Concentrations of polar pesticide residues in the surface waters of selected areas of Coast region, Tanzania

John Andrew Mahugija Marco and Michael Andrew Kishimba

Chemistry Department, University of Dar es Salaam, P.O. Box 35061 Dar es Salaam, Tanzania

E-mail: mahugija@udsm.ac.tz (Mahugija)

Abstract

The concentrations of 60 polar pesticide residues were investigated in surface waters from eleven sites in two rivers, a pond and four drinking water wells in Coast region, Tanzania. The extracts were analyzed by Gas Chromatography-Nitrogen Phosphorus Detection (GC-NPD) and confirmed by high-performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS). Quantification of analytes was done by using the peak heights with two different m/z for each analyte. The compounds detected were atrazine, isoproturon and diuron. The highest concentrations of atrazine were 13 ng/l in drinking water, 16 ng/l in pond water and 172 ng/l in river water. The highest concentrations of isoproturon and diuron in river water were 18 ng/l and 12 ng/l, respectively. Atrazine was the most predominant pollutant in water. The results indicate that the source of contamination is due to the agricultural use of these pesticides in the nearby areas. The concentrations of atrazine, isoproturon and diuron in drinking water were far below the WHO guidelines for drinking-water quality.

Keywords: Atrazine; Isoproturon; Diuron; Surface Waters; Tanzania

1. Introduction

Polar pesticides include a wide variety of compounds that are used as insecticides, herbicides, acaricides, nematicides and fungicides. Polar pesticides vary widely in physico-chemical properties like water solubility, K_{ow}, vapour pressure, molecular weight and thermal stability (Buchel, 1983). Due to their low molecular masses, very polar and/or thermolabile nature, difficulties are experienced in their analysis especially at low levels. Problems encountered include rapid deterioration of system performance, analyte losses in the inlet, large response differences between pesticides in extracts and the same concentration in clean solvent (complicating quantification), peak tailing, insufficient selectivity (matrix interferences) and, probably due to all this, poor repeatability (Hajslova and Zrostlikova, 2003; Mol *et al*, 2003). Thus, caution must be exercised when choosing the methods for residue analyses of polar pesticides.

Presence of organic compounds in water is a direct consequence of natural processes in the environment as well as of various anthropogenic activities in the industrial, agricultural and municipal sectors. While the occurrence of the organic compounds of natural origins, e.g. humic substances, which are part of the nature's life cycle, usually does not pose any remarkable problems to the environment, the presence of the anthropogenic organic micropollutants has an adverse impact on the quality of the aquatic ecosystem (Literathy *et al*., 2001). Based on the established quality standards a number of priority pollutants are being monitored regularly in surface waters such as the river basins in developed countries, but no such monitoring programmes are done in Tanzania and most of the developing countries.

In this study, we investigated the concentrations and distribution of polar pesticide residues in pond water, river water and drinking (well) water. The concentrations of residues in drinking water are compared with the WHO guidelines for drinking-water quality for indications of potential public health risks. The pond, rivers and wells studied play very important roles as the major sources of water for domestic uses, agricultural uses and to provide habitats for many species of plants and animals.

2. Materials and methods

2.1 Sampling

The samples which included river water from Chombe and Ruvu Rivers, pond water, and drinking (well) water were collected in September 2002 and May 2003. Water samples from Chombe River were collected from nine sampling points (points 6-10 and 12-15, Fig.1). Four sampling points were located for Ruvu River near the Upper Ruvu water works at Ruvu Darajani (points 16-19, Fig.1). Drinking

water samples were collected from four dug wells (points 1, 2, 3 and 11, Fig.1). Pond water samples were collected from two points (4 and 5) at the same pond (Fig.1). The samples were collected in one litre Teflon stoppered glass sampling bottles, in which sodium chloride (100 g) was added for preservation. The samples were transported to the laboratory and kept in a refrigerator at < 4 °C until extraction.

