NATIONAL SURVEY OF PESTICIDES IN GROUNDWATER 2010

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Murray Close & Alex Skinner
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Prepared by

M. Close & A. Skinner

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Executive Summary

In 2010 ESR co-ordinated a survey of pesticides in groundwater throughout New Zealand, with the well sampling being carried out by Regional and Unitary Authorities. Samples were analysed for acidic herbicides and a suite of organochlorine, organophosphorus and organonitrogen pesticides. One regional council provided results for an additional six wells that had been sampled as part of a separate investigation. These results are included in this report to give a national perspective.

Wells were selected on the basis of the importance of each aquifer to the region, the application or storage of pesticides in the area, and the vulnerability of the aquifer to contamination, recognising that shallower, unconfined aquifers would be more at risk than deeper aquifers. If possible, where a well had been sampled for previous surveys, it was also included in this survey to give a temporal comparison. The majority of the selected wells were from unconfined aquifers.

There were a total of 162 wells sampled for the 2010 National Survey, including the additional 6 wells sampled by Environment Southland. There were 38 wells (24%) with pesticides detected, with 15 wells having 2 or more pesticides detected. There were one or more wells with pesticides detected in 9 of the 14 regions. Pesticides were not detected in wells from the Bay of Plenty, Taranaki, Hawke's Bay, Marlborough and Canterbury regions. There was one well in the 2010 survey with a pesticide concentration greater than the maximum acceptable value (MAV) for drinking water (Ministry of Health, 2008). There were a total of 22 different pesticides detected. Herbicides were the most common pesticide group detected (17) followed by insecticides (3) and fungicides (2). There were a total of 66 pesticide detections and of these detections, 60 (91%) were herbicides. There were 40 detections (61%) of triazine herbicides. Levels of only 3 of the 67 pesticide detections exceeded 1 mg m^{-3}.

There were significant differences between wells with and without detected pesticides for nitrate levels, with higher levels being associated with pesticide detections. Differences for other parameters were not significant.

There has been a decrease in the detection limits for many pesticides since the earlier surveys in 1990 and 1994. If the detection limits for the earlier surveys were applied to the 2010 survey then there would be a total of 12 wells out of the 162 sampled (7.5%) with pesticides detected. This compares with, 7% of the 82 wells in 1990 with detectable pesticides, 13.6% of the 116 wells in 1994, 11% of the 95 wells in 1998, 9% of the 133 wells in 2002, and 8% of the 163 wells in 2006, all adjusted for lower detection limits. This indicates that a similar percentage of wells have had detectable pesticides in each survey once correction for variable detection limits has been made.

Introduction

Groundwater is an important source of drinking water in New Zealand. Half of the community drinking water supplies use a groundwater source and many rural households also rely on groundwater for their drinking water (Close *et al.*, 2001; Davies, 2001). In many regions of New Zealand the volume of groundwater abstracted is increasing. There is also a need to demonstrate good groundwater quality to show that our agricultural systems are environmentally responsible. This has implications with respect to trade and non-tariff barriers.

National surveys of pesticides in groundwater have been carried out at four yearly intervals since 1990, and making this current survey the sixth in the series. Previous national and regional groundwater surveys in New Zealand have shown low levels of pesticides in some groundwater systems, particularly those shallow unconfined systems that are vulnerable to pollution. While the concentrations of detected pesticides have generally been less than 1% of the respective maximum acceptable value (MAV), there have been occasional exceedances of the MAVs. Triazine pesticides are the group of pesticides most commonly detected. Further details of the earlier surveys are summarised in Gaw et al. 2008, Close and Flintoft (2004), Close and Rosen (2001), Close (1996) and Close (1993). In addition to the national surveys some regions have also undertaken their own more intensive monitoring programmes (Hadfield and Smith, 1999; TRC, 1995).

