# National Survey of Pesticides and Emerging Organic Contaminants (EOCs) in Groundwater 2018

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# EXECUTIVE SUMMARY

In 2018 ESR coordinated a survey of pesticides in groundwater throughout New Zealand. The survey has been completed every four years since 1990 with 2018 being the eighth consecutive survey. Regional and Unitary Authorities carried out the well sampling and the 2018 survey was the first time that glyphosate, glufosinate and their metabolites, and a suite of Emerging Organic Contaminants (EOCs) were included. The pesticide and glyphosate analyses were carried out by AsureQuality and samples were analysed for acidic herbicides and a suite of organochlorine, organophosphorus and organonitrogen pesticides, and for glyphosate and three of its metabolites. The EOCs were analysed by Northcott Research Consultants Ltd. 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 based on 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. If possible, where a well had been sampled during previous surveys, it was included in the current survey to give a temporal comparison. The majority of the selected wells were from unconfined aquifers, recognising that shallower, unconfined aquifers would be more at risk than deeper aquifers.

Two regional councils provided pesticide results that were sampled outside of this survey. The Waikato Regional Council provided results for an additional 41 wells that had been sampled as part of a regional survey in December 2016. Environment Canterbury also provided results for an additional 71 wells that had been sampled in late 2018. Both these datasets have been included in this report to give a national perspective.

There were a total of 279 wells sampled and analysed for the pesticide suites, including the 41 wells from Waikato Regional Council and the additional 71 wells from Environment Canterbury. There were 68 wells (24.4%) with pesticides detected, with 28 of these wells having two or more pesticides detected. The maximum number of pesticides detected in one well was six. Herbicides were the most frequently detected pesticide group with 98 detections (88%) of 17 different herbicides and their metabolites. There were three pesticide detections exceeding 1 μg/L with none of the sampled wells exceeding the Maximum Acceptable Value (MAV) for drinking water. The highest detection as a percentage of the MAV was dieldrin, which was detected at a concentration of 0.025 μg/L that was 62.5% of the MAV of 0.04 μg/L

(Ministry of Health 2018). Most pesticide detections were less than 0.5% of the MAV. Note that μg/L = mg $m^{-3}$ = ppb.

A total of 135 wells were analysed for glyphosate, glufosinate and their principal metabolites. There was only one detection of glyphosate at a concentration of 2.1 μg/L. This well showed evidence of poor well-head protection and the contamination likely came from containers that were stored near the well. No MAV for glyphosate in drinking water has been set in New Zealand. New Zealand follows WHO guidelines when setting its MAVs but there is currently no WHO guideline; however, WHO does have a Health Based Value for glyphosate of 900 μg/L (WHO 2017). The detected level of 2.1 μg/L is far below this value.

121 wells were sampled and analysed for a suite of EOCs, with a total of 227 EOCs detected in the 85 wells (70%). All regions that had samples analysed for EOCs had at least three wells with EOCs present. There were 29 different EOCs in the analytical suite and 25 different EOCs were detected in at least one well with the maximum number of EOCs detected in a single well being 13. Most EOCs are used extensively by people or are produced by people (eg estrogenic steroid hormones) and most do not have significant human toxicity when used under normal conditions. There are no MAVs for drinking water associated with these EOCs. However, some of these compounds have shown some endocrine disrupting effects in surface waters and the main concerns with these EOCs are environmental or ecological impacts. There are no or very few guideline values for EOCs regarding ecological impacts as the relevant studies are sparse. Some EOCs, such as sucralose and caffeine, can act as tracers of the presence of human activities or wastewater impacts in the groundwater system.

The most commonly detected EOC was bisphenol-A (BPA) that was detected in 40 wells, with the UV filter compounds, OMC and BP3 next most common with 33 and 24 detections, respectively. Sucralose, an artificial sweetener, was next most common with 18 detections. The highest concentration measured was 655 ng/L for sucralose.

These results indicate that EOCs, sourced from either animal or human effluents/activities, are making their way into shallow groundwater systems and can be detected at low concentrations. Currently there is a lack of knowledge of the fate and effects of many EOCs and whether the levels measured in this study are likely to have impacts for ecological systems. We recommend that monitoring of EOCs in groundwater resources is extended and that research is carried out to quantify the likely risks for the EOCs most frequently detected in this study.

There is limited discussion in this report about temporal variation of pesticides in groundwater with time, the correlation of pesticide detections with parameters such as well depth and groundwater chemistry, and the occurrence of different classes of EOCs that were detected in the groundwater survey. It was felt that it was more important to provide the actual results of the survey of pesticide and EOC concentrations 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.

# 1. INTRODUCTION

When this series of surveys began in 1990, groundwater was, and it continues to be, an important source of drinking water in New Zealand. Around 40% of the community drinking water supplies around New Zealand utilise groundwater (Davies 2001). In addition, many individual rural households rely on groundwater for their drinking water needs. 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 (MfE & StatsNZ, 2019).

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, Emerging Organic Contaminants (EOCs) and in particular if glyphosate is reaching the groundwater systems. In an increasingly globalised world the consumers of our export products value and demand traceability as well as ensuring that our agricultural systems are environmentally responsible (Ministry for Primary Industries, 2019). 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 active ingredient/ha) followed by arable, forestry and pastoral sectors (Manktelow et al., 2005).

Glyphosate (common name Roundup) is widely used in New Zealand and other countries as a general purpose herbicide. It binds to soil and is readily degraded and therefore is not expected to leach to groundwater. It is commonly found in surface waters. However, a recent study in the USA (Battaglin et al., 2014) compiled data from a range of sources including groundwater, that had been analysed using an improved analytical method with a reporting limit of 0.02 μg/L (Note that μg/L = mg $m^{-3}$ = ppb). They found low levels of glyphosate in 5.8% of samples from groundwater and similarly low levels of its metabolite, aminomethylphosphonic acid (AMPA) in 14.3% of groundwater samples. In early 2017 Environment Waikato analysed 40 wells for glyphosate and AMPA (Hadfield, 2017). The samples were analysed at AsureQuality with a detection limit of 1 μg/L. No glyphosate was detected in any of the samples but AMPA was detected in one well at a concentration of 1.9 μg/L. There is no Maximum Acceptable Value (MAV) for glyphosate or its metabolites with respect to drinking water and the US Environmental Protection Agency has stated that glyphosate is no more than slightly toxic to birds, fish, and aquatic invertebrates and exhibits low oral and dermal toxicity to humans (USEPA 1993).

