National Survey of Pesticides in Groundwater 2022

June 2023

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CLIENT REPORT No: **CSC23010**

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ACKNOWLEDGEMENTS

ESR wishes to thank the Regional and Unitary Authorities who funded this survey and whose support ensures the continuation of long-term monitoring of pesticides in groundwater throughout New Zealand.

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		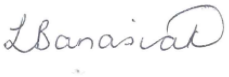
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		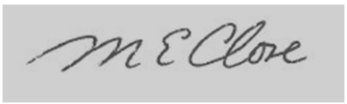
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CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. EXECUTIVE SUMMARY

In 2022, ESR coordinated a survey of pesticides in groundwater throughout Aotearoa New Zealand. The pesticide survey has been completed every four years since 1990, with 2022 being the ninth consecutive survey. Regional and Unitary Authorties carried out the well sampling and the 2022 survey was the first time that per- and polyfluoralkylsubstances (PFAS) were included in the suite of compounds analysed. The pesticide analysis was carried out by Hills Laboratories. Emerging Organic Contaminants (EOCs) were also analysed but the results are not available for this report. ESR's role was to coordinate the survey, advise on well selection, collate and interpret the results and produce a summary report.

Wells were selected based on several factors including the importance of an aquifer to a region, the known application and storage of pesticides in the area, and the perceived vulnerability of the aquifer to pesticide contamination. Where possible, wells sampled in previous surveys were included in the 2022 survey to give a temporal comparison. Most of the sampled wells are screened in unconfined aquifers and were selected because shallower unconfined aquifers are at greater risk of contamination than confined, deeper aquifers.

In total, 184 wells were sampled, including an additional 21 wells from Waikato Regional Council that had been sampled as part of their regional surveys between January 2020 and June 2022. Pesticides were detected in 17 wells (9.2%), with 6 (3.3%) of these wells having two or more pesticides detected. The maximum number of pesticides detected in one well was six. Pesticides were not detected in wells from Auckland Council (8 wells), Bay of Plenty Regional Council (10 wells), Hawkes Bay Regional Council (12 wells), and Greater Wellington Regional Council (8 wells). Sixteen different pesticides were detected in the sampled wells, with herbicides being the most frequently detected pesticide group with 19 detections (66%) of 12 different herbicides and their metabolites. The most commonly detected pesticide was terbuthylazine (detected in 6 wells), followed by desethyl terbuthylazine (DET) (detected in 4 wells). Only one pesticide detection concentration exceeded 1 µg/L (clopyralid, 1.1 µg/L). There is no Maximum Acceptable Value (MAV) for drinking water available for clopyralid. Dieldrin was detected above the MAV for drinking water in one well, at a maximum concentration of 0.053 µg/L (i.e., 133% of the MAV of 0.04 µg/L (Taumata Arowai (2022)). Concentrations of other detected pesticides were less than 4% of their respective MAV.

Compared to the pesticide survey of 2018, the number of pesticide detections has decreased. In 2018 24% of wells had pesticides detected but in the 2022 survey this had dropped to 9%. Analysis of wells sampled in 2022 that had been sampled in multiple previous surveys indicate that there were 2 wells with significant ($p<0.05$) decreases over time and a further well with a decrease at the $p<0.1$ level. 26 of the 56 wells that had been sampled in 2022, and had also been sampled in 4 or more previous surveys, had no pesticides detected on any occasion. 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. Overall, our data from the 2022 national groundwater survey indicate a decrease in the frequency and concentration of pesticide residues detected in groundwater relative to previous surveys.

There is limited discussion in this report about the correlation of pesticide detections with parameters such as well depth and groundwater chemistry. It was felt that it was more important to provide the actual results of the survey of pesticides in groundwater to the regional councils as soon as possible. Further analysis of the data is continuing, and more extensive discussion will be provided in a journal paper that will be prepared for publication and sent to all the councils as soon as it is ready.

2. INTRODUCTION

Aotearoa New Zealand's first nationwide pesticide survey was undertaken in 1990 and has been repeated every four years since. Groundwater is a critical resource for New Zealand, providing drinking-water to 40% of New Zealanders (LAWA, 2022). In most regions throughout Aotearoa New Zealand, the volume of abstracted groundwater is continuing to increase due to growing demand from agricultural (irrigation) and other industry sectors, as well as from drinking water use. However, in many areas nationwide, groundwater quality has been degrading for decades and is owing to land use intensification (MfE & StatsNZ, 2019). Thus, identification of contaminants in aquifers (e.g., via routine monitoring and surveys such as the one presented here) are an essential component for informing careful management and protection of sensitive aquifers and their recharge zones.

Regional councils and unitary authorities are responsible for managing groundwater quantity and quality and maintain groundwater monitoring programmes. However, these monitoring programmes rarely include pesticide analysis. Nevertheless, councils, authorities and local communities are becoming increasingly concerned about whether pesticides are present in groundwater. Pesticides, including 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 active ingredient/ha), with more than 300 pesticides approved for use on fruit and vegetables grown in New Zealand. Pesticides are also widely used by arable, forestry and pastoral sectors (Manktelow et al., 2005).

National surveys of pesticides in groundwater have been carried out every four years since 1990, with the 2022 survey being the ninth consecutive survey. Previous national and regional groundwater surveys in New Zealand have shown low levels of pesticides in some groundwater systems, with a particular focus on shallow unconfined systems that are typically most vulnerable to contamination. While the concentrations of detected pesticides have generally been less than 1% of their respective MAV, there have been some exceedances of the MAVs. Triazine pesticides, which are commonly used to kill weeds, are the group of pesticides most detected. Further details of previous surveys are summarised in Close et al. (2021), Close and Humphries (2016), Close and Skinner (2012), Gaw et al., (2008), Close and

Flintoff (2004), Close and Rosen (2001), Close (1996) and Close (1993). In addition to the national surveys, some regional councils have also undertaken their own more intensive pesticide monitoring programmes (Hadfield and Smith, 1999; Taranaki Regional Council, 1995; Hadfield, 2013).

The most previous survey in 2018 sampled 279 wells including an additional 41 wells sampled by Waikato Regional Council and 71 additional wells sampled by Environment Canterbury (Close et al., 2021). Pesticides were detected in 68 wells (24.4%), including 28 with two or more pesticides detected. The maximum number of pesticides detected in one well was six. Pesticides were not detected in sampled wells from Bay of Plenty (25 wells) and Hawkes Bay (14 wells). In total, twenty-five different pesticides, including metabolites, were detected. Herbicides were the most frequently detected pesticide group with 98 detections (88% of total pesticide detections) of 17 different herbicides and their metabolites. There were three pesticide detections where concentrations exceeded 1 μg/L, however, pesticide concentrations did not exceed the Maximum Acceptable Value (MAV) for drinking water in samples. The highest detection relative to its respective MAV was dieldrin, which was detected at a concentration of 0.025 μg/L (i.e., 62.5% of the MAV of 0.04 μg/L (Taumata Arowai (2022)). Most pesticide detections were less than 0.5% of their respective MAV.

