Ministry for the Environment
Manatū Mō Te Taiao

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Client Report 2001/05

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Determination of non-point source chemical groundwater quality indicators for New Zealand aquifers

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April 2001

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Prepared for

MINISTRY FOR THE ENVIRONMENT

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EXECUTIVE SUMMARY

The New Zealand Ministry for the Environment commissioned the Institute of Geological & Nuclear Sciences Ltd. to develop indicators of groundwater quality through a grant from the Sustainable Management Fund. The development of groundwater indicators is part of the overall Environmental Performance Indicators programme administered by the Ministry for the Environment. This report summarises the testing and selection of groundwater quality indicators for non-point source (diffuse) chemical contamination of groundwater using the "pressure-state-response" framework. "Pressure" indicators were chosen qualitatively based on the most important national pressures effecting groundwater quality. The "state" indicators that were chosen are based on statistical principal component analysis of chemical data taken from the National Groundwater Monitoring Programme. In addition, descriptive evaluation of "state" indicators was included for those parameters where significant temporal data were not available (pesticides and metals). Land use information and geological knowledge of the aquifers included in the survey were used to test the significance of the "state" indicators chosen.

Eight primary "pressure" and "state" indicators and five secondary "state" indicators have been chosen to assess changes in groundwater quality with time. The recommendation section of this report lists the indicators chosen. The indicators selected will be valuable in assessing changes in groundwater quality from non-point source contamination caused by fertiliser applications, impacts of human and animal wastes applied to land, leaching of animal wastes from pastoral farming, pesticide application, contaminants from sheep dips, and corrosion of metals from urban settings. "Response" indicators were not evaluated in this study. It will be beneficial for the regional authorities and the Ministry for the Environment to evaluate and choose "response" indicators based on the "pressure" and "state" indicators developed in this report.

RECOMMENDATIONS

The recommendation of this report is that the following non-point source "pressure" and "state" indicators for groundwater quality be implemented:

Pressure Indicators

1. Percentage change of each land use in an aquifer area (both recharge areas and confined areas)

2. Measurement of stocking rates on pastoral land uses

3. Amount and type of fertiliser applied to land (e.g. NPK or urea) or produced and imported

4. Amount of triazine pesticides applied to land (or produced and imported)

5. Number of well with appropriate wellhead protection per unit area

6. Number of sites with contaminated soils detected

7. Percent change in chemical indicators of recharge water quality from streams, lakes and rivers

8. Abstraction volume of groundwater per aquifer

"State" Indictors

Major ions:

Primary indicators	Potassium, sulphate, chloride
Secondary indicators	Alkalinity, sodium, bromide, magnesium (in Tasman district)

Nutrients:

Primary indicators	Nitrogen as total nitrogen, or nitrate and/or ammonium depending on aquifer conditions and expected contaminants.

Metals:

Primary indicators	Total arsenic and total lead (total dissolved arsenic and lead may also be used)
Secondary indicators	Total copper (total dissolved copper may also be used)

Pesticides:

Primary indicator	Atrazine: High sensitivity atrazine test kits with detection limits of at least 0.015 mg m^{-3} have been shown to be a cost effective method of testing for atrazine.

These "state" indicators should be used in the following context related to the "pressure" indicators:

Pressure indicator	Related state indicator
Percentage change of each land use in an aquifer area (both recharge areas and confined areas)	Percent average change in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to land use in an aquifer
Measurement of stocking rates on pastoral land uses	Percent average increase in indicator chemical (nitrogen, chloride, sulphate) concentrations relating to stocking numbers in an aquifer
Amount and type of fertiliser applied to land (e.g. NPK or urea) or produced and imported	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations relating to fertiliser use in an aquifer
Amount of triazine pesticides applied to land (or produced and imported)	Percent detection of atrazine in wells, percent change in copper concentrations relating to a given land use.
Number of well with appropriate wellhead protection per unit area	Percent average change in indicator chemical (nitrogen, potassium, chloride, sulphate, magnesium) concentrations. *(microbiological indicators may be more appropriate for this state indicator)*.
Number of sites with contaminated soils detected	Number of detections of arsenic and lead in groundwater
Percent change in chemical indicators of recharge water quality from streams, lakes and rivers	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, sulphate, magnesium) concentrations in wells in the recharge area of an aquifer
Abstraction volume of groundwater per aquifer	Percent average change in indicator chemical (nitrogen, potassium, sodium, chloride, bromide, sulphate, magnesium) concentrations per land use in an aquifer

This list of both the "pressure" and "state" indicators is intended to cover as many major issues for non-point source groundwater contamination as possible. It is not intended that all of these possible indicators be monitored in all areas of the country. Two major constraints will be the data and resources available in each region to monitor some of the "pressure" indicators. However, to insure that a national indicator programme for groundwater contamination is useful, some common "pressure" and "state" indicators should be chosen that are monitored throughout the country.

