An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1984 to September 1985

AJ Hassett*, PT Viljoen and JJE Liebenberg
National Institute for Water Research, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, South Africa.

Abstract

During the period September 1984 to September 1985, monthly grab samples were taken from fifteen major surface water resources in the Orange Free State (OFS). Analyses for fourteen chlorinated pesticides were conducted by gas chromatography, electron capture detection. Sales figures for the more commonly used chlorinated pesticides were obtained for the years 1982 to 1984 as background information. Analytical results indicate high maximum values of Atrazine in surface waters in the northern and north-western OFS as well as a single point in the south-eastern OFS. Contamination occurred mainly during January and February. Concentrations of less than 0,8 $\mu g/\ell$ of pp'-DDT were detected in all samples but only during the period September to March. Endrin was detected on three separate occasions in single samples taken from three individual sampling points, at concentrations between 2-4 $\mu g/\ell$. Contamination by other chlorinated pesticides was infrequent, distributed randomly over the period and generally at concentrations below 0,1 $\mu g/\ell$.

Introduction

The presence of large numbers of organic compounds in water, many of which are known to be toxic, or carcinogenic, has caused considerable and wide-spread concern. There is mounting evidence that long-term exposure to low concentrations of certain organic chemicals can be a significant factor in the development and manifestation of some chronic diseases (Fielding and Packham, 1977; National Research Council, 1982). It is further believed that between 80 and 90 per cent of cancer cases have an environmental origin and therefore contaminants present in potable water supplies come under suspicion (Fielding and Packham, 1977).

Most organochlorine pesticides are known to be carcinogenic (National Research Council, 1982). It has been shown that these pesticides are resistant to biodegradation (Tabak *et al.*, 1981) and they and their biologically active metabolites are extremely persistent in soils and surface waters (Phingara *et al.*, 1978).

The organochlorine pesticides DDT, dieldrin and DDE have been taken off the market in the Republic of South Africa (RSA) and are no longer available to the public. Unfortunately little is known as to whether these compounds still occur in South African potable water supplies. The extensive use of the herbicide, Atrazine (2-chloro-4-ethylamino-6-isopropylamino-5-triazine) may prove to be an ecological hazard (Brockway *et al.*, 1984) as it is reportedly toxic to algae at concentrations as low as 1 $\mu g/\ell$.

A high degree of contamination of surface waters occurs from agricultural runoff and atmospheric fall-out (Bedding *et al.*, 1982). The Orange Free State is predominantly a crop farming area and the major producer of maize and wheat in the RSA, consequently it was decided to investigate this area for the occurrence of organochlorine regulatory agents in surface waters.

Pesticide usage

Prior to the selection of sampling sites, a survey was done to assess the type and quantity of chlorinated pesticides and herbicides that were being used by the farming community (Table 1).

Sales figures obtained from various Agricultural Cooperatives covering the period 1982 to 1984, show an increase in Atrazine sales of 670 t in 1983 to 2 900 t in 1984. Sales of other chlorinated herbicides and insecticides fluctuated slightly between 1983 and 1984 (Table 1).

TABLE 1
QUANTITIES OF THE MOST COMMONLY USED CHLORINATED REGULATORY AGENTS SOLD IN THE OFS (1982-1984)

		Quantity (t)		
Active ingredient	**Type**	**1982**	**1983**	**1984**
Atrazine	Herb.	843	670	2 934
Terbutylazine	Herb.	191	69	45
Metolachlor	Herb.	124	61	50
2,4-D	Herb.	90	70	91
Alachlor	Herb.	51	28	15
Chlorpyrifos	Insect.	34	6	9
MCPA	Herb.	16	14	17
Endosulfan	Insect.	13	28	25
Propachlor	Herb.	13	9	13
Cyanizine	Herb.	11	5	3
Trichlorphon	Insect.	5	9	17
Dichlorvos	Insect.	4	0,7	1,5
gamma-BHC	Insect.	2	0,7	0,9
Permethrin	Insect.	2	4	3
Paraquat	Herb.	1,6	0,7	1,1
Fenvalerate	Insect.	1,4	1,4	0,7

Herbicides are usually applied at the time of planting, whereas insecticides are generally applied at an advanced stage of growth. The extended drought experienced by the country during 1984, resulted in poor crop yields and consequently a low occurrence of crop pests. This may explain the increased usage of the herbicide, Atrazine.