Glyphosate and AMPA was analysed using a separate extraction and LC-MS/MS detection. Glufosinate and one of its metabolites, MMPA, are also detected using this method. Glufosinate is a naturally occurring broad-spectrum systemic herbicide produced by several species of Streptomyces soil bacteria. The compound irreversibly inhibits glutamine synthetase, an enzyme necessary for the production of glutamine and for ammonia detoxification, giving it antibacterial, antifungal and herbicidal properties. Application of glufosinate to plants leads to reduced glutamine and elevated ammonia levels in tissues, halting photosynthesis, resulting in plant death (Wikipedia, accessed June 2017). While their spectrum of control is comparable for several weed species, glufosinate tends to be more effective on annual broadleaf weeds than annual grasses, while glyphosate is more effective on grasses. Glufosinate is a "contact" herbicide, in contrast to glyphosate being extensively translocated within the plant.

For the first time EOCs have been included to determine their prevalence in groundwater. There are a wide range of organic compounds that are used widely in the domestic, industrial and agricultural sectors. Some of these compounds have been detected in freshwater systems and are known as emerging contaminants. Some of these compounds are more likely to be transported into surface water systems rather than groundwater depending on their mobility and persistence characteristics. EOCs include personal care products, for example, shampoos, insect repellants, and sun screens, anti-biotics and other pharmaceuticals, estrogens, recreational compounds such as caffeine and nicotine, industrial compounds and compounds from plastic packaging (bisphenol A). There are a few studies on their leaching properties that have been carried out for some of these compounds and there is work being carried out on their presence in wastewaters. However, we know little about most of their transport characteristics and almost nothing about their occurrence in New Zealand groundwater systems. Two regional studies have been recently carried out looking for EOCs in groundwater. A MSc study looked for a suite of 25 EOCs in Canterbury groundwater (van der Krogt, 2018) and found at least one EOC in 26 out of 33 samples taken from 18 wells. The five most commonly detected EOCs were BPA, octyl phenol (industrial compounds), BP3 (UV filter), methyl paraben and propyl paraben (preservatives). A regional study has been carried out in the Waikato region using a wide-screening approach (723 compounds) for EOCs in groundwater (Moreau et al., 2019). They sampled 61 wells and found EOCs in 91% of the baseline sites (51 wells) in 2018. Most of the EOCs detected (75%) were pesticides, with pharmaceutical and industrial chemicals being the next most common groups.

National surveys of pesticides in groundwater have been carried out at four yearly intervals since 1990 with this current survey being the eighth 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 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 Humphries (2015), 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; Taranaki Regional Council, 1995; Hadfield, 2013).

The seventh national survey in 2014 sampled 165 wells from regions throughout New Zealand, including the additional 40 wells sampled by Waikato Regional Council (Close and Humphries, 2016). There were 28 wells (17%) with pesticides detected, with 10 wells having two or more pesticides detected. There were one or more wells with pesticides detected in six of the 13 regions. Pesticides were not detected in wells from the Hawke's Bay, Taranaki, Horizons (Manawatu-Wanganui), Greater Wellington, Marlborough, Canterbury and Otago regions. There was one well in the 2014 survey with a pesticide concentration greater than the MAV for drinking water (Ministry of Health, 2008). There were a total of 21 different pesticides detected in the 2014 survey. Herbicides were the most common pesticide group detected followed by insecticides and fungicides. There were a total of 51 pesticide detections and of these detections, 44 (86%) were herbicides. There were 31 detections of triazine herbicides. Levels of only four of the 51 pesticide detections exceeded 1 μg/L.

This report gives the results from the eighth national survey. The sampling for this survey was carried out in late 2018, mostly between September and November. The Waikato Regional council provided results for an additional 41 wells that had been sampled in late 2016 as part of their regional survey. Environment Canterbury also provided additional results for 71 wells that had been sampled in late 2018. Both these datasets have been included in this report to give a national perspective.

There is limited discussion in this report about temporal variation of pesticides in groundwater with time, the correlation of pesticide detections with parameters such as well depth and groundwater chemistry, and the occurrence of different classes of EOCs that were detected in the groundwater survey. It was felt that it was more important to provide the actual results of the survey of pesticide and EOC concentrations 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. 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 2018 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.

Fourteen of the Regional and Unitary Authorities with groundwater management responsibilities participated in the 2018 survey. The West Coast Regional Council did not participate in the 2018 survey. The Waikato Regional Council carried out their own regional survey in 2016 as did Environment Canterbury in late 2018. The results from 41 wells from the Waikato Region and the additional 71 wells from the Canterbury region were included in this survey (Figure 1). 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.

A total of 121 wells were selected and sampled from 12 regions and analysed for a suite of EOCs. The Waikato Regional Council had participated in a regional survey of EOCs earlier in 2018 (Moreau et al., 2019) so did not take part in this survey. The distribution of wells sampled for EOCs in shown in Figure 2.