Groundwater sampling for the 2002 survey was mostly undertaken between September and December 2022. However, this report also includes data from 21 wells sampled as part of Waikato Regional Council's regional surveys between January 2020 and June 2022. There is limited discussion in this report about temporal variation of pesticides in groundwater, the correlation of pesticide detections with parameters (e.g., depth of the screen, land use, and groundwater chemistry). The aim of this report is to provide a summary of the survey results to the regional councils as soon as possible. More detailed analysis of the data is ongoing, and an extensive discussion will be included in a journal paper.

3. METHODOLOGY

3.1 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, wells sampled in previous surveys were included in the 2022 survey to allow 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 predominant land use in the catchment. 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 (e.g., drinking water). Most of the selected wells are screened in unconfined aquifers.

All fifteen of the Regional and Unitary Authorities with groundwater management responsibilities participated in the 2022 survey. A total of 184 wells were sampled and analysed for the pesticide suites, including the 21 wells from the Waikato Regional Council. The Waikato Regional Council carried out their own regional survey between January 2020 and June 2022, whereby 21 wells were sampled. The data from the Waikato Region were included in this survey (Figure 1).

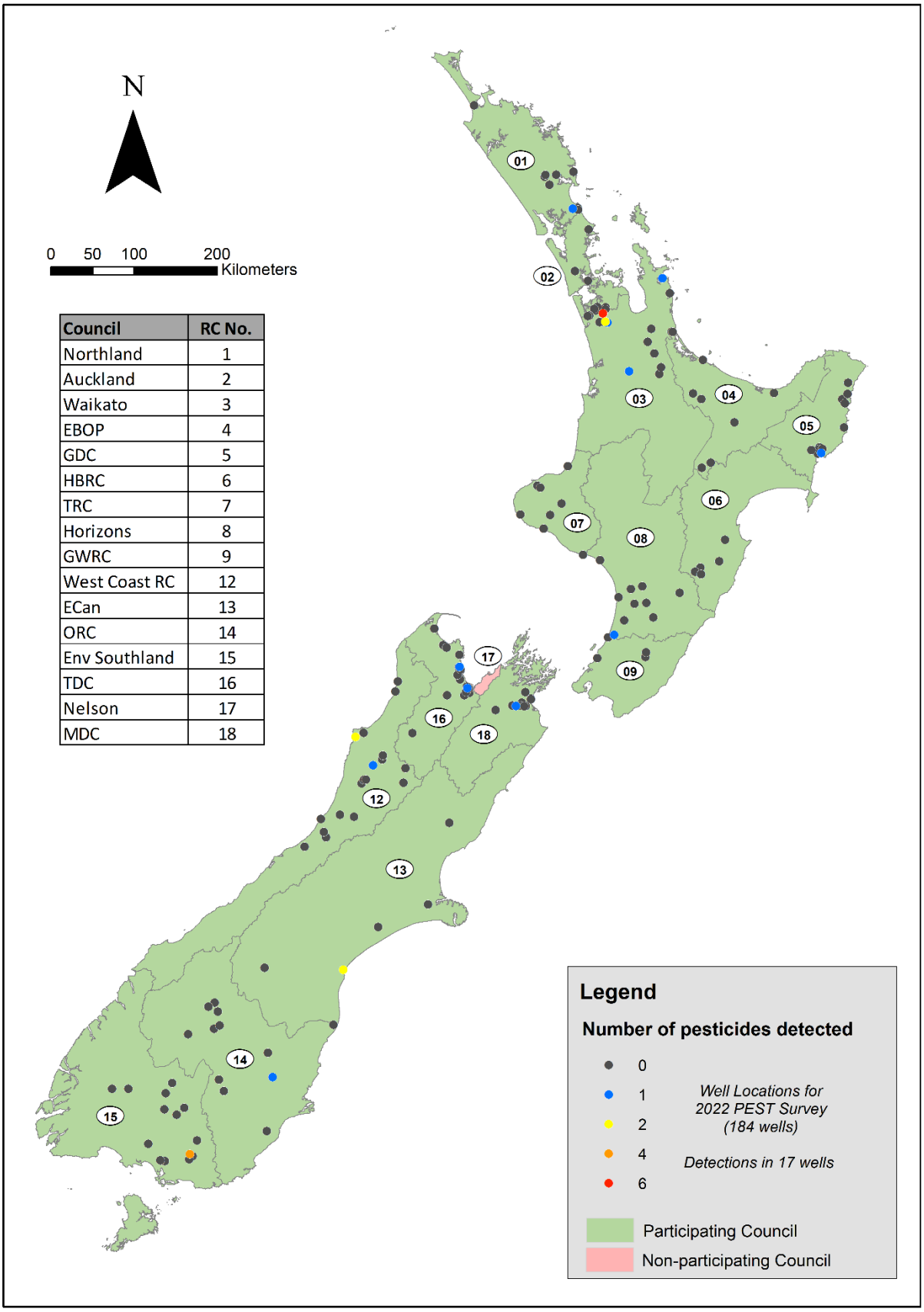

FIGURE 1: Regions and sampling locations for the 2022 survey of pesticides in groundwater.

3.2 SAMPLING

Samples were collected following ESR's procedure for sampling pesticides (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 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 taken following stabilisation of parameter values. For each sampling event, a field sheet was completed and returned to ESR (Appendix B). Glass bottles for pesticide analysis were supplied by Hill Laboratories (an IANZ accredited laboratory). Samples from 7.6% of wells were collected in duplicate so that blind-duplicate analysis could be undertaken for Quality Assurance (QA) purposes.

3.3 LABORATORY ANALYSIS

Samples for the pesticide analysis suites were sent to Hill Laboratories and analysed for acidic herbicides and a suite of organo-chlorine, organo-phosphorus, and organo-nitrogen pesticides (OC/OP/ON). Upon receipt by Hill Laboratories, sample bottles were checked for damage, correlated against the supplied inventory and sampling details, and stored in the dark at 4˚C. The acid herbicide analysis involved liquid chromatography with tandem mass spectrometry (LC-MS-MS). The OC/ON/OP pesticides were analysed using liquid-liquid extraction-gas chromatography–mass spectrometry (LLE-GC-MS). The pesticides assayed and their limits of detection (LOD) are provided in Appendix C. The detection limits are slightly lower than in previous surveys.

4. RESULTS

4.1 ASSESSMENT OF SURVEY METHODOLOGY

Blind duplicate samples from 14 wells (7.6%) were submitted to the analytical laboratory as an additional QA measure. None of the blind duplicate samples had detectable pesticides present and there was very clear consistency for all duplicate analyses (Table 1).

Table 1: Comparison of Blind Duplicate samples for pesticides suite.