Sampling and methods

A total of fifteen surface waters (Table 2) in intensive crop farming areas, were selected for sampling (Fig. 1).

*To whom all correspondence should be addressed.
Received 10 September 1986.

TABLE 2 SELECTED SAMPLING SITE IDENTIFICATIONS	
Site Number	Sampling Site
1	Vaal River (Villiers)
2	Wilge River (Frankfort)
3	Vaal River (Parys)
4	Vaal River (Balkfontein)
5	Laaispruit (Marquard)
6	Meulspruit (Ficksburg)
7	Liebenbergsvlei River (Bethlehem)
8	Liebenbergsvlei (Reitz)
9	Renoster River (Viljoenskroon)
10	Vals River (Kroonstad)
11	Vet River (Hoopstad)
12	Sand River (Senekal)
13	Leeu River – Armenia Dam
14	Caledon River (Ladybrand)
15	Caledon River – Welbedacht Dam

Monthly grab samples, over the period September 1984 to September 1985, were taken from these sampling points. Sample containers consisted of 50 mℓ amber glass bottles, sealed with teflon-lined screw caps. The sample containers were cleaned by washing in detergent, rinsing thoroughly with distilled water and baking at 200°C for 12 h. Pesticides were extracted from 10 mℓ of sample with 200 $\mu\ell$ solvent (van Rensburg and Hassett, 1982) and analysed by high resolution capillary gas chromatography with electron capture detection.

Separations were done on an HP5710 gas chromatograph with a Ni^{63} electron capture detector and a split injector with a split ratio of 1:20. The detector temperature was maintained at 300°C and the injector temperature at 220°C. The analytical column was a 30 m × 0,32 mm ID, 1 μm film thickness, J & W DB5 (J & W Scientific Inc., 3871 Security Park Drive, Rancho Cordova, CA 95670 USA) fused silica capillary column. Helium was used as carrier gas at a flow rate of 2 mℓ/min and the detector make-up gas was 10% methane in Argon at a flow rate of 30 mℓ/min. A 2 $\mu\ell$ aliquot of the extract was injected with the column at 70°C and after an initial hold time of 2 min the oven was programmed to 150°C at 8°C/min and then to 290°C at 4°C/min with a final hold-time of 5 min.

Figure 1
Distribution of sampling sites.

Aldrin was used as internal standard at a concentration of 0,4 $\mu g/\ell$. A standard pesticide mixture obtained from Foxboro/Analabs (Foxboro/Analabs, 80 Republic Drive, North Haven, CT., 06473 USA) was used for calibration purposes. All the unidentified compounds detected were assigned a response factor of 1,00 and their concentrations calculated relative to the internal standard. The identification of the compounds detected was done by gas chromatographic retention-time only.

Results and discussion

The median value has been used for the statistical evaluation of the data, in preference to the mean value because the data obtained are not normally distributed. The median value is not affected by data points at the extremes of the distribution, thus reflecting a true central tendency (Reckhow, 1980). The interquartile range (25%-75%) is also a better measure of the spread of the data than the standard deviation since its values do not depend on the mean value (Reckhow, 1980).

Analyses were carried out for fourteen chlorinated pesticides, listed in Table 3. The compound found in the highest concentration was Atrazine. The highest concentration level detected was 82,3 $\mu g/\ell$, found in a sample taken at Balkfontein (Fig. 1, Sampling point 4).

The highest concentrations of Atrazine were detected in samples taken during January and February (Fig. 2).

The interquartile range shows a large spread of concentrations over these months. Concentrations decrease through to April and May. This decrease may be accounted for by the relative stability of Atrazine which has a half-life of between two and three months (Frank and Sirons, 1985).

TABLE 3 FOURTEEN CHLORINATED PESTICIDES FOR WHICH ANALYSIS WAS DONE	
1.	Atrazine
2.	alpha – BHC
3.	beta – BHC
4.	gamma – BHC
5.	delta – BHC
6.	Heptachlor
7.	Heptachlor Expoxide
8.	alpha – Endosulfan
9.	pp'-DDE
10.	Dieldrin
11.	Dieldrin
12.	beta-Endosulfan
13.	pp'-DDD
14.	pp'-DDT

The greatest contamination by Atrazine occurred in the northern and north-western OFS and in the Welbedacht Dam, situated on the Caledon River in the south-eastern OFS (Table 4).

