National Survey of Pesticides in Groundwater 2014

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		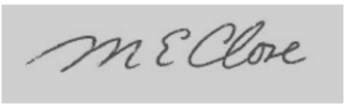
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EXECUTIVE SUMMARY

In 2014 ESR coordinated a survey of pesticides in groundwater throughout New Zealand. The survey has been completed every four years since 1990 with 2014 being the seventh consecutive survey. The well sampling was carried out by Regional and Unitary Authorities while the analysis was completed by AsureQuality. Samples were analysed for acidic herbicides and a suite of organo-chlorine, organo-phosphorus and organo-nitrogen pesticides. ESR's role was to coordinate the survey, advise on well selection as needed, collate and interpret the results and provide a national summary report.

Wells were selected on the basis of the importance of an aquifer to a region, known application and 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 during previous surveys, it was also included in the current survey to give a temporal comparison. The majority of the selected wells were from unconfined aquifers. The Waikato Regional council provided results for an additional 40 wells that had been sampled as part of a regional survey in 2012. These results have been included in this report to give a national perspective.

There were a total of 165 wells sampled including the 40 wells from the Waikato Regional Council. There were 28 wells (17%) with pesticides detected, with 10 of these wells having two or more pesticides detected. The maximum number of pesticides detected in one well was seven. There were one or more wells with pesticides detected in 6 of the 13 participating regions. Pesticides were not detected in sampled wells from Hawkes Bay (12 wells), Taranaki (5 wells), Horizons (23 wells), Greater Wellington (11 wells), Marlborough (17 wells), Canterbury (5 wells), and Otago (8 wells). Twenty one different pesticides were detected in this survey. Herbicides were the most frequently detected pesticide group with 4 insecticides and 2 fungicides also detected. There were 31 detections (61%) of triazine herbicides with terbuthylazine being the most frequently detected pesticide (16 detections). There were four pesticide detections exceeding 1 mg m^{-3} with only one of the sampled wells exceeding the maximum acceptable value (MAV) for drinking water. Dieldrin was detected at a concentration of 0.043 mg m^{-3} which was slightly in excess of the MAV of 0.04 mg m^{-3} (Ministry of Health 2008). The next highest detection relative to the MAV was for terbuthylazine at 17% of the MAV (Table 2) with the remainder of detections being less than 5% of the MAV.

Of the 101 wells that had been sampled on 4 or more surveys, using the sum of all pesticides detected as the comparison measure, 55% of wells had no pesticides detected for any of the surveys, 7% of wells showed an increasing trend, 8% of wells showed a decreasing trend, 20% showed a mixture of pesticides being detected and not detected with no trend, and 10% of wells had positive detections of pesticides for each survey sampled but with no trend. This indicates that the detections of pesticides is similar to previous surveys with no overall increasing or decreasing trend in totals levels of pesticides detected.

This information, combined with the similar levels of detections in the last four surveys, indicates similar levels of pesticide detections in groundwater over the last 12 years, with higher levels of detections before that time. The majority of wells sampled in each national survey have detected no pesticides and the concentrations of pesticides detected are mostly very low.

1. INTRODUCTION

Groundwater is an important source of drinking water in New Zealand. Nearly 40% of the community drinking water supplies around New Zealand utilise groundwater with many individual rural households additionally relying on groundwater for their drinking water needs (Close et al., 2001; Davies, 2001). In the majority of regions throughout New Zealand the volume of abstracted groundwater is increasing due to increased demand from the agricultural (irrigation) and industry sectors as well as from drinking water use. Groundwater quality however in some urban and rural areas has been steadily degrading and is increasingly under pressure as land use intensifies. Regional councils are responsible for the management of our water resources and carry out regular monitoring programmes to assess their quality. There is interest from the community about whether pesticides are reaching the groundwater systems as well as from our export markets who are concerned that our agricultural systems are environmentally responsible. Pesticides, which include insecticides, fungicides, herbicides and plant growth regulators, are commonly used in New Zealand to control insects, diseases and weeds in primary industries such as agricultural farming, forestry and horticulture (Manktelow et al., 2005). The horticultural sector is the most intensive user of pesticides on a land area basis (13.2 kg a.i./ha) followed by arable, forestry and pastoral sectors (Manktelow et al., 2005).