Details of how and when these indicators should be applied are detailed in this report.

7.5.5 Results

The results from the 95 wells where groundwater was sampled indicate that there were a total of 33 wells (35%) where groundwater contained detectable pesticides, including triazine metabolites. Groundwater from some 18 wells (19%) had two or more pesticides detected (Table 7.5, Figure 7.10a). There were one or more wells where groundwater contained pesticides detected in 11 out of the 15 regions. Groundwater from one well had pesticides detected at levels greater than the maximum acceptable value (MAV) for drinking water (Ministry of Health, 1995).

Table 7.5 GC-MS results compared to atrazine test kits and HS atrazine test kit results for the same groundwater samples (from Rosen et al., 2000).

Region (number of wells sampled)	**Well**	**Pesticide detected**	**GC-MS ($mg\ m^{-3}$)**	**Atrazine test ($mg\ m^{-3}$)**	**High sensitivity atrazine test ($mg\ m^{-3}$)**
Northland (5)	8301	Terbuthylazine	0.28	<0.046	0.054
Waikato (8)	61.93	Atrazine	0.06	<0.046	0.18
		Metolachlor	0.21		
	64.511	DEA	0.02	<0.046	
Bay of Plenty (9)	1132	DEA	0.01	<0.046	
	3045	DEA	0.01	<0.046	
	WR2000	DEA	0.01	<0.046	
Gisborne (6)	GPM 007	Atrazine	0.02	<0.046	0.06
		Alachlor	0.02		
		DEA	0.03		
	GPF 032	Atrazine	0.04	<0.046	0.11
Taranaki (2)	810	Simazine	0.03	<0.046	0.02
Wellington (10)	Betty	Simazine	0.03	<0.046	0.026
	Edhouse	Alachlor	0.25	<0.046	0.09
		Pirimiphos methyl	0.01		
	SPTyres	Simazine	0.04	<0.046	0.09
		Terbuthylazine	0.01		
Tasman (14)	FP 4140	Simazine	0.01	<0.046	Not analysed
	WWD 285	Simazine	0.02	<0.046	0.026
		Terbuthylazine	0.04		
	WWD 417	Simazine	0.01	<0.046	Not analysed
	WWD 508	Diazinon	0.03	<0.046	0.07
		Simazine	0.02		
	WWD 524	Propazine	0.01	<0.046	Not analysed
	WWD 3115	Diazinon	0.01	<0.046	Not analysed
	WWD 3216	Diazinon	0.02	<0.046	0.08
		Simazine	0.02		
	WWD 4096	Simazine	0.03	<0.046	0.15
		Terbuthylazine	0.03		
	WWD 8036	DEA	0.02	<0.046	<0.015
		DIA	0.03		
		Simazine	0.04		
	WWD 8043	Simazine	0.02	<0.046	0.24
		Terbuthylazine	0.45		
Marlborough (7)	P28w/2600	Simazine	0.32	No sample	No sample
		Procymidone	0.17		
	P28w/1873	Triclopyr	0.14	<0.046	No sample
Canterbury (8)	M35/1382	Simazine	0.01	<0.046	Not analysed
	K38/0268	Atrazine Simazine	0.01 0.05	0.32	0.18
		Terbuthylazine	1.3		
	K38/0172	2,4-D	0.9		
		Atrazine	0.03	1.55	0.40
		Cyanazine	1		

Region (number of wells sampled)	**Well**	**Pesticide detected**	**GC-MS ($mg\ m^{-3}$)**	**Atrazine test ($mg\ m^{-3}$)**	**High sensitivity atrazine test ($mg\ m^{-3}$)**
		DEA	0.07		
		DIA	0.26		
		Diazinon	0.03		
		MCPA	61		
		MCPB	2.1		
		Mecoprop	420		
		Metribuzin	1.2		
		Picloram	0.3		
		Simazine	0.04		
		Terbuthylazine	0.04		
		Triclopyr	0.3		
Otago (7)	G43/0027	Simazine	0.02	<0.046	0.02
	I44/0101	Terbuthylazine	0.01	<0.046	Not analysed
		Trifluralin	0.02		
	J41/0008	Pendimethalin	0.03	<0.046	.042
		Propazine	0.01		
	J41/019	Atrazine	0.01	<0.046	Not analysed
		Simazine	0.02		
		Terbuthylazine	0.02		
Southland (9)	90519-04	DEA	0.04	0.3	0.90
		Hexazinone	0.12		
		Propazine	0.23		
	90519-05	Atrazine	0.08	No sample	No sample
		DEA	0.15		
		DIA	0.02		
		Hexazinone	0.23		
		Metribuzin	0.14		
		Propazine	2.5		
		Simazine	0.31		
		Terbuthylazine	3.5		
	Edendale	Not detected	-	0.07	0.08
Auckland (2)		None detected			
Hawkes Bay (3)		None detected			
Manawatu-Wanganui (2)		None detected			
West Coast (3)		None detected			

DEA = Desethyl atrazine; DIA = Desisopropyl atrazine.