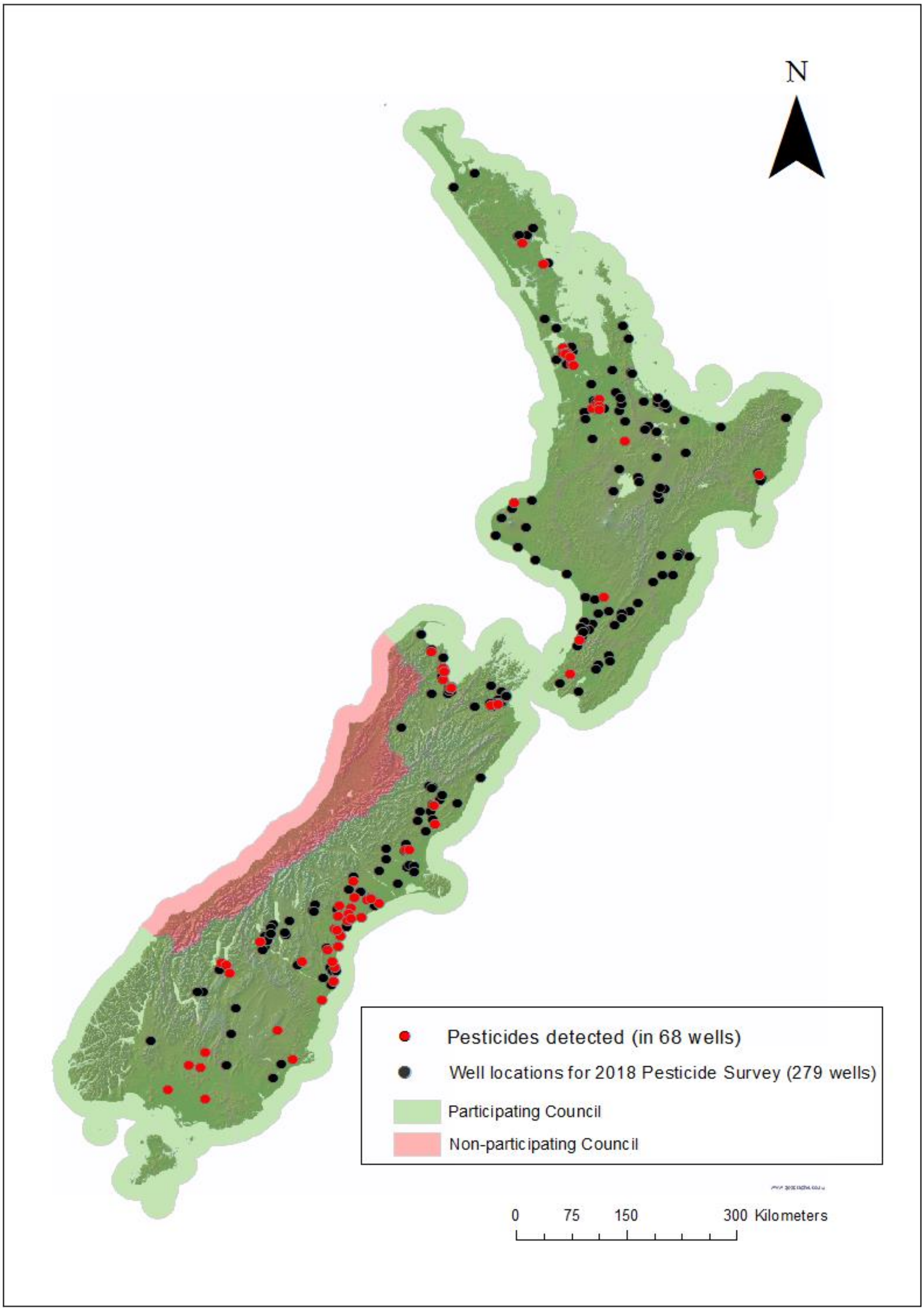

**Figure 1: Regions and sampling locations for the 2018 survey of pesticides in groundwater.**

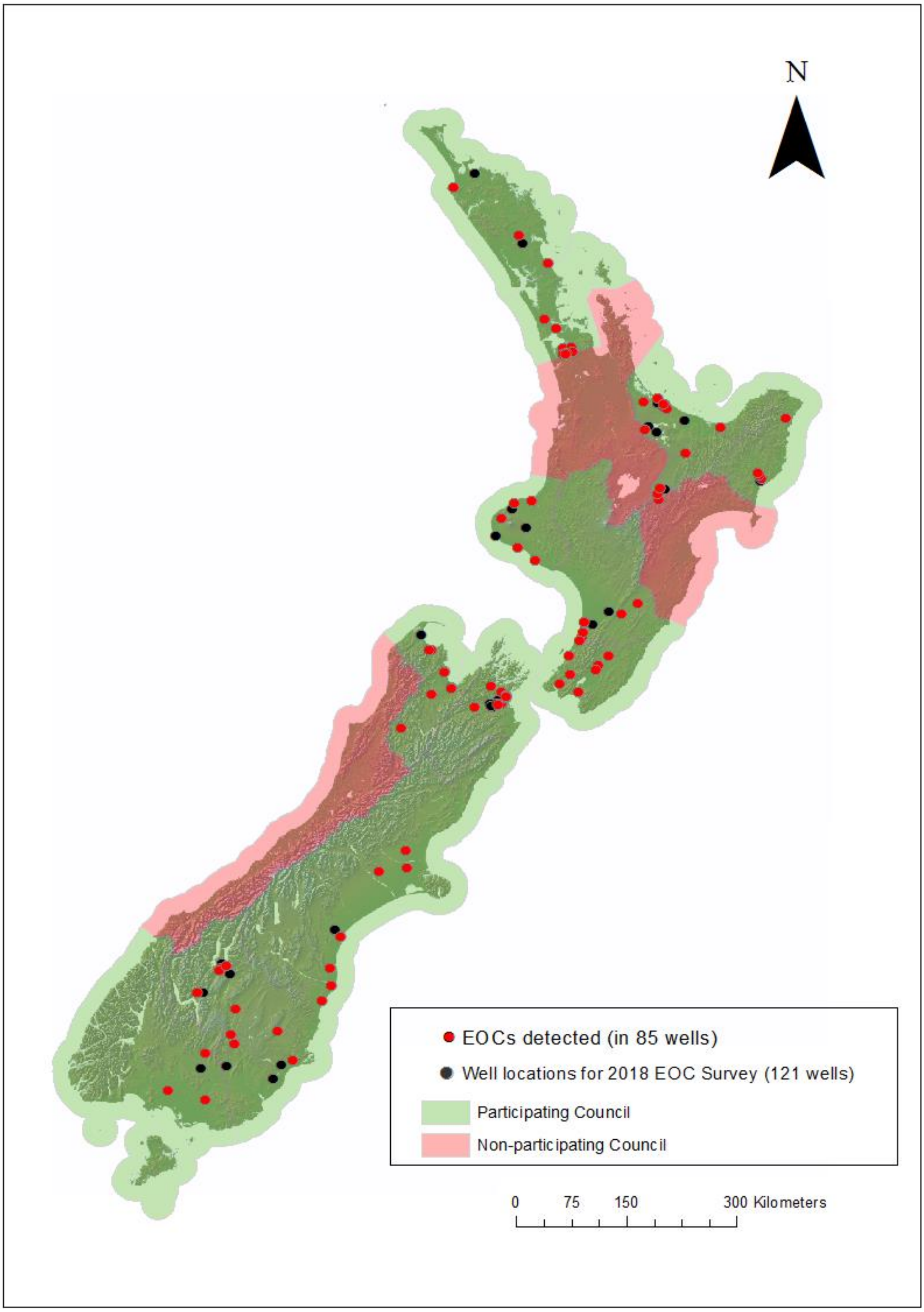

**Figure 2: Regions and sampling locations for the 2018 survey of EOCs in groundwater.**

## 2.2 SAMPLING

Samples were collected according to the ESR procedures for sampling pesticides and EOCs (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). Bottles for pesticide and glyphosate analysis were supplied by AsureQuality and bottles for EOC analysis were supplied by Northcott Research Consultants Ltd.