The fifth national survey in 2006 sampled a total of 163 wells from regions throughout New Zealand (Gaw et al, 2008). There were 31 wells (19%) with pesticides detected and in 13 of these wells; two or more pesticides were detected. There were one or more wells with pesticides detected in 11 of the 14 participating regions. Nineteen different pesticides were detected in the sampled wells. Herbicides were the pesticide group most commonly detected with 12 different herbicides detected followed by insecticides (5) and fungicides (2). There were a total of 50 pesticide detections and of these detections, 37 were herbicides. There were 25 detections of triazine herbicides. Simazine and terbuthylazine were the two most frequently detected pesticides. Levels of only 2 of the 50 pesticide detections exceeded 1 mg m^{-3}. One pesticide, alachlor, was detected in one well at a concentration of 34 mg m^{-3}, which is greater than the maximum acceptable value (MAV) for alachlor in drinking water of 20 mg

m^{-3} (Ministry of Health, 2008). For the majority of the detected pesticides, concentrations were less than 1% of the MAV.

This report gives the results from the sixth national survey. The sampling was carried out in late 2010. Results for an additional six wells from Southland were also included in the 2010 national dataset.

Methodology

Well Selection

The well selection criteria were; the importance of each aquifer to the region, the application or storage of pesticides in the area, and the vulnerability of the aquifer to contamination, recognising that shallower, unconfined aquifers would be more at risk than deeper aquifers. If possible, where a well had been sampled for previous surveys it was also included in this survey to provide a temporal comparison. Wells were also added for regions that were under-represented or not sampled in the last survey. For each well the following information was requested; well location, water level, depth of the well screen, the type of aquifer, and the general land use in the area. A balance was sought between selecting wells that were most vulnerable to contamination (shallow and screened near the water table) and wells that reflected the general usage of the aquifer. Most of the selected wells were from unconfined aquifers.

Fourteen of the regional councils and unitary authorities with groundwater management responsibility participated in the 2010 survey. The level of involvement and number of wells sampled in each region depended on the usage of pesticides in the region, the importance of groundwater resources to the region, and whether the council had recently carried out regional monitoring of pesticides.

Sampling and Analysis

Samples were collected from selected wells by the Regional Council and Unitary Authority staff and sent to AsureQuality, Wellington for analysis. Samples were collected by either down hole pumps or at in situ pumps as close to the borehead as possible. The bores were flushed for three well volumes where possible.

All samples were analysed for acidic herbicides and a suite of organochlorine, organophosphorus and organ nitrogen pesticides (OC/OP/ON) using gas chromatography with mass spectrometry detector (GC-MS). The acid herbicide analysis involved solid phase extraction and derivatisation of the extract with diazomethane followed by GC-MS analysis using single ion monitoring. The OC/ON/OP pesticide analysis involved extraction with dichloromethane and a pre-concentration step followed by GC-MS analysis in scan mode. Samples from six percent of wells were collected in duplicate as blind duplicate samples for quality control purposes.

The pesticides assayed and their detection limits are provided in Appendix 1. The detection limits for this survey were similar to the 1998, 2002, and 2006 surveys but significantly lower than the limits for the 1994 and 1990 national surveys by a factor of between 5 and 10.

Data analysis

Information on well depth, position of screen, water level at the time of sampling, groundwater temperature, and type of aquifer (confined or unconfined) were obtained for as many wells as possible. Conductivity, pH, and nitrate were also obtained for each well where possible. These were either measured on samples taken at the same time as the pesticide samples or medians were taken of previously collected data.

Each well was classified for presence or absence of pesticides. T-tests were carried out for the presence/absence data and the variances were tested for homogeneity using the F statistic to determine whether the variances should be pooled or kept separate.

Results

A total of 156 wells from 14 regions were sampled in this survey. Results for six additional samples from Environment Southland are also included in the national survey results, giving a total of 162 samples.

Assessment of Survey Methodology

Blind duplicates

Blind duplicate samples from 8 wells (5%) were submitted to the analytical laboratory as a quality control measure. Most of the blind duplicate samples did not have detectable pesticides present and there was good agreement for all duplicate analyses (Table 1). Terbuthylazine was detected in one set of duplicate samples at levels of 0.084 and 0.086 mg m^{-3}.

Table 1: Comparison of Blind Duplicate samples.