Twenty different pesticides were detected, usually at very low concentrations, as well as the two triazine metabolites. Fifty seven out of the 75 pesticide detections (76%) belonged to the triazine group, with 5 of these (9%) being greater than 1 $mg\ m^{-3}$ and 74% of these being less than 0.1 $mg\ m^{-3}$. Three of the 18 non-triazine pesticides (17%) were greater then 1 $mg\ m^{-3}$ with all 3 detections being in groundwater from well K38/0172. Forty four of the non-triazine pesticides were below 0.1 $mg\ m^{-3}$.

However, of the 95 wells where groundwater was sampled, atrazine was detected in groundwater from only 4 wells using the "normal" atrazine test kit.

The wells where atrazine was detected in groundwater were two Canterbury wells, and two Southland wells, none of which had atrazine concentrations greater than 0.08 mg m^{-3}. Groundwater from one well (Edendale) did not contain any detectable pesticides using the GC-MS method, but both the "normal" and high sensitivity atrazine test kits indicated that atrazine was present. This sample could be identified as the only false positive in the testing, assuming that the GC-MS testing is infallible. It is also possible (but highly unlikely) that the GC-MS result is a false negative. Testing of groundwater from other wells in the area have detected triazine group pesticides. Groundwater from the other three wells contained significant concentrations of triazine compounds that show cross reactivity to the atrazine test kit. Terbuthylazine, propazine, simazine, DEA and DIA all show cross sensitivities to the test, although the least detectable dose for DIA is 0.800 mg m^{-3} for the "normal" atrazine test kit (Table 7.6).

Table 7.6. Compounds that show cross reactivity to both "normal" and high sensitivity atrazine test kits and their least detectable dose. Data from the Ohmicron RaPID Assays® method sheet (from Rosen et al., 2000).

"Normal" atrazine test kit		High sensitivity atrazine test kit	
Compound	**Least detectable dose (mg m^{-3})**	**Compound**	**Least detectable dose (mg m^{-3})**
Atrazine	0.046	Atrazine	0.015
Propazine	0.033	Propazine	0.005
Prometryn	0.054	Prometryn	0.013
Prometon	0.056	Prometon	0.015
Ametryn	0.053	Ametryn	0.019
Terbuthylazine	0.310	Terbuthylazine	0.019
Simazine	0.340	Simazine	0.019
DEA	0.062	DEA	0.027
Terbutryn	0.090	Terbutryn	0.027
Cyanazine	1.0	Cyanazine	0.036
DIA	0.800	DIA	0.156
2-Hydroxy Atrazine	1.1	6-Hydroxy Atrazine	0.158

The main reason why pesticides were not detected using the normal atrazine test kit is because the least detectable dose (LDD) for atrazine is 0.046 mg m^{-3}, which is greater than most of the atrazine detections using GC-MS and most of the LDDs for the cross sensitive compounds are even higher (Table 7.6).

The high sensitivity (HS) atrazine test kits on the other hand detected pesticides in 20 samples that were tested (Figure 7.10b). One false positive was detected (Edendale well) that also tested positive for the "normal" atrazine test kit (see above). The HS kits also detected all sites at which triazine compounds were detected by GC-MS (that were above the HS atrazine test kit LDD). Although concentrations of the atrazine detected by the test kit did not always match the GC-MS concentrations, this is because many samples had multiple pesticides present, some of which had cross sensitivities to the test. In some cases, the HS atrazine test kit result was higher than the GC-MS result, but there were no other pesticides present in the GC-MS sample analysed. This suggests that absolute concentrations measured by the test kits should be used with caution, as they may not be as accurate as the GC-MS results. Groundwater from one well from Wellington (Edhouse well) tested positive for the HS atrazine test kit method, but no triazine compounds were detected in the GC-MS sample. However, alachlor and pirimiphos methyl were both detected in the GC-MS sample. Alachlor is known to have no cross reactivity to the HS atrazine test kit according to the information supplied by Ohmicron. However, no data are given for pirimiphos methyl in the Ohmicron literature, so that it is possible that a cross reactivity exists for this compound.