## 2.3 LABORATORY ANALYSIS

### 2.3.1 Pesticide analysis

All samples for the pesticide analysis suites 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 7% 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, 2010, and 2014 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 and Environment Canterbury were analysed by Hill Laboratories which had similar methods but slightly lower detection limits.

### 2.3.2 Glyphosate and Glufosinate analysis

The samples for the pesticide analysis suites were sent to AsureQuality in Wellington and analysed for glyphosate, glufosinate and their principal metabolites, AMPA (from glyphosate) and MPPA (from glufosinate). The analysis used liquid chromatography with a tandem mass spectrometry detector (LC-MS/MS). The pesticides assayed and their detection limits are provided in Appendix C.

### 2.3.3 Emerging Organic Contaminants (EOCs)

Upon receipt by NRC Ltd at Plant and Food Research in Hamilton the bottles of groundwater samples were checked for damage, correlated against the supplied inventory and sampling details, and immediately transferred into a walk-in chiller and stored in the dark at 4°C.

Particular care was taken to avoid potential contamination of the groundwater and Quality Assurance (QA) samples with EOCs during all steps of the preparatory, extraction and purification process. Laboratory personnel undertaking these tasks were required to avoid drinking coffee and tea for a period of 16 hours proceeding, and for the duration when working with the samples. These same personnel were similarly asked to refrain from applying cosmetics and skin moisturisers and were required to where nitrile gloves when handling the samples.

#### Sample preparation

The bottles of groundwater samples were removed from storage at 4°C and the pH adjusted to <2.5 by the addition of 6M sulphuric acid. The aqueous samples were filtered through a glass microfiber filter (47 mm, Labservice) topped with diatomaceous earth filter aid media (Hyflo SuperCel) to remove particulate material. The sample filtrate was collected in pre-cleaned 2L Glass Schott bottles.

The filtered groundwater samples extracted for the analysis of EOCs excluding pharmaceutical compounds were spiked with a solution of carbon-13 labelled analogues of target EOCs for use as surrogate recovery compounds. Filtered groundwater samples being extracted for pharmaceuticals were spiked with the acidic herbicides dichlorprop, flamprop and MCPB, and the plant growth regulator naphthalene acetic acid for use as surrogate recovery compounds

### Sample extraction and purification

Emerging organic contaminants (EOCs) in the filtered groundwater samples (dissolved phase) were extracted by solid-phase extraction (SPE). Neutral and phenolic EOCs were extracted by SPE using Waters Oasis HLB cartridges and pharmaceuticals using Waters Oasis MCX cartridges. The EOC sample extract was split into two equal portions- one for analysis of neutral EOCs and the other for polar EOCs requiring chemical derivatisation for analysis by gas chromatography mass-spectrometry (GCMS). The portions of split sample extract were transferred into vials, capped and sealed and stored under refrigeration for analysis. One half of the EOC sample extract was exchanged into acetone, deuterated internal standards added, and transferred into GC vials for the analysis of non-polar neutral EOCs.

### Sample extract derivatisation

A solution of deuterated polar internal standards was added to the second portion of the EOC sample extracts and the polar EOCs (steroid hormones, phenolic antimicrobials, paraben preservatives, UV filters, succralose) were derivatised to their respective trimethylsilyl ethers using a catalytic mixture of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), ammonium iodide, and mercaptoethanol.

An internal standard mixed solution containing deuterated monocarboxylic phthalate acid esters and ibuprofen-d3 was added to the pharmaceutical sample extracts which were evaporated to dryness and converted to their respective tertiary-butyl dimethyl silyl esters by reaction with N-tert-butyldimethyl- silyl-N-methyltrifluoroacetamide (MTBSTFA) with 1% t-butyldimethylsilyl chloride (TBDMSCl).

### Instrumental analysis of EOCs

The analysis of the different classes of EOCs required the use of different GCMS instruments and instrumental analysis methods. Paraben preservatives, phenolic antimicrobials and UV filters were analysed using an Agilent 6890N gas chromatograph coupled to a 5975 mass spectrometer operating in single ion monitoring mode. Quantitation of target EOCs was achieved by internal standard quantitation using Agilent Chemstation MS software. Steroid hormones, neutral EOCs, BPA and acidic pharmaceuticals were analysed using an Agilent 7000 series triple quadrupole GCMS operating in MS/MS mode. Quantitation of target EOCs was achieved by internal standard quantitation using Agilent Mass Hunter Quantitative Analysis software.

### Quality assurance procedures

Each individual sample was spiked with a mixed solution of surrogate recovery standards at a concentration of 50 ng/L (parts per trillion) and 25 ng/L, respectively for neutral and polar EOCs and pharmaceuticals. Quality Assurance (QA) samples incorporated into the analysis of ground water samples included blank SPE cartridges, Milli-Q water blank samples, Milli-Q water samples spiked with target analytes. The QA Milli-Q water spike samples were spiked with mixtures of the target analytes at an equivalent concentration of 50 ng/L and 25 ng/L respectively for neutral and polar EOCs and pharmaceuticals.

Comparative standards, comprising the same volume of each individual QA spike solution incorporated into each batch of extracted samples, were prepared by dispensing aliquots of the individual QA spike solutions into labelled vials at the same time they were added to each batch of samples. The percentage recovery of surrogate and target compound spikes was determined by directly comparing the concentration of analytes measured in QA and sediment samples against that measured in the corresponding comparative standard(s).