Council	Well Number	Pesticide Concentration (mg m^{-3} or ug/L)
NRC	207244	Terbuthylazine 0.086
		Terbuthylazine 0.084
TRC	GND0814	ND
		ND
MDC	P28W/3222	ND
		ND
TDC	59	ND
		ND
HBRC	40829	ND
		ND
ARC	7419009	ND
		ND
GW	S26/0457	ND
		ND
HORIZONS	336114	ND
		ND

Overall Survey Results

Of the 162 wells sampled there were 38 wells (24%) with pesticides detected and in 15 of these wells; two or more pesticides were detected (Table 2). The maximum number of pesticides detected in one well was five. There were one or more wells with pesticides detected in 9 of the 14 participating regions. Pesticides were not detected in sampled wells from Bay of Plenty (6 wells), Taranaki (8 wells), Hawkes Bay (11 wells), Marlborough (17 wells) and Canterbury (5 wells) regions. Twenty two different pesticides were detected in the sampled wells. Herbicides were the pesticide group most commonly detected with 17 different herbicides detected followed by insecticides (3) and fungicides (2). There were a total of 66 pesticide detections and of these detections, 60 (91%) were herbicides. There were 40 detections of triazine herbicides. Simazine and terbuthylazine were the two most frequently detected pesticides. Levels of only 3 of the 66 pesticide detections exceeded 1 mg m^{-3}. Only one pesticide was detected at levels greater than the maximum acceptable value (MAV) for drinking water. Dieldrin was detected in one well at a concentration of 0.13 mg m^{-3} (MAV for dieldrin equals 0.04 mg m^{-3} - Ministry of Health, 2008).

The range of concentrations found, MAV values, groundwater ubiquity scores (GUS), and the mobility and degradation characteristics of each pesticide are given in Table 3. The mobility and degradation values come from the National Pesticide Information Center which hoists several pesticide properties databases (http://npic.orst.edu) as at April 2011, unless otherwise noted. The selected value listed in this database, plus the range of values in the literature, are given in Table 3. The mobility is represented by the soil organic carbon sorption coefficient (K_{oc}). K_{oc} is calculated by measuring the ratio, K_d, of sorbed to solution pesticide concentrations after equilibrium of a pesticide in a water/soil slurry and then dividing by the weight fraction of organic carbon present in the soil. High K_{oc} values indicate compounds with high adsorption to soils and low mobility. The soil half life is the time it would take for half the amount of pesticide to degrade in soil, assuming a first order degradation process. The GUS scores are a simplified assessment of whether a pesticide is likely to leach or not (Gustafson, 1989) and are calculated as:

$$GUS = \log_{10}(\text{soil half life}) \times (4 - \log_{10}(K_{oc}))$$

GUS values greater than 2.8 indicate that the compound would leach relatively readily and a GUS score of less than 1.8 indicated a "non-leacher". There was a transitional zone between 1.8 and 2.8 where pesticides could leach under favourable conditions. In this report a wider transitional zone was used. The GUS values suggested by Primi *et al.* (1994) of 1.5 and 3.0 were used to differentiate leachers and non-leachers.

Table 2: Summary of gas chromatography-mass spectroscopy (GC-MS) results from the 2010 groundwater survey.