National surveys of pesticides in groundwater have been carried out at four yearly intervals since 1990 with this current survey being the seventh consecutive survey. 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 contamination. 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, which are commonly used to kill weeds, are the group of pesticides most commonly detected. Further details of previous surveys are summarised in Close and Skinner (2011), Gaw et al. (2008), Close and Flintoff (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 sixth national survey in 2010 sampled a total of 162 wells from regions throughout New Zealand, including the additional 6 wells sampled by Environment Southland (Close and Skinner, 2011). 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 pesticides concentration greater than the MAV for drinking water (Ministry of Health, 2008). There were a total of 22 different pesticides detected in the 2010 survey. Herbicides were the most common pesticide group detected followed by insecticides and fungicides. There were a total of 66 pesticide detections and of these detections, 60 (91%) were herbicides. There were 40 detections of triazine herbicides. Levels of only 3 of the 66 pesticide detections exceeded 1 mg m^{-3}. Note that mg m^{-3} is equivalent to $\mu g\ L^{-1}$ which is equivalent to ppb.

This report gives the results from the seventh national survey. The sampling was carried out in late 2014 with the exception of Hawke's Bay Regional Council which conducted its sampling in January 2015. The Waikato Regional council provided results for an additional 40 wells that had been sampled as part of their regional survey in late 2012. These results have been included in this report to give a national perspective.

2. METHODOLOGY

2.1 WELL SELECTION

In collaboration with ESR wells were selected by each participating council using the following criteria:

- shallow, unconfined and vulnerable aquifers
- significant and important aquifers
- past or present land use
- known or suspected pesticide storage and use

If possible, where a well had been sampled during previous surveys it was also included in the 2014 survey to provide a temporal comparison. Wells were also selected in areas that were under-represented or not sampled in previous surveys. For each well the following information was requested from the council: 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.

Twelve of the Regional and Unitary Authorities with groundwater management responsibilities participated in the 2014 survey. Bay of Plenty and West Coast Regional Councils did not participate in the 2014 survey, and the Waikato Regional Council carried out their own regional survey in 2012. The results from 40 wells from the Waikato Region were included in this survey. The 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.