### Background concentration of EOCs

Residues of three EOCs, namely Bisphenol-A (BPA), octinoxate and oxybenzone were detected in SPE cartridge blanks and Milli-Q water blanks at mean equivalent concentrations of 2.33, 2.15 and 2.19 ng/L respectively. No residues of pharmaceutical compounds were detected in any of the QA blank samples.

The results reported for BPA, octinoxate and oxybenzone were corrected against the blank concentration measured in each batch of extracted samples.

### Method detection limits

Method detection limits (MDLs) for individual EOCs were calculated using a signal-to-noise ratio of 3:1 and by assessment of the mean concentration of target EOCs detected in the QA blank samples. The higher of these two values was adopted as the MDL for each individual compound. The resulting confirmed MDLs obtained for the target analytes are listed in Table 7. The final MDLs obtained for seven target EOCs were higher than initially estimated. The final MDLs obtained for bisphenol-A, octinoxate and oxybenzone increased because of their presence as background contaminants in the QA SPE and Milli-Q water blanks. The MDLs for the stimulants caffeine, 1,7-dimethylxanthine, nicotine and cotinine increased above initial estimates due to the relatively low intensity of their respective mass ions combined with increased background contributions of these low mass ions impacting on the sensitivity of mass detection.

# 3. RESULTS

A total of 167 wells were sampled and the groundwater samples sent to AsureQuality in Wellington. The Waikato Regional Council provided results for an additional 41 wells that had been sampled as part of their regional survey in December 2016 and were sent to Hill Laboratories. Environment Canterbury also provided results for an additional 71 wells that were sampled as part of a regional survey and were analysed by Hill Laboratories. Both these additional datasets were included in this report to give a national perspective, giving a total of 279 wells for the pesticide suites. Glyphosate, Glufosinate and their metabolites were analysed on samples from 135 wells and the EOC suite was analysed on samples from 121 wells.

## 3.1 ASSESSMENT OF SURVEY METHODOLOGY

### 3.1.1 Pesticides

Blind duplicate samples from 12 wells (7 %) 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 very good agreement for 11 of the 12 duplicate analyses (Table 1). Well 7428105 from Auckland had 2,4-DB detected in one duplicate and bentazone detected in the other duplicate sample, both at concentrations just above the detection limits. All of the blind duplicate samples had no detections for Glyphosate as there was only one detection from all the sampled wells and that particular well was not sampled as one of the blind duplicates.

### 3.1.2 Emerging Organic Contaminants

Blind duplicate samples from 5 wells (4%) were submitted to the analytical laboratory as an additional quality control measure. There was very good agreement for four of the five duplicate analyses (Table 2), with well GND2515 having 9 different EOCs detected in both duplicates with reasonably similar concentrations in each sample. There were differences in the samples from well 362397, with one sample having detections of caffeine and octinoxate (OMC) and the other sample having no detections of any EOC.

**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 | 1355 (Blind Duplicate) | | ND (ND) |
| Auckland Council | 7428105 (Blind Duplicate) | 2,4-DB<br>Bentazone | 0.11 (<0.1)<br><0.1 (0.11) |
| Bay of Plenty Regional Council | 1001289 (Blind Duplicate) | | ND (ND) |
| | 1001290 (Blind Duplicate) | | ND (ND) |
| Hawkes Bay Regional Council | 16095 (Blind Duplicate) | | ND (ND) |
| Taranaki Regional Council | GND2515 (Blind Duplicate) | Terbuthylazine | 0.028 (0.030) |
| Horizons Regional Council | 315027 (Blind Duplicate) | Bentazone | 0.13 (0.14) |
| | 338005 (Blind Duplicate) | | ND (ND) |
| | 372136 (Blind Duplicate) | | ND (ND) |
| Tasman District Council | 524 (Blind Duplicate) | Bentazone | 0.35 (0.36) |
| | 6342 (Blind Duplicate) | | ND (ND) |
| Otago Regional Council | G41/0045 (Blind Duplicate) | | ND (ND) |

## Surrogate standard recovery for EOCs

The results obtained from quality assurance procedures met or exceeded accepted standards for laboratories undertaking trace analysis of organic contaminants and pesticides.

The recovery of surrogate standards spiked into all of the analysed ground water, and Milli-Q water blank and spiked QA fell within the accepted range of 70% to 130 % (Table 3). The relatively narrow 95% confidence intervals for the mean recovery of surrogate standards reflects in part the high total number of ground water and QA samples from which this data was derived (N = 147). Regardless, the recovery data obtained of the surrogate spike compounds demonstrates good overall reproducibility of the sample extraction and analysis method.

**Table 2: Comparison of Blind Duplicate samples for EOC suite.**

(ND, not detected)

| Council | Well ID (Blind duplicate) | Pesticide Concentration (ng/L) | |
|---|---|---|---|
| Horizons Regional Council | 362397 (Blind Duplicate) | Caffeine | ND (3.12) |
| | | Octinoxate | ND (13.2) |
| Taranaki Regional Council | GND2515 (Blind Duplicate) | Bisphenol-A | 5.05 (5.55) |
| | | Caffeine | 7.08 (4.39) |
| | | Carbamazepine | 73.1 (72.1) |
| | | Diclofenac | 89 (107) |
| | | 4-methylbenzylidene camphor | 11.8 (12.7) |
| | | Octinoxate | 7.85 (10.7) |
| | | o-phenylphenol | 7.31 (4.93) |
| | | Oxybenzone | 26.5 (24.3) |
| | | Sucralose | 266 (1043) |
| Otago Regional Council | F40/0045 (Blind Duplicate) | Bisphenol-A | 55.1 (42.6) |