Council Region (no. detections/ no. wells sampled)	Well number	Pesticide Detected	GCMS Concentration (mg m^{-3})
Northland Regional Council (4/12)	205038	Linuron	0.043
	207244	Terbuthylazine	0.084
	208287	Simazine	0.018
		Bromacil	0.057
	209851	Terbuthylazine	0.030
Auckland Council (5/12)	43915	Alachlor	0.023
		Metolachlor	0.096
		Bentazone	0.17
		Acetochlor	0.091
	6487015	Terbuthylazine	0.014
	7419126	Metribuzin	0.026
		Metalaxyl	0.013
	7419127	Bentazone	0.10
	7428031	Alachlor	0.025
		Metolachlor	0.047
		Metribuzin	0.020
		Bentazone	0.20
		Acetochlor	0.080
Environment Waikato (3/6)	61_113	Metribuzin	1.7
		Procymidone	0.056
		Bentazone	0.24
	70_21	Simazine	0.011
		Terbacil	0.048
	70_22	Simazine	0.011
		Terbacil	0.051
Gisborne District Council (2/6)	GDF 032	Atrazine	0.042
	GPE 015	Atrazine	0.022
Horizons (7/35)	301011	Terbuthylazine	0.024
	314025	Terbuthylazine	0.031
	323007	Terbuthylazine	5.8
	324067	Terbuthylazine	0.026
	357109	Acetochlor	0.063
	372034	Alachlor	12.000
		Metalaxyl	0.091
		Metribuzin	0.720
		Pendimethalin	0.055
	372071	Picloram	0.36
Greater Wellington Regional Council (2/10)	R27/6418	Terbuthylazine	0.059
	S25/5125	Norflurazon	0.040
Tasman District Council (5/15)	508	Simazine	0.017
	524	Desethyl atrazine	0.023
	3216	Simazine	0.013
	3393	Terbuthylazine	0.027
	4096	Simazine	0.021

Council Region (no. detections/ no. wells sampled)	Well number	Pesticide Detected	GCMS Concentration (mg m^{-3})
Otago Regional Council (2/8)	G43/0027	Simazine	0.13
	J41/0008	pp-DDT	0.033
		Alachlor	0.760
		Metribuzin	0.460
Environment Southland (8/11)	E44/0036	Terbuthylazine	0.080
	E46/0093	Simazine	0.014
		Terbuthylazine	0.019
	E46/0156	Dieldrin	0.13
		Simazine	0.039
		Terbuthylazine	0.014
	F44/0055	Atrazine	0.016
		Terbuthylazine	0.029
	F46/0239	Hexazinone	0.093
		Propazine	0.12
		Terbuthylazine	0.69
	F46/0240	Chlorpyrifos	0.056
		Hexazinone	0.11
		Propazine	0.18
		Terbuthylazine	0.44
	F46/0243	Terbuthylazine	0.028
	F46/0249	Hexazinone	0.74
		Propazine	0.24
		Simazine	0.058
		Terbuthylazine	0.49

Table 3: Characteristics of detected pesticides. Field half-lives and Koc values are from the ARS Pesticide Properties Database: selected value with range in parentheses. (GUS classes: L = leacher; N = non-leacher; T = transitional. NA = not available. MAV = maximum acceptable value.)

Pesticide	**FAO Classification**	**Field half-life (days)**	**Koc (ml g^{-1})**	**GUS score**	**No. of Wells**	**Range (mg m^{-3})**	**MAV (mg m^{-3})**
Herbicides							
Acetochlor	Amide	20 (13.5 – 55)	200 (74 – 428)	2.21 T	3	0.063-0.091	
Alachlor	Amide	27 (7–80)	124 (43–209)	2.73 T	4	0.02-12	20
Atrazine	Triazine	173 (13–402)	147 (38–288)	4.10 L	3	0.016-0.042	2
Bentazone	other herbicide	27 (7–98)	35	3.52 L	4	0.1-0.24	400
Bromacil	Uracil	207 (61-349)	32 (2–72)	5.78 L	1	0.057	400
Desethyl atrazine	Triazine	#	#	# L	1	0.023	#
Hexazinone	Triazine	79 (30 - 180)	54 (34 – 74)	4.30 L	3	0.093-0.74	400
Linuron	Urea derivative	82 (30 - 230)	496 (93 – 863)	2.50 T	1	0.043	7§
Metolachlor	Amide	141 (12–292)	70 (22–307)	4.63 L	2	0.047-0.096	10
Metribuzin	Triazine	47 (23–128)	52 (3–95)	3.82 L	5	0.02-1.7	70
Norflurazon	other herbicide	163	353	3.21 L	1	0.04	50*
Pendamethalin	Dinitroaniline	174 (8 – 480)	13400 (6500 – 29000)	-0.29 N	1	0.055	20
Picloram	Other hormone type	108 (31-206)	29 (7 – 48)	5.16 L	1	0.36	200
Propazine	Triazine	123 (35-347)	161 (100-600)	3.75 L	1	0.24	70
Simazine	Triazine	89 (26–186)	140 (103–230)	3.61 L	10	0.01-0.13	2
Terbacil	Uracil	200 (50–250)	63 (41–120)	5.06 L	2	0.048-0.051	40
Terbuthylazine	Triazine	60†	220 (162–278)†	2.95 T	18	0.014-5.8	8
Insecticides							
Chlorpyrifos	Organophosphate	43 (4 – 139)	9930 (6000 – 14000)	0.01 N	1	0.056	40
pp-DDT	Organochlorine	700 - 5500	$4x10^5$ ($2x10^4$–$7x10^6$)	-0.90 N	1	0.033	1
Dieldrin	Organochlorine	1000 (225 – 1260)	12000 (4000 – 39000)	-0.24 N	1	0.13	0.04
Fungicides							
Procymidone	Dicarboximide	34 (7–120)	580‡	1.89 T	2	0.076-0.19	700
Metalaxyl	other fungicide	77 (27-296)	171 (30-284)	3.33 L	4	0.05-0.085	100

