

Pesticides and Heavy Metals in Agricultural Soil of Kanpur, India

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Received: 28 August 2000/Accepted: 1 June 2001

Most potential contaminants are necessary for agricultural production but become hazardous when they occur in excess in the soil. Much soil contamination is the result of human activity, including the entry of industrial wastes into soil through atmospheric deposition or application of agro-chemicals and sewage waste to the land. These organic (industrially derived compounds such as agricultural pesticides which are intentionally applied to the soil) and inorganic (heavy metals derived mainly from industrial processes although they may occur naturally in soil) contaminants reduce the soil quality for agricultural production. Soils thus play an important role for the global flux of pesticides and heavy metals in the environment.

The fate of a pesticide applied to soil depends largely on its persistence and solubility properties. Once applied to cropland, pesticides may either be taken up by plants (Nair et al, 1993) or ingested by animals, insects, worms, or microorganisms in the soil, or may move downward in the soil (Sujatha and Chacko, 1992) and either adhere to it or dissolve in water or may vaporize (Maguire, 1992) and enter the atmosphere or may breakdown via microbial and chemical pathways into other, less toxic compounds (Samuel and Pillai, 1989) or may be leached out (Li and Migita, 1992) of the root zone by rain or irrigation water. Heavy metals like arsenic, cadmium, chromium cobalt, copper, lead, mercury, nickel and zinc, enter soil (Zanini et al, 1992) as a result of human activities like mining, metallurgy, use of fossil fuels and application of soil amendments and fertilisers. These heavy metals are persistent and their negative effect in soil are long lasting. They are absorbed by crops (Oladipo and Bodunde, 1993) and subsequently enter the human food chain.

In spite of the ban to pesticides like DDT, developing countries like India (Matthews and Graham, 1993) still use these insecticides due to cost benefit efficacy and broad spectrum toxicity. In an agricultural country like India (Mehrotra and Kailash, 1993), DDT and HCH contribute to more than 70% of the pesticide consumption. Hence it becomes imperative to ascertain their levels specially in the tropical part of the country like the Kanpur city (latitude 26.28N, longitude 80.24E) in Uttar Pradesh (Fig.1). The presence of high amounts of pesticides in some winter vegetables and fruits (from Kanpur) that we analysed

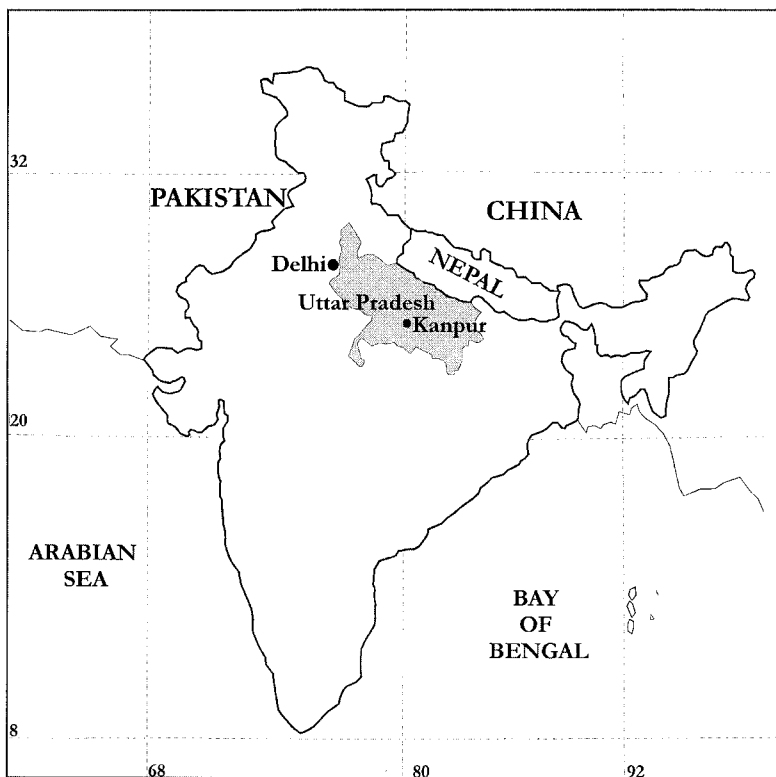


Figure 1. Geographical location of Kanpur in India

(Sanghi and Sasi, 2001), prompted us to take up the monitoring of the agricultural soil where most of these vegetables are locally grown. We explored the possibility of the presence of residues of some commonly used pesticides and absorption of heavy metals, in the soil samples from Kanpur, India. Although monitoring studies of the soil from various countries are available (Babkina, 1992), not much data is available on the tropical part of India (Pillai, 1986). In this paper, we provide information about the levels of organic (pesticides) and inorganic (heavy metals) contaminants in agricultural soil from Kanpur and nearby villages.