(ND, not detected)

Council	Well ID (Blind duplicate)	Pesticide Concentration (µg/L)
Northland Regional Council	331726 (Blind Duplicate)	ND (ND)
Auckland Council	6475015 (Blind Duplicate)	ND (ND)
Bay of Plenty Regional Council	1000147 (Blind Duplicate)	ND (ND)
	170047 (Blind Duplicate)	ND (ND)
Gisborne District Council	GTA044 (Blind Duplicate)	ND (ND)
Hawkes Bay Regional Council	16503 (Blind Duplicate)	ND (ND)
Taranaki Regional Council	GND0827 (Blind Duplicate)	ND (ND)
Horizons Regional Council	347056 (Blind Duplicate)	ND (ND)
Tasman District Council	GW 8036 (Blind Duplicate)	ND (ND)
	GW 23759 (Blind Duplicate)	ND (ND)
Marlborough District Council	20226247 2993 (Blind Duplicate)	ND (ND)
Otago Regional Council	H42/0214 (Blind Duplicate)	ND (ND)
Environment Southland	E46/0867 (Blind Duplicate)	ND (ND)
West Coast Regional Council	Kirby @ Waitaha bore (Blind Duplicate)	ND (ND)

4.2 SURVEY RESULTS

Including 21 wells sampled by Waikato Regional Council, total of 184 wells were sampled. Pesticides were detected in 17 wells (15.8%); a significant decrease compared to the 2018 survey where 68 wells (24.4%) out of a total of 279 wells sampled had pesticides detected. The additional wells sampled by Waikato Regional Council had a higher detection frequency (28.6%) compared to the national detection frequency. It should be noted that five of the Waikato Regional Council wells were sampled on a more frequent basis to provide a more detailed understanding of temporal variability of pesticides in groundwater and three of these wells had a previous history of pesticide contamination. Pesticides were detected in at least one or more well in 10 of the 15 participating regions (Table 2), with regional detection rates varying from 0 to 28.6% (note that most of the higher rates of detection were for a smaller number of sampled wells). Pesticides were not detected in wells from Auckland Council (8 wells), Bay of Plenty Regional Council (10 wells), Hawkes Bay Regional Council (12 wells), and Greater Wellington Regional Council (8 wells). Across all survey data, two or more pesticides were detected in 6 wells (3.3%) (Table 2). The maximum number of pesticides detected in an individual well was six (Waikato, 61_113), with four being detected in a well from Southland (F45/0239). Sixteen different pesticides were detected in the sampled wells (Table 3).

In total, sixteen difference pesticides were detected (Table 3). Herbicides were the most frequently detected pesticide group with 19 detections (i.e., 66% of all herbicide detections) of 12 different herbicides, with two insecticides and two fungicides detected in the sampled wells. There were 13 detections (45%) of triazine herbicides with terbuthylazine being the most frequently detected pesticide (6 detections, 21%), though these concentrations were below the MAV for drinking water. The highest detection as a percentage of the MAV was dieldrin, which was detected at a maximum average concentration of 0.04 μg/L (i.e., 100% of the MAV of 0.04 μg/L (Taumata Arowai, 2022)). Two samples had been collected from this well 11 months apart, with both samples having dieldrin detected at concentrations of 0.027 and 0.053 μg/L, giving an average concentration of 0.04 μg/L. The next highest detections relative to the MAV were for terbuthylazine, simazine and diuron at 3.9%, 2.5% and 2.3% of their MAV's, respectively. The remainder of the pesticides were detected at concentrations below 0.6% of their respective MAVs.

Concentration ranges, MAVs, 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 of May 2023, unless otherwise noted. The selected value listed in this database, plus the range of values in the literature, are given in Table 3. The degree to which pesticides sorb to organic carbon particles in sediment or soil during transport i.e., its mobility, in water is estimated by the pesticide-specific organic-carbon partition coefficient (*K*oc) and the pesticide-specific octanol-water partition coefficient (*K*ow) or the pesticide- and soil-specific distribution coefficient (*K*d). The *K*ow is a useful descriptor of the tendency of a compound to associate with hydrophobic or hydrophilic substances. There will be some sorption of the detected pesticides to soils, sediment, and aquifer media (Sarkar et al., 2020), therefore some pesticides persist in an aquifer or groundwater system and will not be removed from a groundwater system as rapidly as they might if they were totally miscible with water.

Leaching potential can be easily predicted using a nomogram based on the mobility and persistence (Gustafson, 1989):

GUS = log10 (soil half-life) x [4 - log10(*K*oc)]

Pesticides with a GUS less than 0.1 are considered to have an extremely low potential to be leached from soil and are, therefore unlikely to infiltrate into groundwater. A 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. Values of 1.0-2.0 are low, 2.0-3.0 are moderate, 3.0-4.0 are high, and values greater than 4.0 have a very high potential to move toward groundwater. The GUS values suggested by Primi et al., (1994) of 1.5 and 3.0 were used to differentiate leachers and non-leachers. Use of laboratory data for persistence (laboratory half-lives in soil of 20–372 days) and sorption (Koc 418–1666) gives GUS of 1.0 to 3.5 and places diuron mainly in the transitional class (short half-life), extending into the probable leacher range (longest half-life and lowest Koc) (APVMA, 2011).

Water solubility describes the amount of pesticide that will dissolve in a known volume of water at a specific temperature. Most of the values reported were determined at room temperature (20°C or 25°C). Highly soluble pesticides are more likely to be removed from the soil by runoff or via infiltration to the vadose zone with excess water.

TABLE 2: Summary of results from the 2022 pesticides in groundwater survey detailing 29 detections in 17 wells out of a total of 201 wells sampled.

Note that µg/L = mg m^{-3} = ppb. 4,4'-DDE = Dichlorodiphenyldichloroethylene. DET = desethyl terbuthylazine=terbuthylazine desethyl.

COUNCIL REGION (# wells with detections / # wells sampled, % detected)	WELL ID	PESTICIDE DETECTED	CONCENTRATION (µg/L)
Northland Regional Council (1/10, 10%)	209851	Terbuthylazine	0.03
Auckland Council (0/8, 0%)			
Waikato Regional Council (6/21, 28.6%)	60_12	Diuron	0.46
	61_113	4,4'-DDE	0.013*
		Metalaxyl	0.10*
		Metribuzin	0.18*
		Procymidone	0.14*
		Propazine	0.06*
		Terbuthylazine	0.03*
	61_230	Dieldrin	0.04*
	61_54	Dieldrin	0.03
		Propazine	0.03
	61_93	Atrazine	0.06*
		Metolachlor	0.10*
	62_5	DET	0.06
Bay of Plenty Regional Council (0/10, 0%)			
Gisborne District Council (1/14, 7.1%)	GPA004	Diuron	0.17
Hawkes Bay Regional Council (0/12, 0%)			
Taranaki Regional Council (0/8, 0%)			
Horizons Regional Council (1/10, 10%)	372034	Alachlor	0.1
Greater Wellington Regional Council (0/8, 0%)			
Tasman District Council (2/22, 9.1%)	GW285	DET	0.05

	GW6342	Terbuthylazine	0.02
Marlborough District Council (1/10, 10%)	P28w/0548	Terbuthylazine	0.02
Environment Canterbury (1/5, 20%)	K39/0033	DET Terbuthylazine	0.31 0.07
Otago Regional Council (1/13, 7.7%)	I44/0821	Hexazinone	0.1
Environment Southland (1/15, 6.7%)	F45/0239	Propazine	0.03
		Simazine	0.05
		Terbuthylazine	0.08
		DET	0.05
West Coast Regional Council (2/18, 11%)	Westport @ Okari	Clopyralid	1.1
		Picloram	0.3
	Porter @ Maimai	Picloram	0.7
	17 wells		**29 detections**

* Average concentration from well sampled multiple times.