† values for terbuthylazine taken from The Pesticide Manual (1994).
# values assumed to be similar to atrazine
‡ Koc and half-life value for procymidone taken from McNaughton *et al.* (1999).
*Health value from the Australian Drinking Water Guidelines 2004 (Australian Government, 2004)
§ Freshwater interim guideline value taken from Hamilton *et al.*(2003).

Effects of Environmental Factors

Where there were sufficient data available, the effects of environmental factors were investigated on the presence/absence of pesticides. The *t*-test results are summarised in Table 4. As with the earlier surveys, there was a significant difference between wells with and without detected pesticides for nitrate levels, with higher nitrate levels being associated with pesticides being detected. There was information on aquifer confinement status for 101 out of the 162 wells that were sampled. Of the 101 wells for which the confinement status was known, 76 were unconfined, 13 were semi-confined, and 12 were confined. There were no pesticides detected in wells that were known to be semi-confined or confined. There were 23 wells with pesticides detected that were unconfined and 15 wells with pesticides detected that had no information on their confinement status. This result is as expected given that unconfined aquifers are more vulnerable to contamination. However, the significant amount of missing data limits the impact of this conclusion.

Table 4: Summary of *t*-test results. (NS = not significant at *p* = 0.05.)

Variable	Pesticide absent			Pesticide detected			Probability
	N	Mean	SD	*n*	Mean	SD	
Well depth (m)	123	23.2	24.4	35	19.7	17.7	NS
Water depth above screen (m)	97	8.43	10.4	22	8.90	15.0	NS
Temperature (ºC)	120	14.6	1.7	37	14.6	2.3	NS
pH	121	6.61	0.76	34	6.42	0.60	NS
Nitrate-N (mg m^{-3})	92	3.89	4.83	23	7.88	8.06	0.03
Conductivity (mS m^{-1})	122	29.3	20.0	36	29.5	19.0	NS
Dissolved oxygen (mg m^{-3})	33	5.14	4.05	8	7.28	2.15	NS

Discussion

Dieldrin was detected in one well at a concentration of 0.13 mg m^{-3} (MAV for dieldrin equals 0.04 mg m^{-3} - Ministry of Health, 2008). Terbuthylazine was detected in one well at a concentration of 5.8 mg m^{-3}, which is 73% of the MAV for terbuthylazine in drinking water of 8 mg m^{-3}. Alachlor was detected in one well at a concentration of 12 mg m^{-3}, which is 60% of the MAV for alachlor in drinking water of 20 mg m^{-3}. For the majority of the detected pesticides, concentrations were less than 1% of the MAV.