MATERIALS AND METHODS

The study included the following parameters: Soil sampled (place of origin) (Table 1), methods used, pesticides and heavy metals tested for and concentrations found for each pesticide and heavy metals (Table 2).

Pesticide analysis was carried out by Gas-Chromatograph (GC), Perkin Elmer Autosystem XL and the heavy metal analysis was carried out by Inductively Coupled Plasma (ICP), GBC Integra XL. Each sample was analysed thrice and the reproducibility of results was almost 95% by the above methods. Recovery studies were performed separately for two soil samples and the results showed recoveries exceeding 90 percent for all the twelve pesticides and 96% for the heavy metals.

Table 1. Place of origin of the soil samples

| sample | locality |
|--------|-----------------------------|
| S1 | Goraha , Bagdaudi Kachhaar |
| S2 | Ratanpur, Hora |
| S3 | Uttaripura, Kanpur Nagar |
| S4 | Kothi, Mandana |
| S5 | Nankari, IIT |
| S6 | Singhpur, Bithoor |
| S7 | Ramnagar, Mandana |
| S8 | Maanpur |
| S9 | Gohliapur, Bilhaur |
| S10 | Mandana |
| S11 | Dhamni nivada, Kanpur Nagar |
| S12 | Chaubepur |
| S13 | Bibipur, Bilhaur |
| S14 | Barajpur, Kanpur Nagar |
| S15 | Tatyaganj, Amliha |
| S16 | Bekhuntpur, Bithoor |
| S17 | Shivrajpur, Kanpur Nagar |

The pesticides chosen for study were obtained from RDH Laborchemikalien GmbH & Co. KG D-30918 Seelze via Promochem India pvt. ltd, Bangalore India. β -BHC was 99% pure and all the other pesticides were above 99.6% purity level. The pesticides were categorized as:

- organophosphates
 - methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate)
 - dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithiote)
 - malathion (diethyl(dimethoxy thiophosphorylthio succinate)
 - ethion O,O,O',O'-tetraethyl S,S'-methylene bis (phosphorodithioate))
- organochlorines
 - BHC (1,2,3,4,5,6-hexachloro cyclohexane)
 - DDT (1,1'-(2,2,2-trichloro ethylidene)bis [4-chlorobenzene])
 - DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethene)
 - Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzadio-xathiepin 3-oxide)
 - Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a,octahydro-1,4,5,8-dimethanonaphthalene)

The heavy metals analysed were copper, cobalt, cadmium, zinc, nickel, mercury, lead, arsenic and chromium. The heavy metal standards were obtained from Perkin Elmer (with 2% HNO₃, 1000 µg/ml). The heavy metals analysed Cd, Cr, Cu, Ni, Pb and Zn are those which in addition to Hg are listed in the EU Directive on the use of sewage sludge in agriculture.

The villages are within 20 kms vicinity of the Kanpur city. A variety of vegetables, wheat, barley, oat etc. are grown in the farms from where soil samples were collected. A total of seventeen sample types of agricultural soil were collected from the upper 15 cm soil layer by the method of Yadav et al (1981) from different sites in Kanpur area. The soil samples were dried at $t < 30^{\circ}\text{C}$ and sieved to pass a 2mm mesh. The subsamples were ground in a mortar and pestle and sieved to pass a 0.42 mm mesh and stored at -10°C until analysis.