Immunoassay testing has been used as a cost effective and rapid method for the screening of pesticides for about the past 20 years. Studies have mainly been confined to the laboratory (Meulenberg et al., 1995), although significant field studies have been completed in the United States of America (Thurman et al., 1992) and Europe. In some respects the utility of the immunoassay method is that each test is specific to a particular pesticide. However, Meulenberg et al. (1995) comment that the tests are not as specific as they could be and therefore do not quantitatively reflect the concentration of the specific compound that is desired. But, for the purposes of a screening technique that is to be utilised as an indicator of pesticide contamination, the desire would be for the test to be even less specific. In New Zealand, previous national pesticide surveys and the current GC-MS survey indicate that triazine group compounds are prevalent in groundwater samples that contain pesticides. In

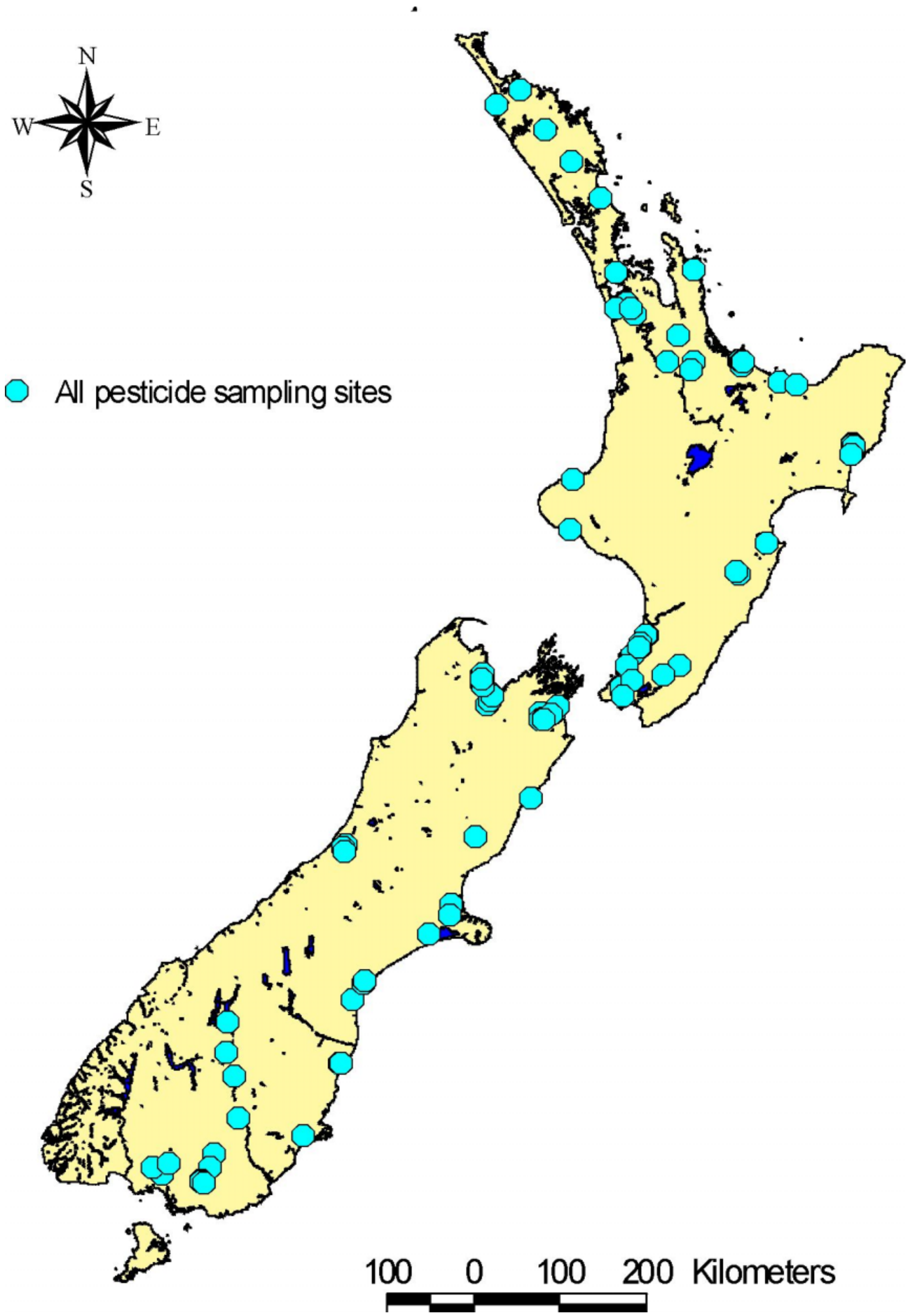

Figure 7.9. Sampling sites for the GC-MS pesticide testing (from Rosen et al., 2000).