Dieldrin was used in New Zealand primarily for the government-required control of ectoparasities on sheep in the 1960's. Most livestock farms in New Zealand would probably have had a sheep or cattle dip site. Even though dieldrin has not been used for this purpose since the mid 1960's, its long persistence means that it can be detected the soil where the dip site wastewater was disposed and occasionally in the underlying groundwater. Hadfield & Smith (1999) carried out an investigation into dieldrin in groundwater in the Waikato region. Their results indicated that dieldrin contamination could be widespread and that concentrations in shallow groundwater (about 5 m bgl) could be expected to increase, even though usage had ceased 30-40 years previously. Dieldrin has a low MAV (0.04 mg m^{-3}), which means that even low concentrations in groundwater can exceed the MAV for drinking water.

Most pesticides were detected at concentrations below 1% of the MAV, indicating that there should be no significant health risk based on the pesticides analysed from drinking the groundwater sampled from the wells in the survey.

Herbicides comprised 60 (91%) of the 66 detections for pesticides. This higher number of detections for herbicides than insecticides and fungicides is consistent with estimates that herbicides comprise at least 60% of the total amount of pesticides sold in NZ annually (Manktelow *et al.*, 2005). Consistent with previous surveys of pesticides in groundwater (Close *et al.*, 2001; Gaw *et al.*, 2008), the triazine group of herbicides were the most frequently detected pesticides, comprising 61% of the detections. Desethyl atrazine, a triazine metabolite, can come from atrazine or propazine. No other pesticides were detected in the same well as desethyl atrazine (Table 2). Although no triazine metabolites were detected in the 2006 survey (Gaw *et al.,* 2008), 6 metabolites were detected in the 2004 survey (Close and Flintoft, 2004), and 12 metabolites were detected in the 1998 survey (Close and Rosen, 2001).

Some of the wells with high levels of pesticides detected in the 2010 survey also had these pesticides detected in the 2006 survey. For example, well 372034 (Horizons) had high (12 mg m^{-3}) levels of alachlor, plus trace levels of metalaxyl, metribuzin and pendimethalin detected in 2010 (Table 2). In 2006 this well had even higher levels of alachlor, plus trace levels of metalaxyl and metribuzin. This indicates either continuing usage of these pesticides in the area or persistence of these pesticides for a long time in the subsurface environment. The soil half life for alachlor is around 1 month so this would imply a much longer persistence below the root zone and in the groundwater. Pesticide persistence in the groundwater can be much longer than in the active root zone (orders of magnitude) as shown by Pang and Close (1999) and Levy and Chesters (1995). Three wells in the Auckland region had low levels of Bentazone in both the 2006 and 2010 surveys and 3 wells from Southland had low levels of terbuthylazine, simazine and propazine in both surveys.

Of the 22 pesticides and metabolites detected, GUS values indicated that 13 were leachers, five were transitional, and four were non-leachers (Table 3). This was a reasonably high proportion of non-leacher pesticides. Detection of non-leacher pesticides can be an indication that normal leaching processes are not responsible for their presence in the groundwater and that other pathways, such as spillages or preferential flow, are taking place. As discussed earlier for dieldrin, it may also be the result of widespread use of the pesticide in previous decades.

The significant decrease in the detection limits for many pesticides for the groundwater surveys undertaken since 1998, compared to the two earlier surveys in 1990 and 1994, needs to be considered before assessing temporal trends. If the detection limits for the 1990 and 1994 surveys were applied to the 2010 survey then there would be a total of 12 wells out of the 162 sampled (7.5%) with pesticides detected. This compares with 8% of the 163 wells in 2006 with detectable pesticides, 9% of the 133 wells in 2002, 11% of the 95 wells in 1998, 13.6% of the 116 wells in 1994 and 7% of the 82 wells in 1990 when adjusted for lower detection limits. This indicates that a similar percentage of wells have had detectable pesticides in each survey once correction for variable detection limits has been made.

There are only two wells that have been sampled for each of the six National Surveys, with another 17 wells that have been sampled for five of the surveys and 44 wells that have been sampled for four of the surveys. Of these 63 wells that have been included in four or more of the surveys, 30 (48%) had no pesticides detected for any of the surveys. If the total concentration of all pesticides detected in the well was used for comparison for the remaining wells, then 15 wells (24%) showed no obvious trend, 12 wells (19%) showed decreasing concentrations, 4 wells (6%) showed increasing concentrations and the other two wells (3%) had positive detections of pesticides on all sampling occasions but showed no obvious trend in pesticide concentrations.