For the pesticide analysis, each soil sample size taken was approximately 1kg, out of which representative subsamples in triplicate (35g) were randomly taken for the analysis. The pesticides were extracted for 8-10 hrs at the rate of 4-5 cycles per hour, in 150 ml of 50%(v/v) acetone in hexane in a soxhlet extractor (Thao et al.1993b, EPA method 3540). The extract obtained was cooled, filtered and concentrated in a rotary evaporator. The concentrate was again extracted in hexane/ water with the help of a separating funnel and dehydrated by passing through sodium sulphate. The solution thus obtained was filtered and concentrated to approximately 5ml. The cleanup and fractionation procedure was carried out with activated florisil packed in a glass column. The fractions obtained on with 20%(v/v) dichloromethane in hexane were analysed for the presence of twelve pesticides, by GC equipped with a split – splitless injection port and selective electron-capture detector (ECD). This detector allows the detection of contaminants at trace level concentrations in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which these detectors do not respond. The column used was PE-17, length 30m, ID 0.25mm, film 0.25mm with a 2ml/min flow. The carrier gas and the makeup gas was nitrogen employing the split mode. The oven temperature was kept at 190°C to 280°C with a ramp of $5^{\circ}\text{C}/\text{min}$. The samples were calibrated (retention time, area count) against 1 and 10 ppm standard mixed solution of all twelve pesticides. Each peak is characterised by its retention time and the response factors in ECD. Sample results were quantitated in ppm automatically by the GC software. The detection limit was 0.001mg/kg for organochlorines and 0.01mg/kg for organophosphate pesticides.

Recovery studies were performed separately for three original sample types by spiking the samples with known quantities of different pesticides and subjecting them to similar analytical procedures. The average recovery was almost 92.8% for organochlorines and 89.1% for organophosphates. The reproducibility of results for all the pesticides was 95.8% and above for all the samples. However, the mean average reading of a particular type of sample analysed in triplicate, was considered.

One GC injection (30 min) of 5 μl covered all twelve pesticides included in the analysis. Hamilton microsyringe injection of the pesticide dissolved in hexane as solvent were made directly onto the coated silanized column solid support, thereby eliminating the possibility of catalytic degradation by metallic surfaces. Pesticides were identified according to their retention times. The actual relative

retention times for the different pesticides were 11.60 (α BHC), 13.04 (β BHC), 13.09 (γ BHC), 13.78 (dimethoate), 14.50 (δ BHC), 15.41 (methyl parathion), 16.10 (malathion), 19.16 (endosulfan), 19.57 (DDE), 20.35 (dieldrin), 22.14 (ethion), 23.46 (DDT). For accurate results the concentration of the standard and concentration of sample to be estimated was kept same. The multiresidue method which can detect all twelve pesticides in one analytical run was preferred. This method is characterised by a broad scope of application, good recoveries and sensitivity and low solvent consumption, coupled with good analytical quality control.

The presence of Malathion (Kid and James,1991), DDE in the samples were further confirmed by ^1H NMR (Jeol, 400MHz) and IR (Bruker) spectral studies. ^1H NMR and IR spectra of the standard pesticide was taken separately and compared with that of the sample containing that particular pesticide.

The heavy metal analysis was carried out by ICP. 5g of soil sample in triplicate was randomly taken out of the 1 kg sample size and dissolved in 10 ml aqua regia with addition of 50 ml distilled water. This was subjected to boiling and then made up to 100 ml. Complete digestion of mineral soil matrix was achieved for all samples. A reagent blank is used to set zero absorbance and the sample solutions were diluted accordingly to bring it to the standard's absorbance range. Samples for which measured values were higher were reanalysed for the relevant metal after redigestion.

RESULTS AND DISCUSSION

Though the concentrations of pesticides in the vegetables grown in the farms (Sanghi and Sasi, 2000) from where the soil samples were collected was quite high (Carrot- 2.45 mg/kg malathion, 0.31 mg/kg DDE, Radish - 6.27 mg/kg malathion, 4.73 mg/kg dimethoate, Onion - 2.48 mg/kg malathion and 1.98 mg/kg BHC), large concentrations of the pesticides in the corresponding soil were not found. The concentrations in the vegetables analysed were much above the recommended 'Maximum residue limits' (MRL) (FAO/WHO, 1986) prescribed by the Indian government and 'acceptable daily intake'(ADI) by international standards. DDT and malathion were detected in almost all the samples and ranged from 0.05–0.98 mg/kg and 0.79-1.34 mg/kg respectively. Very low concentrations (0.02 - 0.14 mg/kg) of dimethoate were detected in samples S2, S6 and S13.