Besides Atrazine, the other chlorinated pesticide most frequently detected in the water samples was pp'-DDT. The maximum concentration found was 0,8 $\mu g/\ell$, in the Welbedacht Dam (Fig. 1, Sampling Point 15). Generally, the concentration levels found were below 0,5 $\mu g/\ell$. The median value of the concentrations detected in all samples was 0,2 μg/ℓ with an interquartile range of 0,17 μg/ℓ-0,63 μg/ℓ. pp'-DDT was detected only in samples taken between September and March, the period during which the OFS receives its rainfall. It has been shown that pp'-DDT is extremely persistent in soils (Frank *et al.*, 1981) and since pp'-DDT has had no official agricultural use since 1976, it is likely that the contamination of the surface waters by pp'-DDT may result from the leaching of soils.

respectively. The other pesticides were detected at random throughout the period and generally at concentrations below 0,5 μg/ℓ. The median, maximum and interquartile range of the total pesticide concentration, excluding Atrazine, for each sampling point is listed in Table 4. None of the samples had 3rd quartile values greater than 0,3 μg/ℓ. Similarly, no median value of the unidentified compounds exceeded 0,5 μg/ℓ and the highest 3rd quartile value observed was 0,53 μg/ℓ (Table 4).

TABLE 4
MEDIAN, MAXIMUM AND INTERQUARTILE RANGE (I) OF ATRAZINE, CHLORINATED PESTICIDES (EXCLUDING ATRAZINE), pp'-DDT AND UNIDENTIFIED COMPOUNDS FOR EACH SAMPLING POINT

	Concentrations (μg/ℓ)											
	Atrazine			Chlorinated pesticides (excluding Atrazine)			pp'-DDT			Unidentified compounds		
Sampling point	Median	Max.	I	Median	Max.	I	Median	Max.	I	Median	Max.	I
1	0,13	21,0	*-3,44	0,27	0,7	*-0,3	0,18	0,66	*-0,26	0,4	1,0	0,23-0,47
2	0,79	18,7	*-2,47	0,18	0,32	*-0,22	0,17	0,27	*-0,18	0,4	0,27	0,14-0,51
3	*	61,5	*-0,42	*	1,07	*-0,13	*	0,53	*-*	0,24	0,47	0,1 -0,3
4	0,38	82,3	*-5,11	*	3,31	*-0,2	*	0,57	*-0,13	0,46	1,0	0,2 -0,6
5	*	8,3	*-1,67	*	3,53	*-0,13	*	0,23	*-0,09	0,42	2,04	0,08-0,53
6	*	3,5	*-1,86	*	1,68	*-0,08	*	0,49	*-*	0,2	2,55	0,09-0,42
7	0,44	21,2	*-5,01	*	4,7	*-0,22	*	0,6	*-0,16	0,4	3,06	0,26-0,47
8	*	6,3	*-*	0,11	0,91	*-0,21	0,07	0,76	*-0,21	0,37	0,44	0,19-0,43
9	*	30,3	*-0,47	0,09	0,47	*-0,26	*	0,4	*-0,15	0,36	1,2	0,13-0,50
10	0,27	6,9	*-3,7	0,13	0,79	*-0,28	0,1	0,36	*-0,19	0,25	0,77	0,12-0,34
11	0,24	6,5	*-0,45	0,12	0,49	*-0,19	*	0,44	*-0,19	0,42	1,78	0,18-0,51
12	*	7,9	*-1,69	*	1,51	*-*	*	0,2	*-0,17	0,38	1,0	0,14-0,51
13	*	11,9	*-*	0,12	5,01	*-0,23	*	0,5	*-0,09	0,28	4,25	0,1 -0,5
14	*	9,7	*-*	*	0,46	*-0,22	*	0,45	*-0,2	0,28	0,69	0,06-0,41
15	*	50,9	*-0,14	*	6,45	*-0,19	*	0,8	*-0,19	0,22	2,58	0,12-0,26

*not detectable

Rainfall data for the whole study area indicate that the monthly rainfall (expressed by the median value) in excess of 50 mm, occurred during October to March (Fig. 3). The highest, total monthly rainfall at each sampling point was also recorded during the period October to March. (Table 5).