Combined with the slight decrease in the number of detections between the last five surveys (adjusted for common detection limits), this indicates that there probably has been a slight decrease in pesticide concentrations in groundwater over the past 16 years. This may result from better application of pesticides by growers, combined with a general move towards use of pesticides with lower persistence and greater selectivity, resulting in lower amounts being applied. However, most of the wells showed no pesticide detections and there are still only a relatively small number of data points over this period so this statement needs to be treated with caution.

The mean nitrate levels were significantly higher for wells with pesticide detections than for wells without pesticide detections. This pattern was also observed in the previous three surveys (Close and Rosen, 2001; Close and Flintoft, 2004; Gaw et al., 2008). Similarly high levels of nitrate were also observed in wells with pesticide detections in a Waikato region survey (Hadfield and Smith, 1999). Seventy six wells (47%) were unconfined and of these, 23 wells had pesticides detected. There were no pesticides detected in semi-confined and confined wells. No other significant relationships were observed between wells with pesticides detected and other factors. This differed from previous surveys where significant relationships between shallower well depths and pesticide detections were observed.

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References

Australian Water and Wastewater Association (1996) *Australian Drinking Water Guidelines - Summary*. Canberra, Australia: Australian Water and Wastewater Association

Close ME (1993) Assessment of pesticide contamination of groundwater in New Zealand. II Results of groundwater sampling. *New Zealand Journal of Marine and Freshwater Research* **27**, 267-273.

Close ME (1996) Survey of pesticides in New Zealand groundwaters 1994. *New Zealand Journal of Marine and Freshwater Research* **30**, 455-461.

Close ME, Rosen MR (2001) 1998/99 National Survey of Pesticides in Groundwater using GCMS and ELISA. *New Zealand Journal of Marine and Freshwater Research* **35**, 205-219.

Close ME, Rosen MR, Smith VR (2001) Fate and transport of nitrates and pesticides in New Zealand's aquifers. In MR Rosen and PA White (Eds.). *Groundwaters of New Zealand*. Wellington, New Zealand: New Zealand Hydrological Society Inc.

Close M, Flintoft M (2004) National Survey of Pesticides in Groundwater 2002. *New Zealand Journal of Marine and Freshwater Research* **38**, 289-299.

Davies H (2001) Groundwater and Health. In MR Rosen and PA White (Eds.). *Groundwaters of New Zealand*. Wellington, New Zealand: New Zealand Hydrological Society Inc.

Gaw S, Close ME, and Flintoft MJ (2008) Fifth national survey of pesticides in groundwater in New Zealand. New Zealand Journal of Marine and Freshwater Research 42, 397–407.

Gustafson DI (1989) Groundwater ubiquity score: A simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry* **8**, 339-357.

Hadfield J, Smith D (1999) *Pesticide contamination of groundwater in the Waikato region. Environment Waikato, 1999/9*. Hamilton, New Zealand: Environment Waikato.

Hamilton DJ, Ambrus A, Dieterle RM, Felsot AS, Harris CA, Holland PT, Katayama A, Kurihara N, Linders J, Unsworth J, Wong S-S. (2003) Regulatory limits for pesticide residues in water. Pure and Applied Chemistry 75 (8): 1123-1155.

Levy, J.; Chesters, G. 1995: Simulation of atrazine and metabolite transport and fate in a sandy-till aquifer. *Journal of Contaminant Hydrology* 20: 67-88.

McNaughton DE, Holland PT, Clothier B, James T (1999) Parameters for environmental persistence of pesticides in horticultural soils. In proceedings of conference "*Environmental Aspects of Pesticide Use*." November 1999, Hamilton, 30 p.

Manktelow D, Stevens P, Walker J, Gurnsey S, Park N, Zabkiewicz J, Teulon D and Rahman A (2005) Trends in Pesticide Use in New Zealand: 2004. Report to the Ministry for the Environment, Project SMF4193. HortResearch Client Report no. 17962.