**Table 3: Recovery of surrogate standards spiked into groundwater and quality assurance samples.**

| Recovery compound | 95% confidence interval for mean % recovery [A] | Range (min-max) |
|---|---|---|
| Bisphenol-A-13C6 | 89.5 ± 1.7 | 78.5 - 102.7 |
| Butyl paraben-13C6 | 102.5± 2.2 | 75.4 – 124.1 |
| Caffeine-13C3 | 76.6 ± 2.5 | 70.3 – 123.1 |
| 17β-estradiol-13C6 | 92.5 ± 1.7 | 75.6 – 122.7 |
| Estrone-13C6 | 92.6 ± 1.9 | 74.6 – 107.3 |
| Methyl paraben-13C6 | 89.5 ± 1.5 | 82.8 – 104.8 |
| 4n-nonylphenol-13C6 | 82.0 ± 1.5 | 71.2- 90.5 |
| Oxybenzone-13C6 | 112.6 ± 6.1 | 86.5 – 127.2 |
| o-phenylphenol-13C6 | 76.9 ± 2.1 | 70.6 – 110.8 |
| Triclosan-13C6 | 96.2 ± 2.1 | 86.5 – 120.8 |
| | | |
| Dichlorprop[B] | 108.9 ± 1.8 | 89.9 – 115.3 |
| Flamprop[B] | 97.1 ± 2.8 | 72.2 – 123.9 |
| MCPB[B] | 117 ± 0.8 | 99.0 – 127.0 |
| NAA[BC] | 98.2 ± 0.7 | 83.9- 106.1 |

[A] N=147; [B]surrogate for acidic pharmaceuticals; [C]napthalene acetic acid

### Target analyte recovery for EOCs

The mean percentage recovery of target analytes spiked into the Quality Assurance Mill-Q water spike recovery samples similarly largely fell within the accepted range of 70% to 130 %. Recoveries of <70% were occasionally obtained for a limited number of target EOCs, principally the more volatile chemicals (Caffeine, nicotine etc) and the highly polar and water soluble sucralose. Despite the occasional recovery of <70% being obtained the corresponding mean recovery for these EOCs were above 70%. Overall, the mean and 95% confidence intervals calculated for the recovery of target EOCs from the QA spike samples demonstrated an acceptable and consistent recovery.

The combined results obtained for the recovery of surrogate compounds and target analyte EOCs from the individual analysed samples and quality assurance spike samples demonstrates the robustness of the employed methodologies.

## 3.2 SURVEY RESULTS

### 3.2.1 Pesticides

With the addition of the 41 wells from the Waikato Regional Council and the 71 additional wells from Environment Canterbury, there were a total of 279 wells sampled with 68 wells (24.4%) having pesticides detected. The additional wells from Waikato had the same detection frequency (24.4%) while the additional wells from Canterbury had a slightly higher detection frequency (32%) compared to the national detection frequency. There were one or more wells with pesticides detected in 6 of the 13 participating regions (Table 4), with regional detection rates varying from 0 to 83% (note that the higher rates were for a small number of sampled wells). Pesticides were not detected in sampled wells from Bay of Plenty (25 wells) and Hawkes Bay (14 wells). In 28 of these wells (10%) two or more pesticides were detected (Table 4). The maximum number of pesticides detected in one well was six. Twenty-five different pesticides, including metabolites, were detected in the sampled wells (Table 5).

Herbicides were the most frequently detected pesticide group with 98 detections (88%) of 17 different herbicides and their metabolites, with seven insecticides and one fungicide detected in the sampled wells. There were 80 detections (71%) of triazine herbicides with terbuthylazine being the most frequently detected pesticide (36 detections). There were three pesticide detections exceeding 1 μg/L with none of the sampled wells exceeding the MAV for drinking water. The highest detection as a percentage of the MAV was dieldrin which was detected at a concentration of 0.025 μg/L which was 62.5% of the MAV of 0.04 μg/L (Ministry of Health 2018). The next highest detections relative to the MAV were for total atrazine and metabolites at 16.5% of the MAV, hydroxyatrazine (another atrazine metabolite) at 11% of MAV assuming the same MAV as for atrazine, then terbacil at 9.5% of the MAV. The remainder of pesticide detections were less than 5% of the MAV.

There was only one detection of glyphosate in the 135 wells (0.7%) that were sampled. This well also had a range of other pesticides detected in the sample including atrazine and its metabolites, diazinon and DDT. This well is a reasonably shallow, large diameter well (depth = 20 m; diameter = 1.0 m). It has been sampled on four previous surveys and has had pesticides detected for three of those surveys. On investigation in 2019 it was found that the condition of this wellhead was poor and there were chemical containers stored close to the well, meaning that ingress of chemicals from the surface was a high possibility.

No MAV for glyphosate in drinking water has been set in New Zealand. New Zealand follows WHO guidelines when setting its MAVs but there is currently no WHO guideline; however, WHO does have a Health Based Value for glyphosate of 900 μg/L (WHO 2017). The detected level of 2.1 μg/L is far below this value.

The range of concentrations found, MAV values, groundwater ubiquity scores (GUS), and the mobility and degradation characteristics of each pesticide are given in Table 5. The mobility and degradation values come from the National Pesticide Information Centre, which hosts several pesticide properties databases (http://npic.orst.edu/) as at September 2019, unless otherwise noted. The selected value listed in this database, plus the range of values in the literature, are given in Table 5. 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:

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

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 4: Summary of results from the 2018 pesticides in groundwater survey detailing 112 detections in 68 wells out of a total of 279 wells sampled.**

Note that µg/L = mg $m^{-3}$ = ppb. DET = desethyl terbuthylazine=terbuthylazine desethyl; DEA = desethyl atrazine = atrazine-desethyl; and DIA = desisopropyl atrazine = atrazine-desisopropyl; p,p'-DDT = 4,4'-DDT.

| Council Region (# detections / # wells sampled) | Well ID | Pesticide Detected | Concentration (µg/L) |
|---|---|---|---|
| Northland Regional Council (2/11) | 7244 | Hexazinone | 0.05 |
| | 9851 | Terbuthylazine | 0.041 |
| Auckland Regional Council (4/8) | 43915 | Bentazone | 0.17 |
| | | Metolachlor | 0.025 |
| | 7419127 | Bentazone | 0.14 |
| | 7428031 | Bentazone | 0.2 |
| | 7428105 | Bentazone | 0.08 |
| | | 2,4-DB | 0.08 |
| Waikato Regional Council (10/41) | 61-54 | Dieldrin | 0.02 |
| | | Propazine | 0.04 |
| | 61-93 | Metolachlor | 0.05 |
| | 61-113 | Metalaxyl | 0.06 |
| | | Propazine | 0.03 |
| | | Terbuthylazine | 0.03 |
| | 61-230 | Dieldrin | 0.025 |
| | 62-5 | DET | 0.05 |
| | 67-4 | Hexazinone | 0.11 |
| | 69-19 | Terbuthylazine | 0.02 |
| | 69-97 | Terbuthylazine | 0.02 |
| | 69-295 | Bromacil | 0.88 |
| | | Endosulfan II | 0.061 |
| | | Terbacil | 3.8 |
| | 70-22 | Endosulfan I | 0.016 |
| | | Endosulfan II | 0.033 |
| | | Endosulfan sulphate | 0.068 |
| | | Terbacil | 0.4 |
| | | Terbuthylazine | 0.09 |
| | | DET | 0.39 |
| Bay of Plenty Regional Council (0/25) | | | |
| Gisborne District Council (1/5) | GPF032 | 2-Hydroxyatrazine | 0.22 |
| Hawkes Bay Regional Council (0/13) | | | |
| Taranaki Regional Council (1/8) | GND2515 | Terbuthylazine | 0.029 |
| Horizons (2/20) | 315027 | Bentazone | 0.14 |