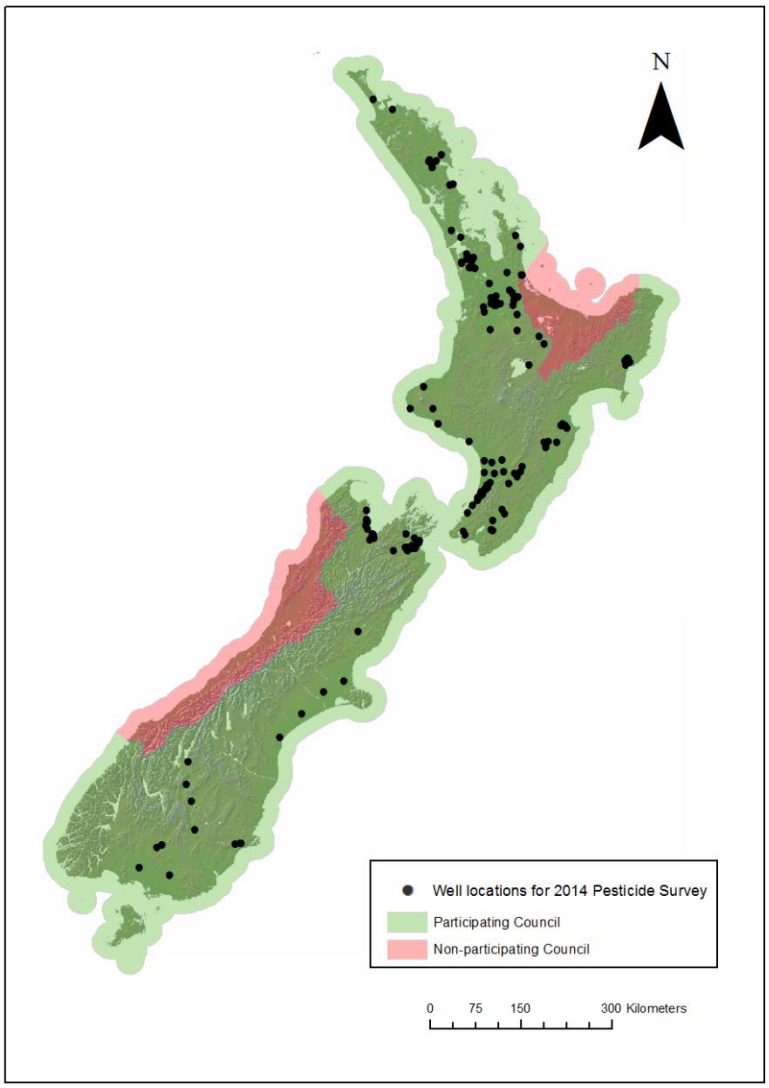

FIGURE 1: Councils participating in the 2014 National Pesticide Survey and their sampled well locations

2.2 SAMPLING

Samples were collected according to the ESR pesticide sampling procedures (Appendix A) with purging procedures based on *"A National protocol for State of the Environment Groundwater Sampling in New Zealand"* (Daughney et al. 2006). According to these procedures each council was asked to purge three well volumes where possible before sampling. Samples were collected by either portable pumps or in situ pumps as close to the well head as possible. In most cases field measurements of pH, dissolved oxygen, conductivity and temperature were recorded and a water sample only taken when these parameters had stabilised. For each well sampled a field sheet was filled out and returned to ESR (Appendix B).

2.3 LABORATORY ANALYSIS

All samples were sent to AsureQuality in Wellington and analysed for acidic herbicides and a suite of organo-chlorine, organo-phosphorus and organo-nitrogen pesticides (OC/OP/ON) using gas chromatography with a 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 8% 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 C. The detection limits for this survey were similar to 1998, 2002, 2006 and 2010 surveys but significantly lower than the limits for the 1994 and 1990 national surveys by a factor of between 5 and 10. The groundwater samples for Waikato Regional Council were analysed by Hills Laboratories which had similar methods but slightly lower detection limits.

3. RESULTS

A total of 125 wells from 12 regions were sampled and the groundwater samples sent to AsureQuality in Wellington. The Waikato Regional Council provided results for an additional 40 wells that had been sampled as part of their regional survey in late 2012. These results have been included in this report to give a national perspective.

3.1 ASSESSMENT OF SURVEY METHODOLOGY

Blind duplicate samples from 10 wells (8 %) 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).

Table 1: Comparison of Blind Duplicate samples.

Council	Well ID	Pesticide Concentration (mg m^{-3})
Northland Regional Council	205044	ND
	Blind Duplicate	ND
Auckland Regional Council	7428105	ND
	Blind Duplicate	ND
Hawkes Bay Regional Council	1558	ND
	Blind Duplicate	ND
Horizons Regional Council	312001	ND
	Blind Duplicate	ND
	316037	ND
	Blind Duplicate	ND
	349012	ND
	Blind Duplicate	ND
Greater Wellington Regional Council	S25/5322	ND
	Blind Duplicate	ND
Tasman District Council	WWD8042	0.014 Terbuthylazine
	Blind Duplicate	0.014 Terbuthylazine
Marlborough District Council	P28W/3222	ND
	Blind Duplicate	ND
Otago Regional Council	G41/0103	ND
	Blind Duplicate	ND

3.2 SURVEY RESULTS

With the addition of the 40 wells from the Waikato Regional Council, there were a total of 165 wells sampled with 28 wells (17%) having pesticides detected. In 10 of these wells two or more pesticides were detected (Table 2). The maximum number of pesticides detected in one well was seven. There were one or more wells with pesticides detected in 6 of the 13 participating regions. Pesticides were not detected in sampled wells from Hawkes Bay (12 wells), Taranaki (5 wells), Horizons (23 wells), Greater Wellington (11 wells), Marlborough (17 wells), Canterbury (5 wells), and Otago (8 wells). Twenty one different pesticides were detected in the sampled wells. Herbicides were the most frequently detected pesticide group with four insecticides and two fungicides detected in the sampled wells. There were 31 detections (61%) of triazine herbicides with terbuthylazine being the most frequently detected pesticide (16 detections). There were four pesticide detections exceeding 1 mg m^{-3} with only one of the sampled wells exceeding the MAV for drinking water. Dieldrin was detected at a concentration of 0.043 mg m^{-3} which was slightly in excess of the MAV of 0.04 mg m^{-3} (Ministry of Health 2008). The next highest detection relative to the MAV was for terbuthylazine at 17% of the MAV (Table 2) with the remainder of detections being less than 5% of the MAV.