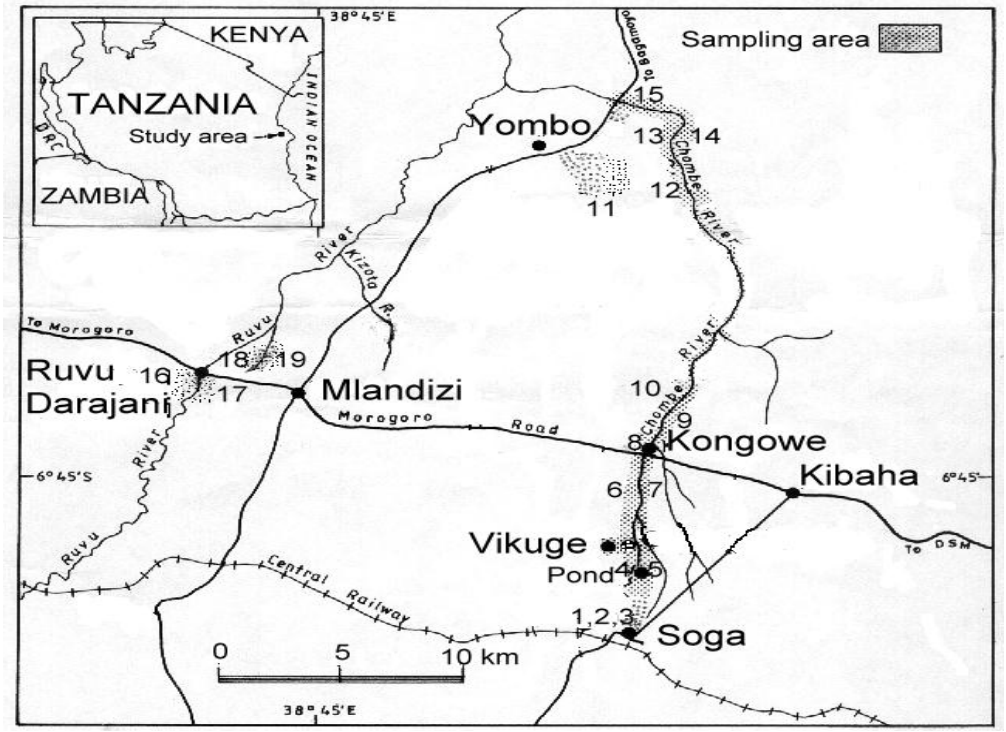


Fig. 1: Map showing the study area

2.2 Chemicals

All pesticide standards were obtained from Dr. Ehrenstorfer, Augsburg, Germany, and most of them were of over 99% certified purity. The concentrations of standard solutions were corrected for the certified purity of standards if below 99%. Individual stock solutions of standard polar pesticides were prepared in ammonium acetate and methanol and they were stored in glass-stoppered flasks at –18 °C. Mixed compounds calibration and measuring standards in ammonium acetate and methanol were prepared from the stock solutions. All solvents were HPLC grade. Laboratory glassware was washed with detergents, rinsed with distilled water and acetone, and then dried in an oven at 110 °C overnight prior to use.

2.3 Extraction and clean up

The unfiltered water sample (1 L) was extracted using the Liquid-Liquid Extraction (LLE) method (Åkerblom, 1995) with ethyl acetate (100 ml, 50 ml, and 50 ml). The organic extracts were dried with anhydrous sodium sulphate (15-20 g) then filtered, and solvent evaporated using a rotavapor at 35 °C and changed to cyclohexane to 1 ml.