Chemical, Biological and Physical forces play an important role in the fate of pesticides in soil. Pesticides remain or persist in soil for a limited time, which may vary from days to years depending on the type of pesticide, soil moisture, organic matter, temperature and pH. Persistence may differ considerably because of varying environmental conditions and application rates. The non-persistent pesticides may disappear from soil in less than a month. Concentration of about 10 parts per billion represents background levels (concentration in soil with no history of pesticide use). Out of the twelve pesticides analysed, only organochlorine DDT, DDE and organophosphate malathion were detected above

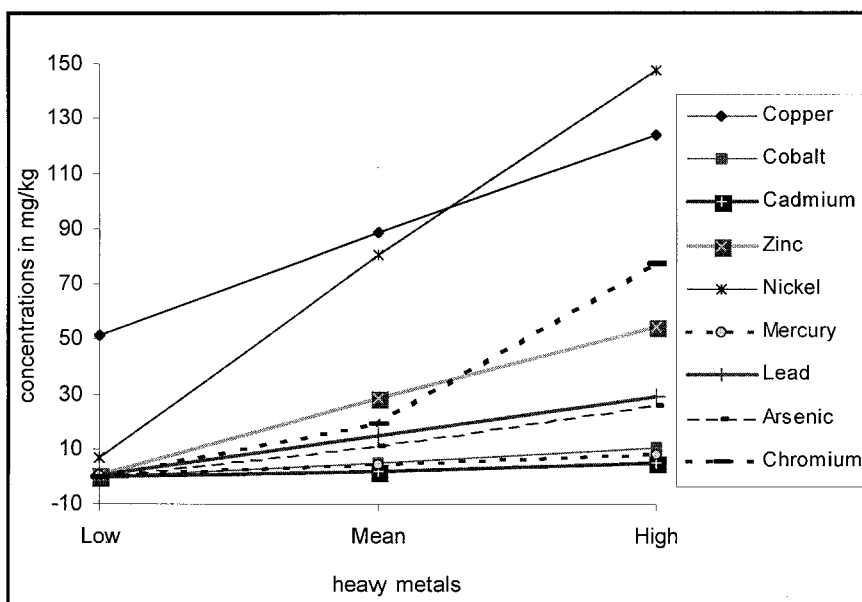


Figure 2. Low and high concentrations of heavy metals in agricultural soil from Kanpur

this limit in the soil samples. The mean values of levels of DDT was 0.25, DDE was 0.16 and malathion was 0.98 mg/kg. The limitation of these studies is that some other pesticides which were not analysed, other then these twelve commonly used ones, may also be present in the soil.

Soils have a natural ability to hold on to metals. The current input of metal contaminants might overload this capacity. Moreover, acidification makes some metals less tightly bound to soil particles, one exception being mercury. Metals freed in this way become available to plants, to which they might be toxic. They may also leach into waterways. Cadmium, zinc and lead become more mobile when acidity increases. They may then move further down in the soil profile.

Large concentrations of heavy metals in mg/kg were found in the soil samples analysed (Table II). It ranged from 'not detectable' (ND) in the case of Cadmium and Arsenic to 147.6 in the case of Nickel. The mean concentrations (Fig.2) of Nickel (80.6 mg/kg) and copper (88.67 mg/kg) were exceptionally high. The standard deviation (SD) for Ni was found to be 63.37 (% RSD 78.62) whereas for copper it was much less at 21.41 (% RSD 24.15). Chromium, Lead, Cobalt, and Zinc were also quite high. The concentrations of Chromium (0.2 – 77.6 mg/kg), Nickel (7.00- 147.6 mg/kg) and Zinc (0.8 – 54.6 mg/kg) varied drastically from locality to locality (Fig.3).

The concentrations of lead in agricultural soil was compared with the soil samples collected and analysed, from the roadways (78 mg/kg). Lower