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 Centre, which hosts several pesticide properties databases (http://npic.orst.edu/) as at April 2015, 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, Kd, 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 absorption 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 value greater than 2.8 indicates that the compound would leach relatively readily and a GUS score of less than 1.8 indicates a 'non-leacher'. There is 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 2014 pesticides in groundwater survey.

Council Region (# detections / # well sampled)	Well ID	Pesticide Detected	GCMS Concentration (mg m^{-3})
Northland Regional Council (2/11)	7244	Hexazinone	0.039
		Terbuthylazine	0.012
	9851	Terbuthylazine	0.021
Auckland Regional Council (4/8)	43915	Acetochlor	0.071
		Bentazone	0.15
		Metolachlor	0.057
	7419127	Bentazone	0.11
	7428031	Acetochlor	0.043
		Bentazone	0.17
		Metolachlor	0.027
	7428105	Bentazone	0.11
Waikato Regional Council (9/40)	60-348	Dieldrin	0.008
	61-113	DEA*	0.08
		Metalaxyl	0.17
		Metribuzin	0.06
		Procymidone	0.08
		Propazine	3.1
		Terbuthylazine	0.08
	61-230	Dieldrin	0.043
	62-5	Desethyl Terbuthylazine	0.1
	64-7	Terbuthylazine	0.04
	67-4	Hexazinone	0.21
	69-295	Bromacil	3.4
	69-374	Simazine	0.06
	70-22	Diuron	0.21
		Endosulfan I	0.01
		Endosulfan II	0.022
		Endosulfan sulphate	0.075
		Terbacil	0.84
		Desethyl Terbuthylazine	0.71
		Terbuthylazine	1.39

Council Region (# detections / # well sampled)	Well ID	Pesticide Detected	GCMS Concentration (mg m^{-3})
Gisborne District Council (2/6)	GPF032	Atrazine	0.017
	GPM007	Acetochlor	0.021
		Terbuthylazine	0.024
Tasman District Council (7/15)	WWD59	Terbuthylazine	0.018
	WWD285	Simazine	0.099
	WWD417	Terbuthylazine	0.032
	WWD3115	Terbuthylazine	0.033
	WWD4096	Simazine	0.015
		Terbuthylazine	0.022
	WWD8036	Dinoseb	0.23
		Terbuthylazine	0.019
	WWD8042	Terbuthylazine	0.014
Environment Southland (4/4)	E44/0036	Terbuthylazine	0.11
	E46/0093	Simazine	0.020
		Terbuthylazine	0.046
	F44/0055	Terbuthylazine	0.018
	F46/0239	Hexazinone	0.076
		Propazine	0.17
		Simazine	0.089
		Terbuthylazine	1.2

* DEA is desethyl atrazine

Table 3: Characteristics of detected pesticides. Field half-lives and Koc values are from the ARS Pesticide Properties Database and National Pesticide Information Centre: 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	0.021 - 0.071	
Atrazine	Triazine	173 (13–402)	147 (38–288)	4.10 L	1	0.017	2
Bentazone	other herbicide	27 (7–98)	35	3.52 L	4	0.11 - 0.17	400
Bromacil	Uracil	207 (61-349)	32 (2–72)	5.78 L	1	3.4	400
DEA	Triazine	†	†	† L	1	0.08	†
Desethyl Terbuthylazine	Triazine				2	0.1 – 0.71	
Dinoseb	Dinitrophenol herbicide	100	124	3.80 L	1	0.23	7[#]
Diuron	Urea derivative	372	477 (418 – 560)	3.40 L	1	0.21	20
Hexazinone	Triazine	79 (30 - 180)	54 (34 – 74)	4.30 L	3	0.039 - 0.21	400
Metolachlor	Amide	141 (12–292)	70 (22–307)	4.63 L	2	0.027-0.057	10
Metribuzin	Triazine	47 (23–128)	52 (3–95)	3.82 L	1	0.06	70
Propazine	Triazine	123 (35-347)	161 (100-600)	3.75 L	2	0.17 – 3.1	70
Simazine	Triazine	89 (26–186)	140 (103–230)	3.61 L	5	0.015-0.099	2
Terbacil	Uracil	200 (50–250)	63 (41–120)	5.06 L	1	0.84	40
Terbuthylazine	Triazine	60*	220 (162–278)*	2.95 T	16	0.012 – 1.39	8
Insecticide							
Dieldrin	Organochlorine	1000 (225 – 1260)	12000 (4000 – 39000)	-0.24 N	2	0.008 – 0.043	0.04
Endosulfan I	Other insecticide	60 (4 – 200)	12,400	-0.17 N	1	0.01	20
Endosulfan II	Other insecticide	‡	‡		1	0.022	