Ministry of Health (2008) *Drinking-Water Standards for New Zealand 2005 (Revised 2008)*. Wellington, New Zealand: Ministry of Health

Pang L, Close ME. (1999) Attenuation and transport of atrazine and Picloram in an alluvial gravel aquifer: a tracer test and batch study. *New Zealand Journal of Marine and Freshwater Research, 1999, Vol. 33:* 279-291

Primi P, Surgan MH, Urban T (1994) Leaching potential of turf care pesticides: A case study of Long Island golf courses. *Ground Water Monitoring and Remediation* Summer 1994, 129-138.

The Pesticide Manual (1994) *The Pesticide Manual, Incorporating The Agrochemicals Handbook*. Hampshire, United Kingdom: The British Crop Protection Council and The Royal Society of Chemistry.

TRC (1995) *Report on an investigation of pesticides in shallow groundwater in Taranaki.*, Report number 95-14. Taranaki Regional Council, 31 p.

Appendix 1: List of pesticides and limits of detection for each method.
Units are mg m^{-3} (ppb). (DDE = dichlorodiphenyldichloroethylene, DDD = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane, DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane.)

(1) Pesticide Screen					
(i)	*Organochlorine pesticides:*			desisopropyl atrazine	0.1
	lindane	0.01		propanil	0.02
	heptachlor	0.02		alachlor	0.02
	heptachlor epoxide	0.03		metolachlor	0.02
	aldrin	0.02		pendimethalin	0.02
	procymidone	0.02		molinate	0.02
	α-chlordane	0.02		metribuzin	0.02
	γ-chlordane	0.02		bromacil	0.03
	dieldrin	0.02		oryzalin	2.0
	p,p'-DDE	0.01		linuron	0.04
	p,p'-DDD	0.01		hexazinone	0.02
	p,p'-DDT	0.01		norflurazon	0.02
	methoxychlor	0.02		metalaxyl	0.01
	cis permethrin	0.01		acetochlor	0.02
	trans permethrin	0.01		oxadiazon	0.01
	BHC	0.01		cyanazine	0.02
	vinclozin	0.02		terbacil	0.02
	endosulfan I	0.02			
	endosulfan II	0.04			
	endosulfan sulphate	0.02	**(2)**	**Acid herbicides**	
	endrin	0.02		mecoprop	0.1
	endrin aldehyde	0.04		MCPA	0.1
	endrin ketone	0.04		MCPB	0.1
				Acifluorfen	0.1
(ii)	*Organophosphorus pesticides:*			Bromoxynil	0.1
	azinphos methyl	0.4		Dicamba	0.1
	diazinon	0.01		dichlorprop	0.1
	pirimiphos methyl	0.02		dinoseb	0.1
	chlorpyrifos	0.02		2,4-D	0.1
				triclopyr	0.1
(iii)	*Organonitrogen herbicides:*			2,4,5-T	0.1
	trifluralin	0.02		2,4-DB	0.1
	simazine	0.01		bentazone	0.1
	atrazine	0.01		fenoprop	0.1
	propazine	0.01		picloram	0.1
	terbuthylazine	0.01		3,5-dichlorobenzoic acid	0.1
	desethyl atrazine	0.02		pentachlorophenol	0.1

www.esr.cri.nz

Institute of Environmental Science & Research Limited

Mt Albert
Science Centre
Hampstead Road
Mt Albert
Private Bag 92 021
Auckland 1142
New Zealand

Tel: +64 9 815 3670
Fax: +64 9 849 6046

Kenepuru
Science Centre
Kenepuru Drive
PO Box 50 348
Porirua 5240
New Zealand

Tel: +64 4 914 0700
Fax: +64 4 914 0770

ESR NCBID - Wallaceville
66 Ward Street
PO Box 40158
Upper Hutt 5140
New Zealand

Tel: +64 4 529 0600
Fax: +64 4 529 0601

Christchurch
Science Centre
27 Creyke Rd
Ilam
PO Box 29 181
Christchurch 8540
New Zealand

Tel: +64 3 351 6019
Fax: +64 3 351 0010