Table 2. Mean concentrations of heavy metals in mg/kg (n=3)

| Sample | Copper | Cobalt | Cadmium | Zinc | Nickel | Mercury | Lead | Arsenic | Chromium |
|--------|------------|----------|---------|----------|-----------|---------|----------|---------|----------|
| S1 | 60.2 | 1.40 | 0.60 | 9.40 | 13.60 | 0.80 | 4.60 | ND | 4.60 |
| S2 | 95.4 | 5.60 | 0.40 | 29.80 | 138.40 | 4.60 | 14.40 | 12.60 | 21.20 |
| S3 | 76.8 | 4.80 | 0.20 | 24.80 | 147.60 | 3.40 | 12.80 | 8.40 | 14.20 |
| S4 | 75.0 | 3.40 | 0.40 | 28.20 | 18.80 | 8.20 | 18.40 | 9.20 | 2.80 |
| S5 | 114.2 | 2.80 | 1.60 | 14.20 | 40.40 | 1.60 | 8.00 | 8.00 | 10.40 |
| S6 | 111 | 6.00 | 3.00 | 47.80 | 136.60 | 2.00 | 19.00 | 16.20 | 19.00 |
| S7 | 81.4 | 5.00 | 2.40 | 31.60 | 147.40 | 5.00 | 18.60 | 12.80 | 16.40 |
| S8 | 67.6 | 5.80 | 2.80 | 31.60 | 147.00 | 4.60 | 17.00 | 19.00 | 117.60 |
| S9 | 106.2 | 2.40 | 1.00 | 14.40 | 55.40 | 3.40 | 7.20 | 7.40 | 9.80 |
| S10 | 101.6 | 4.40 | 2.00 | 29.40 | 11.80 | 7.00 | 13.60 | 7.60 | 16.40 |
| S11 | 63.2 | 5.40 | 2.60 | 37.20 | 147.60 | 4.20 | 15.20 | 10.20 | 17.60 |
| S12 | 95.8 | 6.60 | 3.00 | 29.40 | 15.60 | 3.20 | 16.60 | 13.60 | 21.00 |
| S13 | 123.8 | 10.00 | 4.80 | 54.60 | 21.20 | 7.20 | 24.80 | 18.00 | 28.20 |
| S14 | 111.4 | 10.20 | 5.00 | 45.20 | 28.40 | 6.00 | 29.20 | 26.20 | 29.40 |
| S15 | 77.2 | 0.20 | ND | 0.80 | 7.00 | 1.00 | 0.60 | ND | 0.20 |
| S16 | 51.2 | 3.60 | 2.40 | 24.60 | 145.80 | 6.00 | 15.80 | 5.00 | 18.40 |
| S17 | 95.4 | 7.00 | 3.40 | 30.20 | 147.60 | 5.40 | 21.00 | 13.60 | 21.60 |
| | | | | | | | | | |
| Mean | 88.67 | 4.98 | 2.09 | 28.42 | 80.6 | 4.33 | 15.11 | 11.05 | 19.34 |
| Range | 51.2-123.8 | 0.2-10.2 | ND-5.0 | 0.8-54.6 | 7.0-147.6 | 0.8-8.2 | 0.6-29.2 | ND-26.2 | 0.2-77.6 |
| S.D. | 21.41 | 2.66 | 1.43 | 13.69 | 63.37 | 2.2 | 7.13 | 5.41 | 17.3 |
| R.S.D. | 24.15 | 53.41 | 68.8 | 48.17 | 78.62 | 50.8 | 47.19 | 48.96 | 89.45 |

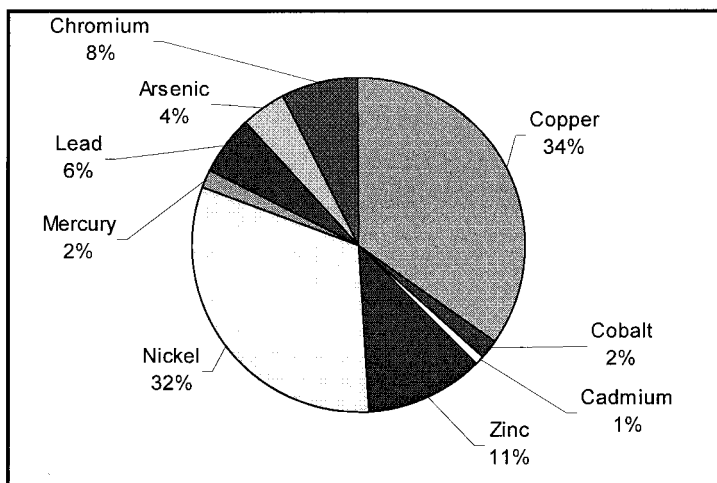


Figure 3. Relative mean concentrations of heavy metals

concentrations of lead in agricultural soil were in conformity to the fact that it is not much exposed to emissions from petrol fume exhausts.

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