Pesticide	FAO Classification	Field half-life (days)	Koc (ml g^{-1})	GUS score	No. of Wells	Range (mg m^{-3})	MAV (mg m^{-3})
Endosulfan sulphate	Other insecticide	‡	‡		1	0.075	
Fungicides							
Procymidone	Dicarboximide	34 (7–120)	580§	1.89 T	1	0.08	700
Metalaxyl	other fungicide	77 (27-296)	171 (30-284)	3.33 L	1	0.017	100

* values for Terbuthylazine taken from The Pesticide Manual (1994); # USEPA drinking water limit for dinoseb = 7 mg m^{-3} (USEPA, 1986); † values assumed to be similar to atrazine; ‡ values assumed similar to Endosulfan I; § Koc data from Close et al. (2008).

4. DISCUSSION

There were four pesticide detections exceeding 1 mg m^{-3} with these detections all being in different wells in the Waikato and Southland regions (Table 2). Only one of the sampled wells exceeding the MAV for drinking water. Dieldrin was detected at a concentration of 0.043 mg m^{-3} which was slightly in excess of the MAV of 0.04 mg m^{-3} (Ministry of Health 2008). The next highest detection relative to the MAV was for terbuthylazine at 1.39 mg m^{-3} which is 17% of the MAV (Table 3) with the remainder of detections being less than 5% of the MAV. These results indicate that there should be little significant health risk based on the pesticides analysed from drinking the groundwater sampled from the wells included in this survey.

Dieldrin was widely 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 in the soil where the dip site wastewater was disposed of 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 in soils near sheep dip sites could be widespread and that concentrations in shallow groundwater (about 5 m below ground level) could increase in certain conditions, even though usage had ceased 30-40 years previously. The low MAV for dieldrin (0.04 mg m^{-3}) means that even low concentrations in groundwater can easily exceed the MAV for drinking water.

Terbuthylazine was the most commonly detected pesticide, being found in 16 wells at levels ranging from 0.012 – 1.39 mg m^{-3} (Table 3), with the next most common pesticide being simazine with 5 detections.

Herbicides were the most frequently detected pesticide group with four insecticides and two fungicides detected in the sampled wells. There were 31 out of the total of 51 detections (61%) of triazine herbicides with terbuthylazine being the most frequently detected pesticide (16 detections). The high detection rate for herbicides is consistent with estimates that herbicides comprise at least 60% of the total amount of pesticides sold in New Zealand annually (Manktelow et al., 2005). The high frequency of triazine detections is consistent with previous surveys of pesticides in groundwater (Table 4).

Of the 21 pesticides detected that had data available for soil half-life and Koc, GUS values indicated that 12 were leachers, 3 were transitional, and 2 were non-leachers (Table 3). This indicates that normal leaching processes are mostly responsible for the presence of the

detected pesticides in the groundwater and that other pathways, such a spills or preferential flow, are less important. The two non-leacher pesticides were dieldrin, which was widely used and is very persistent, as discussed above, and endosulfan. Endosulfan is an organochlorine but not nearly as persistent as dieldrin (Table 3). It was used in New Zealand from the 1960s onwards to control insects in crops such as potatoes, citrus and berry fruit crops, and on turf for earthworm control. Its use had been declining from the mid-1990s to mid 2000s and it was de-registered by ERMA in December 2008.

