 1991). Certainly it would be wise to treat pesticides as potentially dangerous and, thus, to handle them with care. We can say they pose a potential danger if they are consumed in large quantities, but, as any experienced scientist knows, you cannot draw factual conclusions unless scientific tests have been done. Various countries or international bodies have published guidelines for setting water quality standards e.g. the WHO (World Health Organisation, 2006), the European Union, Canada (Environment Canada, 1999), Australia, USA. The World Health Organization's guideline values for drinking water for those pesticides exhibiting threshold toxicity effects are derived from the tolerable daily intake (TDI) or acceptable daily intake (ADI) by assuming daily consumption of 2 litres of water by a 60-kg adult. For pesticides that are highly persistent, have a high bioaccumulation potential, and are often found in food, only 1 % of the TDI is allocated to drinking water. In other cases, a default value of 10 % TDI is allocated to drinking water. Some pesticides have had a designated Maximum Contaminant Limit (MCL) in drinking water set by EPA (Cova et al., 1990) and WHO. Also, combining more than one pesticide in drinking water might be different than the effects of each individual pesticide alone. Certain pesticides are found to disturb the enzymatic activities of the body which leads to different types of diseases (Vettorazzi, 1979). A list of most commonly used pesticides with acceptable daily intake (Guidelines WHO, II edn., 1996) is given in Table 1 (Imran Ali and Jain, 1998). The various diseases/adverse effects produced due to some commonly used pesticides are listed in Table 2 (Imran Ali and Jain, 1998).

2. STUDY AREA

The Godavari River rises near the Trimbak in the district of Nasik in the Indian state of Maharashtra. The river is approximately 1,465 km long and has a total catchment area of 31 mha. It flows in the eastward direction through the states of Maharashtra and joins the Bay of Bengal in Andhra Pradesh. The principal tributaries of the River Godavari are Penganga, Pranahita, Sabari, Indravati, Manjeera and Manair. It is the second largest river in India. River Godavari is under the serious threat as a result of the growing Urbanization and industrialization. The river has been dying at an alarming rate due to the pollution created by the factories. Parbhani district covers an area of about 6250.58 km^2. The district is divided into 9 administrative Sub-units (Tahsils)-Parbhani, Gangakhed, Sonpeth, Pathri, Manwath, Palam, Selu, Jintur, and Purna. Godavari is the only main river in the district. Dudhana and Purna are other sub-rivers of Godavari. The length of the river is 79 km in the district and flows from west to east through Pathri, Gangakhed and Palam talukas and enters in to Nanded district. A sub river of Godavari, Dudhana flows in Selu, Jintur, Parbhani and Purna talukas and enters to Hingoli district. A Yeldari dam is constructed on Purna River at Jintur taluka of the district. We know that other rivers are polluted in some parts of the country (CPCB, 2009), (CPCB Report, 2009). The high organic matter content in the soil dissolves the pesticides and checks their transportation into the soil (Mahananda et al., 2010). The leachability of the pesticides in groundwater is controlled by the nature of the soil and the pesticides themselves (Hamilton, et al., 2003). The pattern of pesticide use, their degradation products, soil texture and the total organic matter in the soil are important factors for this process. Fine texture soils, in general, inhibit pesticide leaching because of either low vertical permeability or high surface area which enhances adsorption of pesticides. pH and the temperature of the soil are also important factors for the leachability of pesticides (Raju et al., 1993; Miliadis et al., 1994; Sherma 1995). However, the mass flow of water through the soil profile is also an important factor for the leaching of pesticides in groundwater (Hanipha et al., 2013).

3. MATERIALS AND METHODOLOGY

3.1. Sampling Methodology

Water samples were collected from Bore Well and Hand Pump (10 Bore Wells and 15 Hand pump) from pre monsoon and post monsoon in two years 2012-14. Water sample were taken directly from Bore well, Hand pump and filled into 500 ml polyethylene bottles, which were previously acid-washed and rinsed with portions of distilled water and water sample, fitted with tight lids. These samples were analyzed for the presence of organochlorine and organophophorus insecticide residues. Eight pesticides were initially selected due to the frequency of their occurrence: endosulfan, heptachlor, HCH and Dichloro-diphenyl-trichloroethane (DDT), Phosphamidon dimethoate, malathion, chlorpyrifos. According to the EPA and WHO they all have been detected in many place, and have the potential to reach levels which exceed health based standards. They are all associated with serious health effects including cancer (Zahm et al., 1998).