TABLE 3: Characteristics of detected pesticides (all herbicides).

Field half-lives, water solubility and *K*oc values are from the National Pesticide Information Centre database (http://npic.orst.edu/): selected value with range in parentheses. GUS classes: L = leacher; N = non-leacher; T = transitional. NA = not available. MAV = maximum acceptable value, are from Taumata Arowai (2022) unless otherwise stated.

PESTICIDE	FAO CLASSIFICATION	FIELD HALF-LIFE (DAYS)	WATER SOLUBILITY (mg/L)	ORGANIC CARBON-WATER PARTITION COEFFICIENT *K*oc (mg/L)	GUS SCORE	# WELLS	RANGE (µg/L)	MAV (µg/L)
Herbicide								
Alachlor	Amide	15	240	170	2.08 T	1	0.1	20
Atrazine	Triazine	60	33	100	3.56 L	1	0.05-0.07	100
Clopyralid	NA	40	300,000	6	5.06 L	1	1.1	-
Diuron	NA	90	42	480	1-3.5 L[1]	2	0.17-0.46	20
Hexazinone	Triazine	90	33,000	54	4.43 L	1	0.1	400
Metolachlor	Amide	90	530	200	3.32 L	1	0.09-0.12	20
Metribuzin	Triazine	40	1220	60	3.82 L	1	0.05-0.59	70
Picloram	Other hormone type	90	200,000	16	5.46 L	2	0.3-0.7	200
Propazine	Triazine	135	8.6	154	3.86 L	2	0.03	70
Simazine	Triazine	60	6.2	130	3.35 L	1	0.05	2
Terbuthylazine	Triazine	86 (34–193)*	6.6[2]	110 (42–575)*	3.79 L	6	0.02-0.31	8
DET	Triazine	#	327.1[2]	#		4	0.05-0.07	
Insecticide								
4,4'-DDE	Organochlorine	1000	0.1	50,000	-2.10 N	1	0.013	1

Dieldrin	Organochlorine	1000	0.2	12,000	-0.24 N	2	0.02-0.04	0.04§
Fungicide								
Metalaxyl	Other fungicide	70	8400	50	3.33 L	1	0.04-0.21	300
Procymidone	Other fungicide	7	4.5	1500	4.26 L	1	0.05-0.22	70

* values for Terbuthylazine taken from Close et al., (2008); DET = desethyl terbuthylazine=terbuthylazine desethyl; # values assumed similar to Terbuthylazine;
§ The sum of aldrin + dieldrin, not each; References: [1] Australian Pesticides and Veterinary Medicines Authority (APVMA, 2011); [2] Pesticide Properties Database, University of Hertfordshire, Agriculture & Environment Research Unit, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm.

5. DISCUSSION

There was one pesticide detection exceeding 1 µg/L (clopyralid at 1.1 µg/L, no MAV currently available) and only one pesticide detected at the MAV for drinking water. The highest detection as a percentage of the MAV was dieldrin, which was detected at a maximum average concentration of 0.04 µg/L, which was 100% of the MAV of 0.04 µg/L (Taumata Arowai, 2022). The next highest detections relative to the MAV were for terbuthylazine, simazine and diuron at 3.9%, 2.5% and 2.3% of their MAV's, respectively. The median concentration of the other detected pesticide detections were lower than 0.6% of their respective MAVs. These results indicate that there is unlikely to be significant risks to human from the pesticides analysed at the wells included in this survey.

In previous surveys, dieldrin concentrations have exceeded the MAV in a small number of samples (Close and Skinner, 2012; Close and Humphries 2016; Close et al., 2021). In the 2018 survey, the maximum concentration of dieldrin was 0.025 µg/L, which was 62.5% of the MAV and 37.5% less than the maximum concentration found in the current study. The comparatively low MAV for dieldrin (0.04 µg/L) means that even concentrations close to the detection limit are more likely (compared to other pesticides) to exceed the MAV for drinking water. Further, dieldrin was widely used in New Zealand in the 1960s, prescribed by Government regulations for the control of ectoparasites on sheep and cattle (MfE, 2006). In the 1960s, most livestock farms operated sheep or cattle dips. Even though dieldrin has not been used since the mid 1960's it persists to this day in many farm soils where dipping operations were completed and dipping wastewater disposed of, and occasionally it is detected in the underlying groundwater. Hadfield and Smith (1999) investigated dieldrin in groundwater in the Waikato region and found widespread dieldrin contamination in soils near sheep dip sites. Further, in shallow groundwater (about 5 m below ground level) proximal to sheep dips, dieldrin concentrations could increase though usage had ceased 30-40 years previously. Many of the other detected insecticides are also persistent legacy chemicals with low mobility (Table 3).

Terbuthylazine was the most detected pesticide, found in 6 wells (21%) at levels ranging from 0.02 to 0.31 µg/L (Table 3). The second most common pesticide was desethyl terbuthylazine (a metabolite of terbuthylazine) with 4 detections ranging in concentration from 0.05 to 0.31 µg/L. None of the detections for terbuthylazine or desethyl terbuthylazine exceeded the MAV

for drinking water. Both dieldrin and picloram were detected in 2 wells, with the remainder of pesticides detected in one well each.

Herbicides were the most frequently detected pesticide group (19 detections out of a total of 29 detections across all pesticide types i.e., 66%) with two insecticides and two fungicides also detected. 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 detection of triazine herbicides (13 detections, 45%), was less common than was observed in previous surveys (Table 4).

Of the 16 pesticides detected that had data available for soil half-life and Koc, GUS values indicated that 12 were leachers, 1 was transitional (diuron was borderline transitional-leacher), and 2 were non-leachers (Table 3). Dieldrin, which was widely used and very persistent as discussed previously, and DDE are non-leacher pesticides that were detected in samples from the Waikato Regional Council. Leaching of extremely persistent pesticides can occur over long time periods to shallow groundwater.