Gel Permeation Chromatography (GPC) clean up of some river water and pond water samples extracts was performed using 50 cm x 1 cm i.d. chromatographic tube, with two adaptors, six-way valve with 1 ml sample injector loop and Teflon tubing (Pharmacia no SR 10/50, Uppsala, Sweden), elution with cyclohexane/ethylacetate (1:1 v/v). The GPC was calibrated using ethion (Åkerblom, 1995). Pesticides were eluted in the range 17 –35 ml. During the clean up, the first fraction (0-16 ml) was discarded. The second fraction (17-36 ml) was collected and concentrated for analyses. The column was cleaned with cyclohexane/ethylacetate (1:1 v/v, 20 ml) before injection of the next sample. The solvent was evaporated and changed to cyclohexane for GC-NPD analyses. The solvent was evaporated and changed to methanol and 10 mM ammonium acetate (1:1 v/v, pH = 6.8) for LC/MS/MS.

2.4 Chromatographic analyses

The gas chromatographic (GC) analyses were conducted using a Varian Star 3400 gas chromatograph, equipped with SE-30 and OV-1701 columns (30 m, 0.32 mm i.d., 0.25 μm film thickness, Hewlett Packard), with Nitrogen Phosphorus Detector (NPD) in the Department of Chemistry, University of Dar es Salaam. Hydrogen was used as both a carrier and make up gas at a flow rate of 30 ± 1 ml/min. The temperature programme was 90 °C held for 1 min, 30 °C/min to 180 °C, 4 °C/min to 260 °C held for 12 min. The injector and detector temperatures were 250 °C and 300 °C, respectively. Standards were injected in the beginning and after every four samples, with parathion being used as an external standard. A volume of 2 μl was injected in every run.

Confirmatory analyses were conducted with LC/MS/MS at the Institute of Ecological Chemistry, GSF-National Research Centre for Environment and Health, Germany. An Agilent (Palo Alto, CA, USA) 1100 HPLC-System (thermoautosampler and quaternary pump) and an API 2000 (Applied Biosystems, Foster City, CA, USA) equipped with an electrospray ionization (ESI) source were used to analyse for polar pesticides. The analytical column was a Phenomenex Synergi MAX-RP 150 x 3 mm (Torrance, CA, USA). Water was purified using a Milli-Q water purification system (Millipore, Bedford, MA, USA). The mobile phase consisted of methanol and 10 mM ammonium acetate (pH = 6.8), at a flow rate of 0.3 ml/min, with the following gradient: from 20% to 70% methanol in the first 5 minutes, increased to 100% the next 10 minutes, held for 2 minutes, then back to 20% in 1 minute and held for the last 7 minutes. Separations were carried out at 20 ^{o}C. The mass detector was operated at 450 ^{o}C nebulizer temperature, 50 psi nebulizer gas pressure, 60 psi turbo gas pressure, 20 psi curtain gas pressure, 1100 V ion spray voltage and 3 psi collision gas pressure. The linearity of the procedure was tested at the 0.01 to 0.5 μ/l levels

Identification of analytes was done by comparing the retention times and relative retention times with parathion as external standard in GC-NPD, and retention times and selected ion monitoring (SIM) mass spectra in LC/MS/MS with those of standards. Quantification of analytes was done by using the peak heights using two different *m/z* for each analyte.

2.5 Analytical quality assurance

A 100 ml aliquot of each solvent was concentrated to 2 ml and used to check the contamination from the reagents used. Two matrix blanks (distilled water) were also obtained. No significant peaks appeared in the chromatograms of the blanks. Chemical recoveries were estimated by spiking the distilled water with pesticide standards at concentrations ranging from 0.01 to 1 μg/ml of each analyte. The average recoveries (± SD, n = 2) were as follows: chlorpyriphos 92.3 ± 2.5%, fenitrothion 90 ± 3.2%, atrazine 80.3 ± 6%, and isoproturon 78 ± 3.2%. The results were not corrected for recoveries since all were within the normal acceptable range of 70 – 120% (Hill, 2000). The detection limit for all analytes was 5 ng/l.