The significant decrease in detection limits for many pesticides for 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 2014 survey then there would only be a total of 16 wells (10%) with detectable pesticides instead of 28 wells (Table 4). Table 4 shows that there has been a similar level of pesticides detected over the past 4 surveys using the more sensitive detection limits. In 1998 35% of wells had pesticides detected but from 2002 to 2014 the percentage of wells with detectable pesticides varied from 17 to 24%. If the earlier less sensitive detection limits were applied then the percentage of wells with detectable pesticides has varied from 7 to 14% over the seven surveys from 1990 to 2014. In all surveys there have been a very small number of wells (between 2 and 4) where pesticides have been detected at concentrations greater than 1 mg m^{-3} and there has been a maximum of one pesticide detected at a concentration greater than the MAV in five out of the seven surveys with the other two surveys having no pesticides detected at a concentration greater than the MAV (Table 4). As these surveys have been focused on shallow unconfined groundwater systems, which are most at risk of pesticide contamination, this indicates that most groundwater in New Zealand should be considered safe to drink with respect to pesticides.

Only one well has been sampled in each of the 7 national surveys, with 11 wells having been sampled in 6 of the surveys. The 101 wells that had been sampled on 4 or more surveys were examined for any trends in the levels of pesticides detected, with the sum of all pesticides detected in a well being used as the comparison measure. 55% of wells had no pesticides detected for any of the surveys, 7% of wells showed an increasing trend, 8% of wells showed a decreasing trend, 20% showed a mixture of pesticides being detected and not detected with no trend, and 10% of wells had positive detections of pesticides for each survey sampled but with no trend. This analysis of wells that have been sampled in 4 or more surveys indicates that the detections of pesticides is similar to previous surveys with no overall increasing or decreasing trend in totals levels of pesticides detected.

This information, combined with the similar levels of detections in the last four surveys (Table 4), indicates that there has been similar levels of pesticide concentrations in groundwater over the last 12 years, with possibly higher levels of detections before that time. The majority of wells sampled in each national survey have detected no pesticides and the concentrations of pesticides detected are mostly very low.

Table 4: Summary statistics for the seven national surveys of pesticides in groundwater in New Zealand.

	Year of survey						
	1990	**1994**	**1998**	**2002**	**2006**	**2010**	**2014**
	(Close 1993)	(Close 1996)	(Close & Rosen 2001)	(Close & Flintoft, 2004)	(Gaw et al. 2008)	(Close & Skinner 2012)	This study
No. of wells in survey	82	118	95	133	163	162	165
No. of regions	6	13	15	15	14	14	13
No. of regions with pesticides detected	4	8	11	9	11	9	6
No. of pesticides detected	7	10	22	21	19	22	21
% of wells with pesticides detected > DL = 0.1 mg m^{-3}	7%	14%	11%	9%	8%	7%	10%
% of wells with pesticides detected > DL = 0.01 mg m^{-3}	-	-	35%	21%	19%	24%	17%
No. of wells with pesticides >1 mg m^{-3}	2	3	3	3	2	3	4
No of pesticides detected > MAV	1	0	1	0	1	1	1
% of detections that were herbicides	50%	95%	92%	92%	74%	91%	86%
% of detections that were triazines	13%	65%	76%	67%	50%	61%	61%

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APPENDIX A: ESR PESTICIDE SAMPLING PROCEDURES

National Survey of Pesticides in Groundwater 2014

Sampling Procedures

Sampling for the National Survey is fairly straightforward.

You will receive the sample bottles (x3 500 mL glass sample bottles which have been preserved with sodium thiosulphate for each well being sampled) from AsureQuality with chain of custody sheet enclosed in a chilly bin with ice pack and packing material for the return trip.

For councils that are sampling more than 7 wells, there is an additional set of sample bottles. This is for the collection of a Blind Duplicate sample, which is a quality control measure for the laboratory analysis. There is no additional cost for the collection of the Blind Duplicate sample. Please collect the Blind Duplicate sample as an extra sample from one of the wells at the same time as collecting the normal sample. There are further instructions relating to the Blind Duplicate samples later.