5.1 TEMPORAL TRENDS FOR PESTICIDES WITH PREVIOUS SURVEYS

For all surveys, most sampling has occurred from October to December (late spring to early summer). Although seasonal patterns in pesticide concentrations are often observed for individual wells (e.g., Hadfield and Smith, (1999); Close et al. (2001)), pesticide variability across different wells is inconsistent. The inconsistency between seasonal trends across different wells is likely due to variable travel times through the soil and vadose (unsaturated) zone and groundwater systems, together with the differences in pesticide mobility and persistence characteristics. This implies that any sampling time can be regarded as representative providing that it is consistent (i.e., sampled in the same season) between surveys, and temporal variability is best assessed using wells that have been sampled in multiple surveys.

The groundwater from some wells has contained detectable concentrations of the same pesticide over multiple surveys. Figure 2 shows selected wells where the same pesticide has been detected in an individual well over five or more surveys. The data for these wells were selected to demonstrate this occurrence for seven different pesticides, with between one and

four pesticides detected within each well. The longevity for these pesticide detections is probably related to both the extended period of time over which application of the pesticide has been occurring (with consistent land use and management taking place in the capture zone of each well), and the recognised increase in the persistence of pesticides once they leach from the soil zone into the vadose zone and groundwater system (Pang and Close,1999; Levy and Chesters,1995).

No wells have been sampled in all nine national groundwater surveys, with 7 wells having been sampled in eight surveys, 10 wells having been sampled in seven surveys, 25 wells having been sampled in six surveys, 36 wells having been sampled in five surveys and 33 wells having been sampled in four surveys. Of the 56 wells that were sampled in 2022 and have been sampled on four or more surveys, using the sum of all pesticide concentrations detected as the comparison measure, 26 wells (46%) had no detectable pesticide concentrations in any of the surveys. There were two wells (F46/0239 and 4096, Environment Southland) that showed a significant ($p < 0.05$) decreasing trend in total pesticide concentrations, and one further well (372034, Horizons Regional Council) showed a decreasing trend in total pesticide concentrations at a significance level of $p < 0.10$).

Well F46/0239 is associated with long-term sources of contamination around Edendale, Southland, with previously high concentrations (> 6 μg/L) of total pesticides being measured in groundwater in the 1994 and 1998 surveys and levels decreasing since that time. Hughes (2000) found several nearby sources were likely involved in the contamination of this well, including a plant nursery, horticultural activities and spraying for weed control around railway yards. Well 4096 is a relatively shallow well (5 m) used for firefighting purposes. It has shown low and consistently decreasing levels of simazine since 1994 (Figure 2), with pesticide concentrations below the detection limit in the 2022 survey. Well 372034 had high levels (34 μg/L) of alachlor detected in 2006, together with trace levels of metalaxyl and metribuzin. Levels of alachlor dropped to 12 μg/L in 2010, to below detection in 2014 and just above detection in 2018 and 2022.

The 1998 survey had the greatest frequency of pesticide detections compared to subsequent surveys. If the higher detection limits (used for the 1990 and 1994 surveys) were applied to subsequent surveys, then the 1994 survey had the highest frequency of pesticide detections (Table 4). Owing to improvements in analytical methods and technology, there has been a

significant decrease in lower detection limits for many pesticides. For example, if the detection limits for the 1990 and 1994 surveys were applied to the 2022 survey, then pesticides would only have been detected in 6 wells (3%) instead of 17 wells (Table 4). Table 4 shows that, while there had been a similar number of pesticides detected in the four surveys prior to the current 2022 survey, there has been a decrease in the number of pesticides detected since the 2018 survey. In 2018, pesticides were detected in 24% of wells compared with 9% in 2022. Analysis of wells sampled in 2022 that had been sampled in multiple previous surveys showed that there were 2 wells with significant ($p<0.05$) decreases over time and a further well with a decrease at the $p<0.1$ level. Twenty-six of the 56 wells that had been sampled in 2022, and had also been sampled in 4 or more previous surveys, had no pesticides detected on any occasion.

In all surveys prior to 2022, a small number of wells (between 2 and 4) have had pesticide concentrations greater than 1 μg/L (Table 4). However, in the 2022 survey, only one well had pesticide concentrations greater than 1 μg/L. In six of the nine surveys, one pesticide was detected at a concentration equal to or greater than the MAV, with the other three surveys having no pesticides detected at a concentration greater than the MAV (Table 5). As these surveys were focused on shallow unconfined groundwater systems, which are most at risk of pesticide contamination, most groundwater in New Zealand should be considered safe to drink with respect to pesticides. Overall, our data from the 2022 national groundwater survey indicate a decrease in pesticide concentrations and total number of detections relative to previous surveys.