(a) GC-MS detections *(b) High sensitivity atrazine test kit detections*

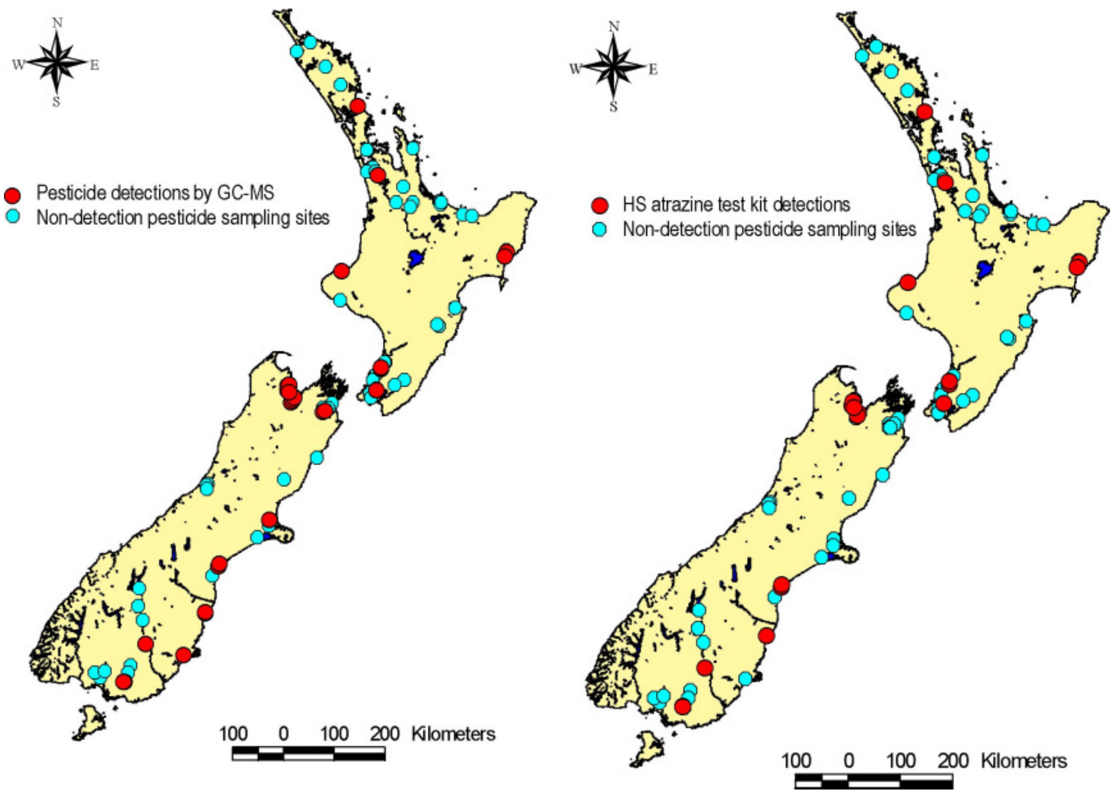

Figure 7.10. (a) Pesticide detections using the GC-MS technique (b). Pesticide detections using the high sensitivity atrazine test kits (from Rosen et al., 2000).

the present survey, 73% of the pesticides detected were from the triazine group. This suggests that a test kit that can detect triazine compounds in general could act as a good indicator of pesticide contamination.

The high sensitivity atrazine test kit used for this study has cross reactivity to many other common triazine group compounds particularly simazine, which was detected in 19 wells by GC-MS. The low detection limit (or LDD) for many of the compounds (see Table 7.2) including atrazine mean that the technique will give comparable results to GC-MS results. However, due to the cross sensitivities, the quantitative concentration given by the ELISA method may not be accurate for atrazine if other triazine compounds are present. Therefore, any positive result using an immunoassay technique should be checked by GC-MS if quantitative results are required.

One apparent false-positive result occurred using the high sensitivity test, which indicates that the HS atrazine test kit could be a useful indicator of pesticides in New Zealand even at a relatively low level of detection. It appears that many pesticides present in New Zealand groundwater are below the LDD of the "normal" atrazine test kit. This limits the ability of this test to act as an indicator and should only be used if the purpose of the study is to track known discharges of atrazine in to receiving waters. Most detections in the GC-MS survey were above the LDD of the HS test kit. Because atrazine is also relatively easily leached to groundwater (Gustafson, 1989), it provides an ideal indicator of contamination by other pesticides.