Before sampling the bore or well:

1) Collect the water level information, this information can be very important.

2) Make sure that at least 3 times the casing volume of water has been purged from the bore.

3) If the bore is a domestic water supply fitted with a down hole pump, make sure the pump is running and allow it to run at least 15 minutes before sampling.

If you are using your own pump for sampling such as a Grundfos MP1 pump, flush the well for at least 15 minutes at a high flow rate before sampling the well. This should also be adequate to rinse the pump between wells. Turn the flow rate down for 2-3 minutes before sampling.

4) Sample as close to the well-head as possible, but NEVER on the downstream side of holding tanks.

5) If you have a pH meter or conductivity meter, make sure that these reading have stabilised before taking the sample.

6) Prepare ice packs by submerging them in water for approximately 30 minutes then place in the freezer.

When sampling the well:

1) Label the bottles before you get your hands or the bottles wet.

2) Make sure your hands are clean and do not touch near the top of the sample bottles.

3) The glass bottles for the pesticide analyses have been washed and rinsed according to a strict protocol. It is important that the samples are collected directly into the bottles and not

into a bucket or other container before filling the sample bottles. **DO NOT RINSE THE BOTTLES.**

a) Fill the bottles to just below the cap thread as each bottle contains a preservative, Sodium Thiosulphate and there may be some expansion on warming. Make sure that you fill three bottles for each well that is sampled.

DO NOT FREEZE THE BOTTLES, OTHERWISE THEY WILL BREAK.

Blind Duplicates:

There will be a number of Blind Duplicate samples collected (about 7% of the total number of samples). If you are sampling more than 7 wells then you will be asked to collect a Blind Duplicate sample. The Blind Duplicate samples should be labelled as for the other samples but the well number on the bottle should be **fictitious** and the time should be omitted. Both the real and fictitious well number should be recorded on the ESR sampling sheet and note that a Blind Duplicate has been collected.

Collect the bottle for the sample and the Blind Duplicate alternatively, for example please sample in the following order:

- 1st 500ml bottle for the sample
- 1st 500ml bottle for the Blind Duplicate
- 2nd 500mL bottle for the sample
- 2nd 500 mL bottle for the Blind Duplicate
- 3rd 500ml bottle for the sample
- 3rd 500ml bottle for the Blind Duplicate

Please fill in an ESR Field Sampling form and an AsureQuality Environmental Sample Submission form for each well sampled. Indicate on the ESR Field Sampling form if there has been a Blind Duplicate taken and record its associated fictitious well number along with what well the Blind Duplicate belongs to. Do not send this sheet to AsureQuality.

Scan and email copies of the ESR Field Sampling forms to Bronwyn Dumbleton (bronwyn.dumbleton@esr.cri.nz) alternatively you can post the forms to: Bronwyn Dumbleton, ESR, PO Box 29-181, Christchurch 8540.

Place the AsureQuality Environmental Sample Submission form in the plastic bag supplied and send it with the samples to AsureQuality.

Once all the samples have been collected:

The glass bottles should be packed in the containers and packaging received in, and couriered to AsureQuality at the following address:

AsureQuality Limited
Wellington Laboratory
1C Quadrant Drive
Gracefield
Lower Hutt
Ph: 04 5708800
Attention: Sample Reception

Please advise AsureQuality of any breakages on Stephanie.Jonassen@asurequality.com and GracefieldSR@asurequality.com so we can send replacement bottles.

Any queries regarding the pesticide sampling should be directed at Murray Close, ESR, Christchurch. (Phone: (03) 351 0014; Fax: (03) 351 6019 or email: murray.close@esr.cri.nz), or Bronwyn Humphries, ESR, Christchurch (Phone: (03) 351 0138 or email: bronwyn.humphries@esr.cri.nz).

Some important things to consider when sampling are:

1. Please do not sample on a Thursday or Friday. If you do this however please send samples with a weekend delivery ticket or refrigerate until Monday. If at all possible please sample on Monday to Wednesday and then send the samples back to AsureQuality immediately via courier.

2. Allow any disused bores to run until at least 3 times the casing volume has been cleared from the bore, if possible, or at least until the parameters such as conductivity and pH have stabilised. Sampling bores that are constantly in use will cut down on purging time.