Of the other chlorinated pesticides (Table 3), Endrin was detected in single samples taken from each of the points 7,13 and 15 (Table 2; Fig. 1) at concentrations of 2,1; 4,2 and 3,0 μg/ℓ

TABLE 5
HIGHEST, TOTAL MONTHLY RAINFALL, AT SAMPLING POINTS

Sampling Site	Maximum (mm)	Month
1. Villiers	140	January
2. Frankfort	111	January
3. Parys	103	December
4. Balkfontein	155	February
5. Marquard	150	February
6. Ficksburg	96	October
7. Bethlehem	130	January
8. Reitz	124	January
9. Viljoenskroon	89	January
10. Kroonstad	158	March
11. Hoopstad	91	October
12. Senekal	104	November
13. Armenia Dam	107	November
14. Ladybrand	129	November
15. Welbedacht	94	February

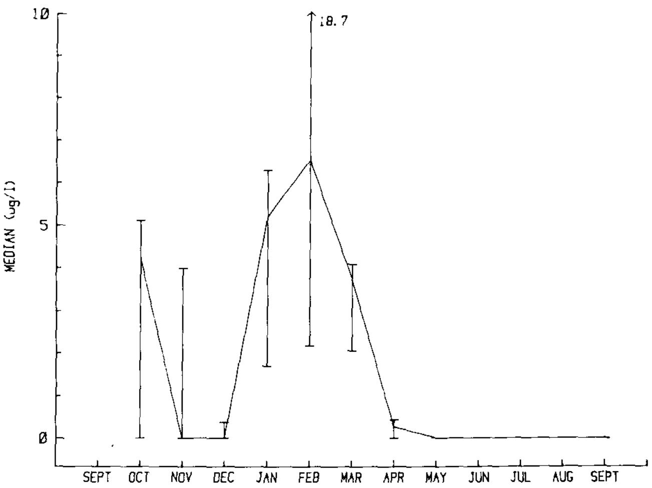

Figure 2
Median value (μg/ℓ) and spread of Atrazine found in the OFS for the period October to September.

Figure 4 is a plot of the normalised monthly median values, at each sampling point of the concentration of all compounds detected, the Atrazine concentrations, the pp'-DDT concentrations and the concentrations of the unidentified compounds. This gives an overall picture of the contamination of the surface waters in the OFS by organochlorine pesticides and herbicides. The normalised data reveal a trend which shows that the greatest contamination occurs mainly during January and February.

Conclusion

Runoff from agricultural land has been shown to be a major source of contamination of surface waters by organic pollutants, particularly pesticides (Bedding *et al.*, 1982). Results of a survey done in the OFS, a large argicultural area, indicate contamination of surface waters by the herbicide Atrazine, with concentration levels reaching 80 $\mu g/\ell$. This compound was, however, only detected in samples taken between October and April. Maximum concentrations were observed in January and February. Sales figures of the commonly used chlorinated pesticides and herbicides, reflect the extensive usage of Atrazine in 1984, with sales of Atrazine five times higher than in 1983. It has been reported (Hallenbeck and Cunningham-Burns, 1985) that Atrazine is mutagenic and causes prenatal damage, however, World Health Organization (WHO, 1984) has not listed this compound in their recommendations for drinking-water quality.

The analytical data on the other chlorinated pesticides indicate their occurrence at low concentration levels, generally below 0,3 $\mu g/\ell$. Low concentrations of pp'-DDT were observed (Table 4) and only during the period September to March. Because of the stability of this compound, the transportation of pp'-DDT from soils to surface waters, due to leaching, must be considered.

The close resemblance of the trends of the median values of the total contamination (Fig. 4) and the median rainfall figures (Fig. 3) would suggest that surface runoff may play an important part in the transport of agricultural pollutants to the surface waters in the study area. The results derived from this investigation form a sound basis for a more detailed study of this subject. In such a study, the identification and characterisation, by gas chromatography – mass spectrometry, of the compounds detected, would be essential.