3.2. Sample Analysis

2 µl of the sample was injected and it was analyzed for the presence of pesticides, by Gas Chromatograph (Thermoquest-Trace GC) with the ^{63}Ni selective electron-capture detector. The capillary column used was DB-5 coated with 5% diphenyl and 95% dimethylpolysiloxane. The carrier gas and the makeup gas used was nitrogen with a 0.4 ml/min and 60-ml/min-flow rate respectively employing the split less mode. In this the oven temperature was kept at 60°C to 300°C with a ramp of 4°C/min. The detector and injector were maintained at 330°C and 260°C, respectively. The samples were calibrated (retention time, area count) against standard mixture of known concentration of all four organochlorine and four organophosphorous pesticides. Each peak was characterized by comparing relative retention time with those of standards. Identifications were confirmed by spiking with known standard and by performing thin layer chromatography of the pooled extract. Solvent systems used was 2% acetone in heptane and 10% chloroform in hexane. In this the spots corresponding to the position of standards were scraped, extracted and analysed by GLC. The identifications as usual were crosschecked with another GLC capillary column – DB- 17- coated with 50% phenyl, 50% methyl polysiloxane (length 30m, ID 0.25 mm and film 0.25 µm).

Table 1

Some most commonly used pesticides with their acceptable daily intake concentrations

Pesticide	Maximum acceptable values (µg/l)
Alachlor	20.00
Aldrin/Dieldrin	0.03
Carbofuran	5.00
Chlordane	0.20
DDT	2.00
HCB	1.00
Heptachlor	0.03
Methoxychlor	20.00

Table 2

Most Commonly used pesticides and their health hazards

Pesticides	Diseases/adverse effects
Aldrin	Attacks the nervous system, convulsion, repeated dosage damages the liver, carcinogenic
BHC	Liver tumour
Captan	Abnormality in the eyes and brain, carcinogenic
Chlordane	Carcinogenic
DDT	Liver damage, carcinogenic, destroys enzymatic activities
Endosulfan	Carcinogenic
HCH	Highly toxic, bone marrow damage, mutagenic, teratogenic, carcinogenic
Heptachlor	Liver damage, carcinogenic
Phosphamidon	anxiety, headache, confusion, convulsions
Dimethoate	moderately toxic compound
Chlorpyrifos	moderately toxic, neuroteratogen
Malathion	Low toxic but sometimes carcinogenic
Methoxychlor	Low toxic but sometimes carcinogenic
Mirex	Carcinogenic

Table 3
Highest concentrations of pesticides recorded in Parbhani District (Year 2012-14)

Pesticide	Dharkhed (mg/l)	Raorajur (mg/l)	Salegaon (mg/l)	Sonpeth (mg/l)	Rampuri Buzurg (mg/l)
Endosulfan	0.0017	0.0018	0.0022	0.0018	0.0020
Heptachlor	0.0005	Nil	Nil	Nil	Nil
HCH	0.0057	0.0056	0.0058	0.0062	0.0070
DDT	0.0028	0.0032	0..0035	0.0042	0.0019
Phosphamidon	0.0012	0.0016	0.0032	0.0040	0.0010
Dimethoate	0.1122	0.1166	0.1543	0.1342	0.1323
Malathion,	0.0649	0.0637	0.0067	0.0746	0.0823
Chlorpyrifos	0.0370	0.0412	0.0376	0.0410	0.0014