3. Results

The results of the analyses of the samples have shown the presence of atrazine, isoproturon and diuron in some water samples. The results of sample analyses are summarized in Table 1. Atrazine was detected in drinking (well) water, pond water and Chombe River water. The levels of atrazine in Ruvu River water were all below the detection limit. The highest concentrations of atrazine were 13 ng/l in drinking water (Soga well 2), 16 ng/l in pond water and 172 ng/l in river water (Chombe River). The highest concentration of atrazine in Chombe River water was about thirteen times greater than the highest concentration in drinking water and was about eleven times greater than the highest concentration in pond water. In comparison, the concentrations of atrazine in Chombe River water were greater than those in drinking (well) water and pond water. The average concentrations of atrazine were 30.8 ng/l in Chombe River water, 15.5 ng/l in pond water and 7 ng/l in drinking water.

Table 1: Concentrations of polar pesticide residues in water (ng/l)

Sampling site	*Sample ID*	*Atrazine*	*Isoproturon*	*Diuron*
Soga well 1	1	6	nd	nd
Soga well 2	2	13	nd	nd
Soga well 3	3	9	nd	nd
Vikuge pond	4	15	nd	nd
	5	16	nd	nd
Chombe River	6	16	nd	nd
	7	5	nd	nd
	8	77	nd	nd
	9	172	nd	nd
	10	7	nd	nd
Well 4	11	nd	nd	nd
Chombe River	12	nd	18	12
	13	nd	nd	nd
	14	nd	nd	nd
	15	nd	nd	nd
Ruvu River	16	nd	nd	nd
	17	nd	nd	nd
	18	nd	nd	nd
	19	nd	nd	nd

nd = not detected

Isoproturon and diuron were detected in Chombe River water only at one site, and their concentrations were 18 ng/l and 12 ng/l, respectively (Table 1). These concentrations were generally lower than the concentrations of atrazine.

4. Discussion

The results of the analyses of the samples have shown the presence of some polar pesticide residues in some water samples. The compounds detected were atrazine, isoproturon and diuron.

Atrazine was detected in 53% of the samples, which indicated that it was a predominant pollutant in water. There is a significant difference in atrazine concentrations between Chombe River and Ruvu River that could indicate atrazine contamination in Chombe River, Soga wells and pond water due to usage in nearby areas.

Atrazine is used for the pre and post-emergence control of annual and broad leaved weeds and perennial grasses. Atrazine is used in the production of maize, sorghum, sugar cane, pineapples, grassland (Tomlin, 2000), with its biggest market in maize production (Hicks, 1998). Atrazine is also applied in combination with many other herbicides, for example with simazine (Tomlin, 2000). Atrazine is a pervasive environmental contaminant (Cox, 2001). It is strongly persistent and is one of the most significant water pollutants in rain, surface, marine, and ground water (Wiegand *et al*., 2001). Its persistence (it has a half-life of 125 days in sandy soils) (IPCS, 1990) and mobility in some types of soils because it is not easily absorbed by soil particles, means it often causes contamination of surface and ground waters (IPCS, 1990). Its persistence in deep lakes may exceed 10 years (Cox, 2001). Atrazine is a pesticide of major concern for a number of reasons including possible negative health effects, effects on aquatic organisms, levels in drinking water and the development of resistance (Cox, 2001). Whilst it is becoming less widely used, the effects of its long-term persistence may still cause health and environmental problems in the future.

The presence of isoproturon and diuron in Chombe River water at one site suggests the use of these pesticides in the areas which are near to that site. Isoproturon is mobile in soil and has been detected in both surface water and groundwater. In water, it is quite persistent and hydrolyses slowly; the half-life is about 30 days (Department of the Environment, 1989). In soil, isoproturon undergoes enzymatic and microbial demethylation at the urea nitrogen and hydrolysis of the phenylurea to form 4-(2-hydroxyisopropyl)aniline. It also undergoes some photochemical degradation; photometabolites

identified include 3-(4-isopropylphenyl)-1-methylurea, 3-(4-isopropylphenyl)urea, 4,4'-diisopropylazobenzene, and 4,4'-diisopropylazoxybenzene. Under field conditions, its half-life is about 40 days in temperate climates and 15 days in tropical climates (Kulshrestha and Muckerjee, 1986).