3. Please try to avoid sampling in the pouring rain so that the risk of contamination is minimised.

4. Please try to keep the bottles provided clean and do not rinse out the bottles as they contain a preservative.

If you have any questions about sampling or if the procedures conflict with your current sampling protocols, please do not hesitate to contact us and we can try to resolve the issues as quickly as possible.

Thanks for participating in the programme; it could not exist without your support. Any questions or comments are welcome.

Regards – The ESR Team

Murray Close (027 4361270) and Bronwyn Humphries (027 2434570)

APPENDIX B: ESR PESTICIDE SAMPLING FIELD SHEET

Field Sampling Form:
2014 National Survey of Pesticides in Groundwater
(please use one form per well)

Regional/District Council:		
Person collecting sample:		
Grid reference (NZTM):		
Council well number/ID:		
Well owners name:		
Address:		
Weather:		
Surrounding land use:		
Well use:		
Well diameter (mm):		
Well depth (m):		
Screened interval (m):		
Pumped (circle one):	*YES / NO*	
Sampling point description:		
Water level (m):		
Date and time of sampling:	*Date:*	*Time:*
Time of pumping before sampling:		
Well volume removed:		
Field measurements:	*DO (mg/L)*	
	Conductivity	
	Temperature	
	pH	
Type of aquifer:		
Name of aquifer (if any):		
Comments:		

APPENDIX C: 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.)

Pesticides Screen						**Acid Herbicides**	
Organochlorine Pesticides		*Organonitrogen Herbicides*		*Organophosphorus Pesticides*			
Aldrin	< 0.01	Acetochlor	< 0.02	Azinphos methyl	< 0.4	Acifluorfen	< 0.4
BHC-alpha	< 0.01	Alachlor	< 0.02	Chlorpyriphos	< 0.02	Bentazone	< 0.1
BHC-beta	< 0.01	Atrazine	< 0.01	Diazinon	< 0.01	Bromoxynil	< 0.1
BHC-gamma (lindane)	< 0.01	Bromacil	< 0.03	Dimethoate	< 0.4	2,4-D	< 0.1
BHC-delta	< 0.01	Carbofuran	< 0.9	Pirimiphos methyl	< 0.02	2,4-DB	< 0.1
Chlordane-alpha	< 0.01	Cyanazine	< 0.02			Dicamba	< 0.1
Chlordane-gamma	< 0.01	Hexazinone	< 0.01			3,5-Dichlorobenzoic acid	< 0.1
DDD(p,p')	< 0.01	Metalaxyl	< 0.02			Dichlorprop	< 0.1
DDE(p,p')	< 0.01	Metolachlor	< 0.02			Dinoseb	< 0.1
DDT(o,p')	< 0.01	Metribuzin	< 0.02			Fenoprop	< 0.1
DDT(p,p')	< 0.01	Molinate	< 0.01			MCPA	< 0.1
Dieldrin	< 0.01	Norflurazon	< 0.02			MCPB	< 0.1
Endosulfan I	< 0.02	Oryzalin	< 2			Mecoprop	< 0.1
Endosulfan II	< 0.04	Oxadiazon	< 0.01			Pentachlorophenol	< 0.1
Endosulfan sulfate	< 0.02	Pendimethalin	< 0.02			Picloram	< 0.1

Pesticides Screen						Acid Herbicides	
Organochlorine Pesticides		*Organonitrogen Herbicides*		*Organophosphorus Pesticides*			
Endrin	< 0.02	Propanil	< 0.01			2,4,5-T	< 0.1
Endrin aldehyde	< 0.04	Propazine	< 0.01			Triclopyr	< 0.1
Endrin ketone	< 0.04	Pyriproxyfen	< 0.5				
Heptachlor	< 0.01	Simazine	< 0.01				
Heptachlor epoxide	< 0.03	Terbacil	< 0.02				
Hexachlorobenzene	< 0.1	Terbuthylazine	< 0.01				
Methoxychlor	< 0.02	Trifluralin	< 0.02				
Permethrin-cis	< 0.01						
Permethrin-trans	< 0.01						
Procymidone	< 0.02						
Vinclozolin	< 0.02						

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