4. RESULTS AND DISCUSSION

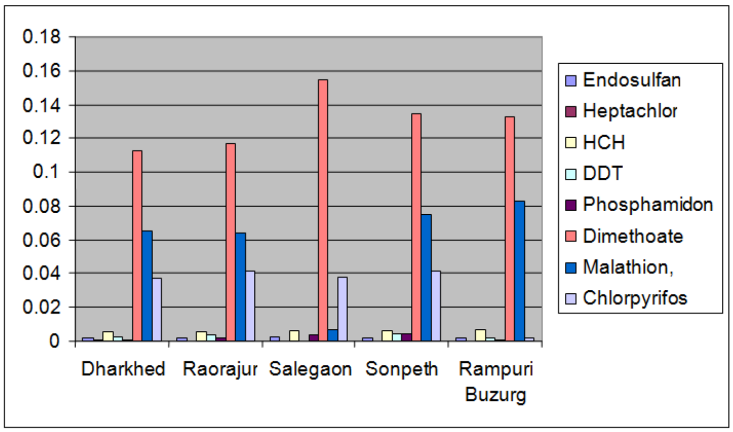

Figure 1
Pesticides present in different villages of Parbhani District in mg/Lit

Endosulfan is a broad-spectrum insecticide and acaricide. Heptachlor (banned with effect from September 20, 1996) is not used. Hexachlorocyclohexane (HCH) is used against sucking and biting pest and as smoke for control of pests in grain sores. It is used as dust to control various soil pests such as flea beetles and mushroom flies. It is in the list of banned pesticides in India (with effect from April 1, 1997). HCH, previously called BHC (benzene hexachloride), its isomer γ-HCH called lindane has powerful insecticidal properties. It is very effective against a wide variety of insects, including domestic insects and mosquitoes. γ-HCH (lindane) appears in the list of pesticides for restricted use. Only γ isomer of HCH is more resistant to biological and chemical degradation under aerobic conditions and is most commonly used. Dimethoate is a systemic and contact insecticide and acaricide, effective against red spider mites and thrips on most agricultural and horticultural crops. Malathion an important and widely used contact insecticide and acaricide for the control of aphids, red spider mites, leaf hoppers and thrips on a wide range of vegetable and other crops. It is also used to control insect vectors like mosquitoes. It is rapidly absorbed by practically all routes including the gastrointestinal tract, skin, mucous membranes, and lungs. Malathion requires conversion to malaoxon to become an active anticholinesterase agent. Most of the occupational evidence indicates a low chronic toxicity for malathion. Chlorpyrifos is a moderately persistent insecticide effective against mosquito and fly larvae, cabbage root fly, aphids. Chlorpyrifos (Qiao et al., 2001) has become one of the most widely applied insecticides in homes restaurants against cockroaches, termites.

Agricultural use of pesticides should be part of an integrated pest management (IPM) strategy that includes biological and cultural control, pest monitoring, crop rotation, and other applicable practices. When a pesticide is needed, its selection should be based on site characteristics and the pesticide's effectiveness, toxicity to non-target species, costs, half-life, etc. Presence of endosulfan isomers (α and β), endosulfan sulfate, predominance of p,p′ -DDT among ΣDDT (Vladimir et al., 2002) reflects that the quality of ground water in the area has deteriorated to a dangerous proportion making it unfit for drinking and irrigation purposes. The greatest concerns with the organochlorines are the long term effects. The U.S. EPA has concluded that DDT, DDE and DDD are probable human carcinogens. The concentrations of Endosulfan, HCH and DDT including organophosphorus pesticide residues especially Dimethoate, Malathion and in some quantities Chlorpyrifos in all the samples were above the permissible limits prescribed by the European Commission (Press release, 2001-2010) Directive for drinking purposes. Pesticides Actually Present Values in the places (Figure 1) in the Godavari River plain near Parbhani recorded highest concentration of them are mentioned in Table 3.

5. RECOMMENDATIONS

Government should implement a public information and education program that emphasizes the importance of proper use (and disposal) of pesticides including the use of non-toxic alternatives whenever possible. The program should be directed to individuals, farmers, appropriate businesses, and government entities. Government should start guiding centers and support to enhance pesticide research, education, and technical assistance. The villages should have a program for pesticide hazardous waste disposal. It is strongly recommended that the government proceed with a full scale program that will establish a series of advisories and controls on the application of pesticide. The district should evaluate the possible impact on water resources of chemical applications of pesticides in wellhead protection areas.

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