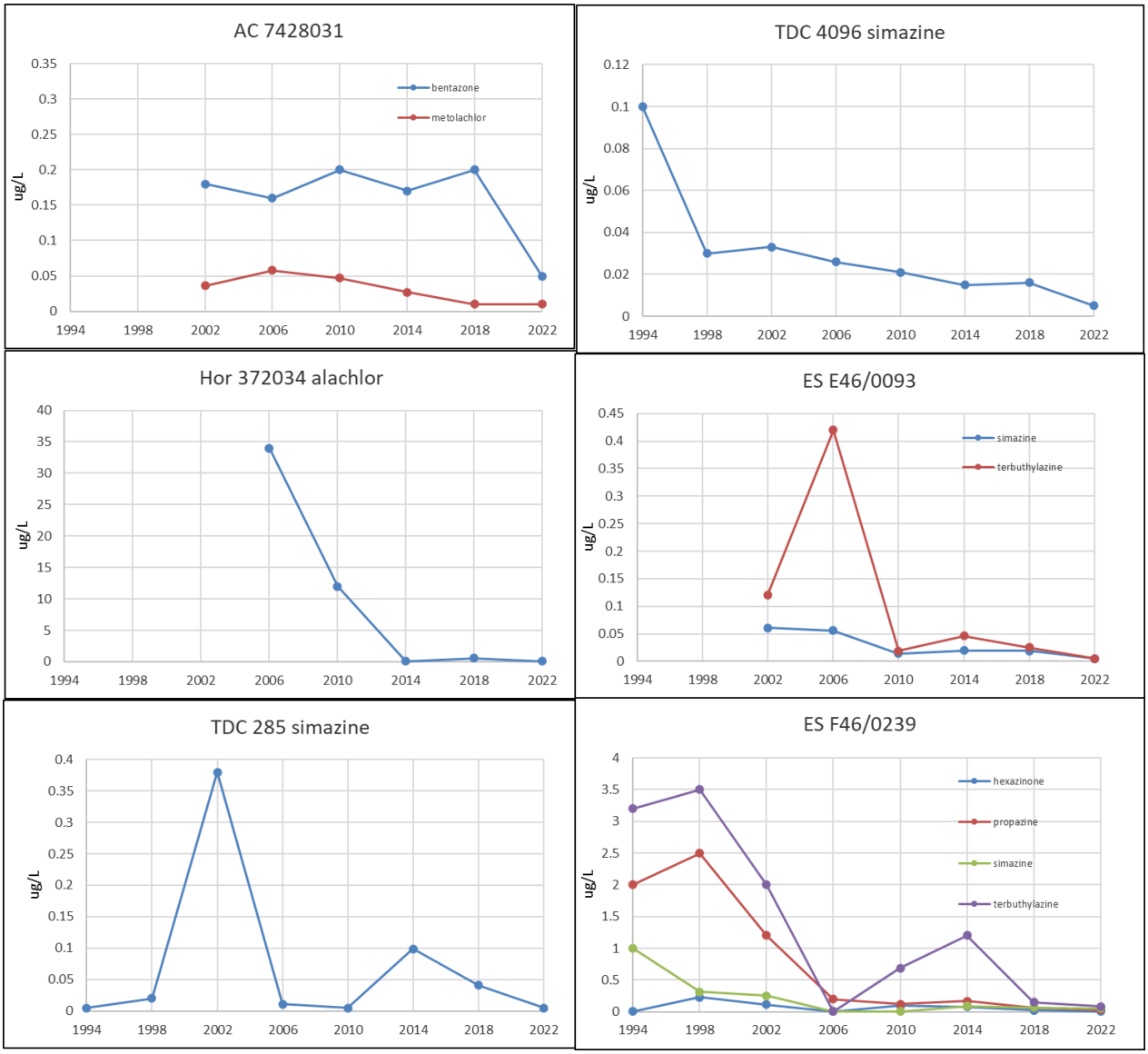

FIGURE 2: Temporal variation of pesticides in selected wells across multiple surveys.

Note: Values < DL have been plotted as 0.5DL

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

* Detection limits have changed over time so detection counts may not be directly comparable over time.

	Year of survey								
	1990	1994	1998	2002	2006	2010	2014	2018	2022
	Close 1993	Close 1996	Close & Rosen 2001	Close & Flintoft, 2004	Gaw et al. 2008	Close & Skinner 2012	Close & Humphries 2015	Close & Humphries 2018	This study
No. of wells in survey	82	118	95	133	163	162	165	279	184
No. of regions	6	13	15	15	14	14	13	14	15
No. of regions with pesticides detected	4	8	11	9	11	9	6	12	10
No. of pesticides detected*	7	10	22	21	19	22	21	28	16
% of wells with pesticides detected > DL = 0.1 μg/L	7%	14%	11%	9%	8%	7%	10%	8%	3%
% of wells with pesticides detected > DL = 0.01 μg/L	-	-	35%	21%	19%	24%	17%	24%	9%
No. of wells with pesticides >1 μg/L	2	3	3	3	2	3	4	3	1
No of pesticides detected > MAV	1	0	1	0	1	1	1	0	1
% of detections that were herbicides	50%	95%	92%	92%	74%	91%	86%	88%	66%
% of detections that were triazines	13%	65%	76%	67%	50%	61%	61%	71%	45%

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APPENDIX A: ESR 2022 PROCEDURES FOR SAMPLING OF PESTICIDES

National Survey of Pesticides, EOCs & PFAS in Groundwater 2022 - Sampling Procedures

To: The Regional or Unitary Authority

Thank you for participating in the National Survey of Pesticides in Groundwater 2022. The survey has occurred every four years since 1990 with this year being the 9th survey.

This document contains details of the required sampling procedures for this year's survey. This set of instructions are for councils that are also collecting samples for PFAS analysis in addition to samples for pesticides and EOC analysis. Four organisations are involved in the survey, ESR, Hill Laboratories, Northcott Research Consultants, and AsureQuality laboratories, with details of their role and what support and services you will receive from them below:

ESR:

- Management of the nationwide survey and full technical support
- Field sampling form
- Analysis of the results and a final report

Hill Laboratories *(Pesticide analysis laboratory)*

- x1 500ml amber glass sample bottle unpreserved (Org500)
- **NOTE: For all Hill Laboratories samples, there are holding time requirements that must be met. Samples must be refrigerated after collection and received at Hill's Hamilton Laboratory within 3 calendar days of collection. Samples should not arrive at the laboratory on a Friday due to sample extraction requirements.**
- Sample submission form
- Polystyrene boxes, ice packs and packing material for the return trip (i.e. bubble wrap)

Northcott Research Consultants *(Emerging Organic Contaminants (EOCs) analysis laboratory)*

- x1 4L amber glass sample bottle
- Sample submission form

- Polystyrene boxes, ice packs and packing material for the return trip (i.e. bubble wrap)

AsureQuality Laboratories *(PFAS analysis laboratory)*

- x1 250ml HDPE sample bottle unpreserved (supplied double-bagged in ziplock bags)
- Sample submission form
- Polystyrene boxes, ice packs and packing material for the return trip

GEAR LIST

- Council Health and Safety Form, first aid kit and cell phone
- Personal Protection Equipment (PPE)
- Sampling gloves (nitrile)
- Sample bottles (x5 bottles for each well)
- Chilly bins, ice packs and packing material (i.e. bubble wrap)
- Portable pump (i.e. Grundfos MP1 or SuperTwister) and power source if needed
- Courier tickets and address information for Hill Laboratories, Northcott Research Consultants Ltd, and AsureQuality.

SOME IMPORTANT THINGS TO REMEMBER WHEN SAMPLING

1. Please do not sample on a Thursday or Friday. If it is unavoidable then 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 Hill Laboratories, Northcott Research Consultants, and AsureQuality immediately via courier.
2. For PFAS sampling there needs to be 2 people in the sampling team to be able to implement a "Clean Hands/Dirty Hands" protocol. Disposable nitrile gloves have been supplied by ESR for use in collection of the PFAS samples. Note that the PFAS samples are collected in replicate. If a Blind Duplicate sample is being collected from the well, there will be a total of 4 HPDE bottles collected from the well.
3. Overalls (100% cotton and washed using water only) should be stored in plastic bags while travelling in the vehicle and put on at each site. A separate set of overalls is **not** required for each site.
4. NOTE: For all Hill Laboratory samples, there are holding time requirements that must be met. Samples must be refrigerated after collection and received at the laboratory within 3 calendar days of collection.
5. Field staff **please strictly avoid the following** on the day of sampling if sampling for EOCs or PFAS:

- Spray deodorants
- Perfume
- Insect repellent
- Smoking
- Coffee and other caffeine containing drinks such as tea, V, coke, pepsi, etc. (no drinking of these caffeine containing drinks on the day of sampling as caffeine is exuded in breath and will influence the results for nicotine and cotinine)

- Sunscreen
- Makeup/cosmetics (these products contain UV filters that are being analysed and will affect the results)

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

WELL SAMPLING PROCEDURE

1. Before putting on gloves, the sampling team removes the bags containing the gloves, 10 L bucket and the plastic groundsheet from the storage containers in which they are packed.