| Council Region<br>(# detections / # wells sampled) | Well ID | Pesticide Detected | Concentration (µg/L) |
|---|---|---|---|
|  | 372034 | Alachlor | 0.59 |
|  |  | Metalaxyl | 0.024 |
| Greater Wellington Regional Council (1/8) | R27/1137 | Terbuthylazine | 0.054 |
| Tasman District Council (8/22) | 285 | Simazine | 0.041 |
|  |  | Terbuthylazine | 0.011 |
|  | 524 | Bentazone | 0.36 |
|  | 3115 | Terbuthylazine | 0.031 |
|  | 4096 | Simazine | 0.016 |
|  |  | Terbuthylazine | 0.034 |
|  | 4140 | Terbuthylazine | 0.038 |
|  | 6601 | Simazine | 0.02 |
|  | 8036 | Hexazinone | 0.095 |
|  |  | Terbuthylazine | 0.014 |
|  | 23604 | Terbuthylazine | 0.018 |
| Marlborough District Council (2/19) | P28w/3069 | Terbuthylazine | 0.064 |
|  | P28w/3222 | Terbuthylazine | 0.016 |
| Environment Canterbury (26/77) | J38/0242 | Simazine | 0.019 |
|  |  | Terbuthylazine | 0.019 |
|  | K39/0033 | Simazine | 0.019 |
|  |  | Terbuthylazine | 0.17 |
|  | M35/8567 | Terbuthylazine | 0.013 |
|  | BY20/0148 | Hexazinone | 0.01 |
|  | CA15/5009 | Bromacil | 2.0 |
|  | CA17/0008 | DEA | 0.015 |
|  | CA18/0020 | Hexazinone | 0.018 |
|  | J37/0012 | Bentazone | 0.22 |
|  | J38/0004 | DET | 0.027 |
|  | J38/0169 | Terbuthylazine | 0.04 |
|  |  | DET | 0.199 |
|  |  | Simazine | 0.011 |
|  |  | DIA | 0.02 |
|  | J39/0135 | DET | 0.015 |
|  |  | Atrazine | 0.021 |
|  | J40/0286 | Terbuthylazine | 0.037 |
|  |  | DET | 0.06 |
|  |  | Hexazinone | 0.013 |
|  | J40/0333 | DEA | 0.011 |

| Council Region (# detections / # wells sampled) | Well ID | Pesticide Detected | Concentration (µg/L) |
|---|---|---|---|
| | | DET | 0.023 |
| | J41/0018 | Terbuthylazine | 0.006 |
| | | DET | 0.011 |
| | K36/0033 | Terbuthylazine | 0.35 |
| | | DET | 0.175 |
| | | 4,4'-DDE | 0.0025 |
| | | 4,4'-DDT | 0.0018 |
| | K37/0147 | Terbuthylazine | 0.019 |
| | | DET | 0.021 |
| | K37/0216 | DEA | 0.015 |
| | K38/0148 | Terbuthylazine | 0.005 |
| | K38/0404 | Atrazine | 0.011 |
| | K38/1017 | DET | 0.011 |
| | K38/2200 | Terbuthylazine | 0.005 |
| | L37/0297 | 4,4'-DDE | 0.0007 |
| | L37/0439 | DET | 0.014 |
| | | Terbuthylazine | 0.022 |
| | M35/6295 | DET | 0.027 |
| | | Terbuthylazine | 0.01 |
| | N33/0064 | DET | 0.03 |
| | | Terbuthylazine | 0.006 |
| | N33/0212 | DET | 0.021 |
| | | Terbuthylazine | 0.01 |
| Otago Regional Council (6/16) | F40/0206 | Simazine | 0.03 |
| | G40/0367 | Picloram | 0.4 |
| | G40/0411 | Terbuthylazine | 0.022 |
| | H43/0132 | Picloram | 0.91 |
| | | Terbuthylazine | 0.16 |
| | I44/0821 | Hexazinone | 0.15 |
| | J41/0008 | Atrazine | 0.032 |
| | | Total Atrazine and Metabolites (max) | 0.33 |
| | | Diazinon | 0.01 |
| | | Glyphosate | 2.1 |
| | | 4,4’-DDT | 0.02 |
| Environment Southland (5/6) | E44/0036 | Terbuthylazine | 0.089 |
| | E46/0093 | Simazine | 0.019 |
| | | Terbuthylazine | 0.025 |

| **Council Region**<br>**(# detections / # wells sampled)** | **Well ID** | **Pesticide Detected** | **Concentration (µg/L)** |
|---|---|---|---|
|  | F44/0484 | Simazine | 0.053 |
|  |  | Terbuthylazine | 0.3 |
|  | F45/0792 | Terbuthylazine | 0.021 |
|  | F46/0239 | Hexazinone | 0.024 |
|  |  | Propazine | 0.062 |
|  |  | Simazine | 0.067 |
|  |  | Terbuthylazine | 0.15 |
|  | **68 wells** |  | **112 detections** |

**Table 5: Characteristics of detected pesticides.**

Field half-lives and Koc 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.