Diuron has a relatively low K_{OC}, which indicates a relatively low tendency to sorb to soils and sediments, while its hydrolysis half-life (1240-2020 days, pH 5-9 at 25 °C) and aqueous photolysis half-life (43.1-2180 days, pH 7 at 25 °C) (DPRPesticide Chemistry Database, 2003) are relatively long. Consequently diuron is both mobile and relatively persistent, and is therefore prone to off-site movement in surface runoff, and migration to ground water.

The concentrations of atrazine in drinking water were far below the WHO guideline for drinking-water quality of 2000 ng/l (WHO, 1996). The concentrations of isoproturon and diuron in drinking water were all below the detection limit (< 5 ng/l) and thus were far below the WHO guideline for drinking-water quality of 9000 ng/l (WHO, 1996).

The concentrations seem to be very low may be because most polar pesticides have limited environmental persistence due to their ready hydrolysis, facile biodegradation and photodegradation (Connell, 1997). There is no any published work that has reported on the presence of atrazine, isoproturon and diuron in surface waters of other areas in Tanzania which we could compare our findings. This is partly because the previous studies did not screen for these pesticides.

4. Conclusions

In general the concentrations of polar pesticide residues in the surface waters from the studied areas of Coast region in Tanzania were very low. This is important for the community in these areas and the water-works especially in the Ruvu River because most polar pesticides are toxicologically important. The Ruvu River serves as the major source of domestic water supply for Coast region and the capital city of Dar es Salaam. The low polar pesticides concentrations can be explained by the fact that most polar pesticides have limited environmental persistence. From all the 60 polar pesticides under investigation (56 of them are listed in Appendix 1) only atrazine, isoproturon and diuron could be found in and along the Chombe River. The highest concentrations were mainly found in the Chombe River, which might be explained by emissions from nearby farms which use these pesticides.

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Appendix I List of polar pesticide residues screened by LC/MS/MS

Analyte	*Mass transition*	*Analyte*	*Mass transition*
Acephate	143 / 95	Isoproturon	207 / 165
Aldicarb	208 / 116	Ketoprofen	255 / 105
Atrazine	216 / 68	Metalaxyl	280 / 192
Butocarboxim	191 / 75	Metazachlor	278 / 210
Buturon	237 / 84	Methabenzthiazuron	222 / 165
Carbaryl	202 / 145	Methamidophos	142 / 94
Carbendazim	192 / 160	Methiocarb	226 / 169
Carbofuran	222 / 165	Methomyl	163 / 88
Chlorotoluron	213 / 72	Metoxuron	229 / 72
Chloroxuron	291 / 72	Mevinphos	225 / 127
Diazinon	305 / 97	Monolinuron	215 / 148
Difenconazole	408 / 253	Monuron	199 / 72
Diflubenzuron	311 / 158	Neburon	275 / 88
Difenoxuron	287 / 72	Omethoate	214 / 125
Dimethoate	230 / 199	Oxamyl	237 / 72
Diniconazol	328 / 70	Pencycuron	331 / 127
Dimefuron	339 / 72	Phentoate	321 / 247
Diuron	233 / 72	Pirimicarb	239 / 72
Epoxiconazole	330 / 70	Promecarb	208 / 109
Etaconazole	328 / 159	Propiconazole	342 / 159
Ethiofencarb	226 / 107	Propoxur	210 / 168
Fenobucarb	208 / 95	Prosulfocarb	252 / 91
Fenuron	165 / 72	Pyrazophos	374 / 222
Fenoxycarb	302 / 116	Terbuconazole	310 / 70
Fluometuron	233 / 72	Thiodicarb	355 / 88
Flusilazole	316 / 247	Thiofanox	219 / 57
Furathiocarb	383 / 195	Triadimenol	296 / 70
Hexaconazole	314 / 70	Triflumuron	359 / 156