2. Select a flat suitable area for sampling and place groundsheet on the ground. Remove sampling equipment from the bags and place on the groundsheet. Place the decontamination equipment, and chilly bin onto the groundsheet.

3. Take the 100% cotton overalls from the plastic bag and put them on.

4. **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves. (A hint is to put on 2-3 pairs of gloves so that putting on a fresh pair of gloves (as in step 12 or if they get contaminated) only involves taking off the uppermost pair of gloves).

5. **CLEAN HANDS** labels the preserved sample bottles and places them back into the zip lock plastic bags.

6. DIRTY HANDS measures the **static water level** within the well. This information can be very important for interpreting the results. The static water level is to be taken from a known or historical council recorded measuring point (i.e. typically the top of the well casing).

> Make sure that **x3 times the casing volume of water** has been purged from the well before a sample is taken. This is to ensure that a representative sample is taken from the surrounding aquifer and not from the stagnant water within the well casing. If the well is a domestic/agricultural water supply fitted with a submersible pump, make sure the pump is running and allow it to run so that x3 well volumes are removed from the well. Take your sample as close to the well head as possible before it enters into a pressure tank or storage tank (**NEVER sample down gradient of a pressure tank or storage tank**).

7. **DIRTY HANDS** opens the tap and allows the water to run for approximately two minutes into a bucket.

8. **DIRTY HANDS** undertakes the physicochemical measurements using a multi-parameter water meter (i.e. pH, temperature, conductivity, dissolved oxygen etc) from the water collected into the bucket and records the readings and site observations. Make sure that these **readings have stabilised** before taking the sample.

9. **CLEAN HANDS** opens the sample and replicate bottles lids and collects the samples by alternately filling 25-33% of each bottle from the running tap.

10. **DIRTY HANDS** operates the tap to ensure the correct flow is maintained.

11. **CLEAN HANDS** replaces the lid on the sample bottles, returns the bottles to their inside bag, and zip-locks the bag.

12. **DIRTY HANDS** turns off the tap and places on a fresh set of gloves.

13. **CLEAN HANDS** then places the zipped bag into the outer bag held by **DIRTY HANDS**.

14. **DIRTY HANDS** zips the outer bag, places the double-bagged sample bottle into a clean chilly bin.

15. Once the PFAS samples are stored away, clearly label the glass bottles for Pesticide and EOC analyses before you get your hands or the bottles wet with the date, time and well ID number.

16. Make sure your hands are clean and once the lid is off do not touch the top of the sample bottle or the inside of the lid.

17. **Hill Laboratories bottles:** The amber glass sample bottles 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.

18. **Northcott Research Consultants bottles:** The glass 4L bottles need to be pre-rinsed twice with approximately 0.5 L of sample before filling with the collected sample. 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.

19. Make sure that you fill the correct number of bottles for each well that is sampled. If your council has opted to sample Pesticides, EOCs and PFAS for the well, there will be a total of 2 glass bottles and 2 HDPE bottles to fill.

11) Once your samples have been collected immediately store them in a chilly bin with ice packs (keep them stored at approx. 4°C) in preparation for transportation to the labs. **DO NOT FREEZE THE BOTTLES, OTHERWISE THEY WILL BREAK.**

BLIND DUPLICATES

For councils that are sampling more than 7 wells, there is an additional set of sample bottles. This is for the collection of blind duplicate samples, 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 samples as an extra sample from one of the wells at the same time as collecting the normal sample. Instructions are below:

- Pick at random which well will be chosen to provide the blind duplicate sample.
- The blind duplicate sample should be labelled the same as the well sample but the well ID number on the bottle should be **fictitious** and the time should be omitted. On the ESR sampling sheet identify the well ID number that is associated with the fictitious blind duplicate well number. **On the Hill Laboratories and the AsureQuality chain of custody forms do not indicate which sample is the blind duplicate sample.**
- For example, if you are sampling between 8 and 21 wells for pesticides then 1 blind duplicate sample is required. If you are sampling more than 21 wells then 2 blind duplicate samples are required. We will advise you regarding the number of blind duplicate samples that you should collect.
- When you are sampling the well collect the water for the sample and the blind duplicate as outlined below. This will ensure that the sample and the blind duplicate are representative of the whole sampling period when both samples are being taken.
- For the PFAS samples we are aiming to collect blind duplicate samples for 10% of the wells being sampled to provide additional quality control and assurance.

    - 250 mL HDPE bottle for the well sample
    - 250 mL HDPE bottle for the well sample (2nd bottle in ziplock bag)
    - 250 mL HDPE bottle for the Blind Duplicate

- 250 mL HDPE bottle for the Blind Duplicate (2nd bottle in ziplock bag)
- 500 mL amber glass bottle for the well sample
- 500 mL amber glass bottle for the Blind Duplicate
- 4L amber glass bottle for the well sample
- 4L amber glass bottle for the Blind Duplicate

FORMS

Please fill in the forms for each well sampled:

- **ESR Field Sampling form** (i.e. the well details and parameters). Record if there has been a blind duplicate sample taken and record the fictitious well ID number along with which well the blind duplicate belongs to.

- **Hill Laboratories Environmental sample submission form** (please place the form in a waterproof plastic bag inside the chilly bin)

- **Northcott Research Consultants Ltd sample submission form** (please place the form in a waterproof plastic bag inside the chilly bin)

- AsureQuality sample submission form (please place the form in a waterproof plastic bag inside the chilly bin)

Scan and email copies of the ESR Field Sampling forms to Laura Banasiak: laura.banasiak@esr.cri.nz, copy to Murray Close, murray.close@esr.cri.nz

COURIERING SAMPLES

The glass bottles should be packed in the chilly bins and packaging received in and couriered to Hill Laboratories and Northcott Research Consultants Ltd (addresses are provided at the end of this document). The HDPE bottles should be packed in the chilly bins and packaging received in and couriered to AsureQuality Laboratories (address provided at the end of this document).

Please advise Hill Laboratories of any breakages at mail@hill-labs.co.nz so that replacement bottles can be sent.

Please advise Northcott Research Consultants Ltd of any breakages nrcltd@hotmail.co.nz or 021 2268474 so that replacement bottles can be sent.

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.

APPENDIX B: ESR PESTICIDES SAMPLING FIELD SHEET

ESR Science for Communities He Pūtaiao, He Tāngata	**Field Sampling Form: 2022 National Survey of Pesticides, EOCs & PFAS in Groundwater** ***(please use one form per well)***	
Regional/District Council:		
Person collecting sample:		
Grid reference (NZTM):		
Council well number/ID:		
Blind Duplicate number if appropriate:		
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 volumes 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 (LOD)

Units are μg/L (ppb).