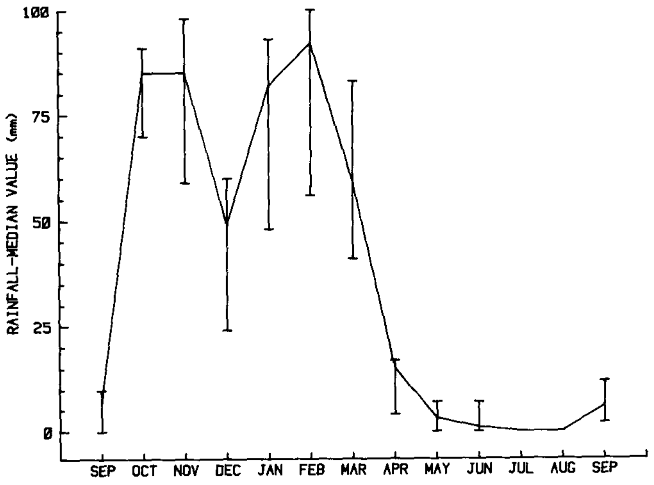

Figure 3
Median value and spread of monthly rainfall for study area.

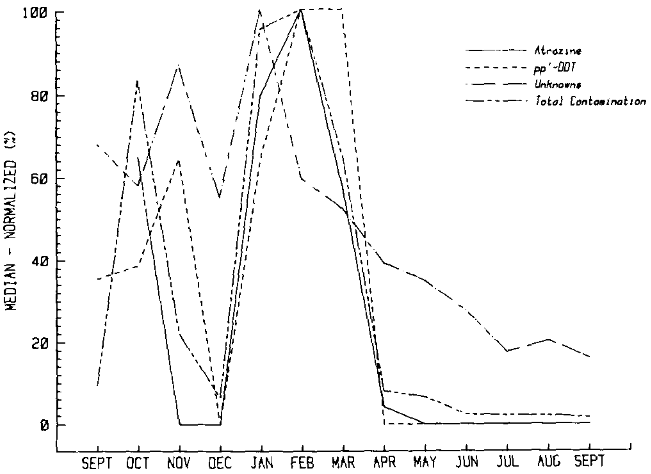

Figure 4
Normalised median value (%) of Atrazine, pp'-DDT, total unknowns and total contamination for the OFS over the period September to September.

Acknowledgements

Rainfall data were supplied by the South African Weather Bureau, Pretoria. This paper is published with the permission of the National Institute for Water Research.

References

BEDDING, N.D., McINTYRE, A.E., PERRY, R. and LESTER, J.N. (1982) Organic contaminants in the aquatic environment. I Sources and Occurrence. *Sci. Tot. Environ.* **25** 143-167.

BROCKWAY, D.L., SMITH, P.D. and STANCIL, F.E. (1984) Fate and effects of Atrazine in small aquatic microcosms. *Bull. Environ. Contam. Toxicol.* **32** 345-353.

FIELDING, W. and PACKHAM, R.F. (1977) Organic compounds in drinking water and public health. *J. Inst. Wat. Eng. Sci.* **31** 353-375.

FRANK, R., BRAUN, H.E. and HOLDRINET, M.V.H. (1981) Residues from past users of organochlorine insecticides and PCB in waters draining eleven agricultural watersheds in southern Ontario, Canada. 1975-1977. *Sci. Total Environ.* **20** 255-276.

FRANK, R. and SIRONS, G.J. (1985) Dissipation of Atrazine residues from soils. *Bull. Environ. Contam. Toxicol.* **34** 541-548.

HALLENBECK, W.H. and CUNNINGHAM-BURNS, K.M. (1985) *Pesticides in Human Health.* Springer-Verlag New York Inc.

NATIONAL RESEARCH COUNCIL (USA) (1982) *Quality Criteria for Water Reuse.* Nat. Academy Press. Washington D.C.

PHINGARA, S.S., WARREN, W.J. and NELSON, P. (1978) Pesticidal residues in rural potable water. *J. Am. Wat. Wks. Ass.* **70** 41-45.

RECKHOW, K.H. (1980) Techniques for exploring and presenting data applied to lake phosphorous concentration. *Can. J. Fish. Aquat. Sci.* **37** 290-294.

TABAK, H.H., QUAVE, S.A., MASHNI, C.I. and BARTH, E.F. (1981) Biodegradability studies with organic priority pollution compounds. *J. Wat. Poll. Control Fed.* **53** 1503-1518.

VAN RENSBURG, J.F.J. and HASSETT, A.J. (1982) A low-volume liquid-liquid extraction technique. *HRC and CC* **5** 574-576.

WHO (1984) *Guidelines for Drinking-water Quality* Vol. 1, *Recommendations.* World Health Organization.