(1) Pesticide Screen			
(i) Organochlorine pesticides:		Cyfluthrin	0.00004
Aldrin	0.000005	Cyhalothrin	0.00004
alpha-BHC	0.000010	Cypermethrin	0.00008
beta-BHC	0.000010	Deltamethrin (including Tralomethrin)	0.00006
delta-BHC	0.000010	Diazinon	0.00002
gamma-BHC (Lindane)	0.000010	Dichlofluanid	0.00004
cis-Chlordane	0.000005	Dichloran	0.0002
trans-Chlordane	0.000005	Dichlorvos	0.00008
2,4'-DDD	0.000010	Difenoconazole	0.00008
4,4'-DDD	0.000010	Dimethoate	0.00008
2,4'-DDE	0.000010	Diphenylamine	0.00008
4,4'-DDE	0.000010	Diuron	0.00004
2,4'-DDT	0.000010	Fenpropimorph	0.00004
4,4'-DDT	0.000010	Fluazifop-butyl	0.00004
Total DDT Isomers	0.00006	Fluometuron	0.00004
Dieldrin	0.000005	Flusilazole	0.00004
Endosulfan I	0.000010	Fluvalinate	0.00004
Endosulfan II	0.000010	Furalaxyl	0.00002
Endosulfan sulphate	0.000010	Haloxyfop-methyl	0.00004
Endrin	0.000005	Hexaconazole	0.00004
Endrin aldehyde	0.000005	Hexazinone	0.00002
Endrin ketone	0.000010	IPBC (3-Iodo-2-propynyl-nbutylcarbamate)	0.0002
Heptachlor	0.000005	Kresoxim-methyl	0.00002
Heptachlor epoxide	0.000005	Linuron	0.00005
Hexachlorobenzene	0.00004	Malathion	0.00004
Methoxychlor	0.000005	Metalaxyl	0.00004
		Metolachlor	0.00004
(ii) OrganoNitrogen & Phosphorus pesticides:		Metribuzin	0.00004
Acetochlor	0.00004	Molinate	0.00008
Alachlor	0.00004	Myclobutanil	0.00004
Atrazine	0.00004	Naled	0.0002
Atrazine-desethyl	0.00004	Norflurazon	0.00008
Atrazine-desisopropyl	0.00008	Oxadiazon	0.00004
Azaconazole	0.00002	Oxyfluorfen	0.00002
Azinphos-methyl	0.00008	Paclobutrazol	0.00004
Benalaxyl	0.00002	Parathion-ethyl	0.00004
Bitertanol	0.00008	Parathion-methyl	0.00004
Bromacil	0.00004	Pendimethalin	0.00004
Bromopropylate	0.00004	Permethrin	0.00002
Butachlor	0.00004	Pirimicarb	0.00004
Captan	0.00008	Pirimiphos-methyl	0.00004
Carbaryl	0.00004	Prochloraz	0.0002
Carbofenothion	0.00004	Procymidone	0.00004
Carbofuran	0.00004	Prometryn	0.00002
Chlorfluazuron	0.00004	Propachlor	0.00004
Chlorothalonil	0.00004	Propanil	0.0002
Chlorpyrifos	0.00004	Propazine	0.00002
Chlorpyrifos-methyl	0.00004	Propiconazole	0.00004
Chlortoluron	0.00008		
Cyanazine	0.00004		

Pyriproxyfen	0.00004	Chlorpropham	0.00008
Quizalofop-ethyl	0.00004	Chlozolinate	0.00004
Simazine	0.00004	Coumaphos	0.00008
Simetryn	0.00004	Cyproconazole	0.00004
Sulfentrazone	0.0002	Cyprodinil	0.00004
TCMTB [2-(thiocyanomethylthio) benzothiazole,Busan]	0.00008	Dichlobenil	0.00004
Tebuconazole	0.00004	Dichlofenthion	0.00004
Terbacil	0.00004	Dicofol	0.0002
Terbumeton	0.00004	Dicrotophos	0.00004
Terbuthylazine	0.00002	Dinocap	0.0003
Terbuthylazine-desethyl	0.00004	EPN	0.00004
Terbutryn	0.00004	Ethion	0.00004
Thiabendazole	0.0002	Etrimfos	0.00004
Thiobencarb	0.00004	Famphur	0.00004
Tolylfluanid	0.00002	Fenarimol	0.00004
Triazophos	0.00004	Fenitrothion	0.00004
Trifluralin	0.00004	Fenpropathrin	0.00004
Vinclozolin	0.00004	Fensulfothion	0.00004
		Fenvalerate (including Esfenvalerate)	0.00004
(iii) Acid Herbicides:		Folpet	0.00008
Acifluorfen	0.0004	Hexythiazox	0.0002
Bentazone	0.0004	Imazalil	0.0002
Bromoxynil	0.0004	Indoxacarb	0.00004
Clopyralid	0.0004	Iodofenphos	0.00004
2,4-Dichlorophenoxyacetic acid (24D)	0.0004	Isazophos	0.00004
		Isofenphos	0.00002
2,4-Dichlorophenoxybutyric acid (24DB)	0.0004	Leptophos	0.00004
		Methacrifos	0.00004
Dicamba	0.0004	Methidathion	0.00004
Dichlorprop	0.0004	Methiocarb	0.00004
Haloxyfop	0.0004	Mevinphos	0.00008
2-methyl-4-chlorophenoxyacetic acid (MCPA)	0.0004	Nitrofen	0.00008
		Nitrothal-isopropyl	0.00004
2-methyl-4-chlorophenoxybutanoic acid (MCPB)	0.0004	Oxychlordane	0.00002
		Penconazole	0.00004
Mecoprop	0.0004	Phosmet	0.00004
Oryzalin	0.0006	Phosphamidon	0.00004
2,3,4,6-Tetrachlorophenol (TCP)	0.0004	Propetamphos	0.00006
		Propham	0.00004
2,4,5-Trichlorophenoxypropionic acid (245TP, Fenoprop, Silvex)	0.0004	Prothiofos	0.00004
		Pyrazophos	0.00004
Fluroxypyr	0.0004	Pyrifenox	0.00004
2,4,5-Trichlorophenoxyacetic acid (245T)	0.0004	Pyrimethanil	0.00004
		Quintozene	0.00008
Pentachlorophenol (PCP)	0.0004	Sulfotep	0.00004
Picloram	0.0004	Tebufenpyrad	0.00002
Quizalofop	0.0004	Tetrachlorvinphos	0.00004
Triclopyr	0.0004	Triadimefon	0.00004
(iv) Multiresidue Extra Pesticides:			
Bendiocarb	0.00004		
Benodanil	0.00008		
Bifenthrin	0.00002		
Bromophos-ethyl	0.00004		
Bupirimate	0.00004		
Buprofezin	0.00004		
Captafol	0.0002		
Carbofenothion	0.00004		
Chlorfenvinphos	0.00004		

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