| Pesticide | FAO Classification | Field half-life (days) | Koc (ml $g^{-1}$) | GUS score | No. of Wells | Range (µg/L) | MAV (µg/L) |
|---|---|---|---|---|---|---|---|
| ***Herbicides*** | | | | | | | |
| 2,4-DB | Phenoxy hormones | 5 | 440 | 0.95 N | 1 | 0.08 | 100 |
| 2-Hydroxyatrazine | Triazine | | | | 1 | 0.22 | 2 |
| Alachlor | Amide | 15 | 170 | 2.08 T | 1 | 0.59 | 20 |
| Atrazine | Triazine | 60 | 100 | 3.56 L | 3 | 0.011 - 0.032 | 2 |
| DEA | Triazine | † | † | | 3 | 0.011 – 0.015 | 2 |
| DIA | Triazine | † | † | | 1 | 0.02 | 2 |
| Bentazone | Other herbicide | 27 (7–98) | 35 | 3.52 L | 7 | 0.08 – 0.36 | |
| Bromacil | Uracil | 60 | 32 | 4.44 L | 2 | 0.88 – 2.0 | 400 |
| Glyphosate | Phosphonyl | 47 | 24,000 | -0.64 N | 1 | 2.1 | 900 |
| Hexazinone | Triazine | 90 | 54 | 4.43 L | 8 | 0.01 – 0.15 | 400 |
| Metolachlor | Amide | 90 | 200 | 3.32 L | 2 | 0.025 – 0.05 | 10 |
| Picloram | Other hormone type | 90 | 16 | 5.46 L | 2 | 0.4 – 0.91 | 200 |
| Propazine | Triazine | 135 | 154 | 3.86 L | 3 | 0.03 – 0.062 | 70 |
| Simazine | Triazine | 60 | 130 | 3.35 L | 10 | 0.011 – 0.067 | 2 |
| Terbacil | Uracil | 120 | 55 | 4.70 L | 2 | 0.4 – 3.8 | 40 |
| Terbuthylazine | Triazine | 86 (34–193)* | 110 (42–575)* | 3.79 L | 36 | 0.005 – 0.35 | 8 |
| DET | Triazine | # | # | | 15 | 0.011 | 0.39 |

| **Pesticide** | **FAO Classification** | **Field half-life (days)** | **Koc (ml g$^{-1}$)** | **GUS score** | **No. of Wells** | **Range (μg/L)** | **MAV (μg/L)** |
|---|---|---|---|---|---|---|---|
| ***Insecticide*** | | | | | | | |
| 4,4’-DDE | Organochlorine | 1000 | 50,000 | -2.10 N | 2 | 0.0007 – 0.0025 | 1 |
| 4,4’-DDT | Organochlorine | 2000 | 2,000,000 | -7.60 N | 2 | 0.0018 – 0.02 | 1 |
| Diazinon | Organophosphate | 40 | 1000 | 1.60 T | 1 | 0.01 | |
| Dieldrin | Organochlorine | 1000 | 12000 | -0.24 N | 2 | 0.02 – 0.025 | 0.04 |
| Endosulfan I | Other insecticide | 50 | 12,400 | -0.17 N | 1 | 0.016 | |
| Endosulfan II | Other insecticide | ‡ | ‡ | | 2 | 0.033 – 0.061 | |
| Endosulfan sulphate | Other insecticide | ‡ | ‡ | | 1 | 0.068 | |
| ***Fungicides*** | | | | | | | |
| Metalaxyl | Other fungicide | 70 | 50 | 3.33 L | 2 | 0.024 – 0.06 | 100 |

† values assumed similar to Atrazine; * values for Terbuthylazine taken from Close et al., (2008); # values assumed similar to Terbuthylazine; ‡ values assumed similar to Endosulfan I; DET = desethyl terbuthylazine=terbuthylazine desethyl; DEA = desethyl atrazine = atrazine-desethyl; and DIA = desisopropyl atrazine = atrazine-desisopropyl; p,p’-DDT = 4,4’-DDT.

### 3.2.2 Emerging Organic Contaminants (EOCs)

There were a total of 227 EOCs detected in the 85 wells (70%) from the 121 wells that were sampled (Table 6), and all regions that had samples analysed for EOCs had at least three wells with EOCs present. There were 29 different EOCs in the analytical suite and 25 different EOCs were detected in at least one well (Table 7). The maximum number of EOCs detected in a single well was 13.

The EOCs were grouped into six categories that reflected their source and usage (Table 7). Most EOCs are used extensively by people or are produced by people (eg estrogenic steroid hormones) and most do not have significant human toxicity when used under normal conditions, such as use of sun screens or anti-inflammatories such as diclofenac (voltaren). There are no MAVs for drinking water associated with these EOCs. However, some of these compounds have shown some endocrine disrupting effects in surface waters (Sellin et al., 2009; Tremblay et al., 2018) and the main concerns with these EOCs are environmental or ecological impacts. However, there are no or very few guideline values for EOCs regarding ecological impacts as the required studies are sparse (Lapworth et al., 2012). Some EOCs, such as sucralose and caffeine, can act as tracers of the presence of human activities or wastewater impacts in the groundwater system (Table 7).

The most commonly detected EOC was bisphenol-A (BPA) which was detected in 40 wells, with the UV filter compounds, OMC and BP3 next most common with 33 and 24 detections, respectively (Table 7). Sucralose, an artificial sweetener, was next most common with 18 detections. The highest concentration measured was 655 ng/L for sucralose (Table 7).

**Table 6: Summary of results from the 2018 Emerging Organic Contaminants (EOCs) in groundwater survey detailing 227 detections in 85 wells.**

| Council Region (# detections / # well sampled) | Well ID | EOC Detected | GCMS Concentration (ng $L^{-1}$) |
|---|---|---|---|
| Northland Regional Council (3/5) | 1002 | Bisphenol-A | 31.4 |
| | | Octinoxate | 31.4 |
| | 5044 | Acetominophen | 1.18 |
| | | Bisphenol-A | 16.7 |
| | | Carbamazepine | 5.49 |
| | | Diclofenac | 12.8 |
| | | 2,4-dihydroxybenzophenone | 3.18 |
| | | Ibuprofen | 5.66 |
| | | Naproxen | 4.83 |
| | 8287 | Oxybenzone | 10.8 |
| Auckland Council (4/8) | 43915 | Caffeine | 45.0 |
| | | 17α-estradiol | 0.95 |
| | 6475015 | Bisphenol-A | 27.0 |
| | | Ibuprofen | 30.8 |
| | 6487015 | Bisphenol-A | 6.73 |
| | | Estrone | 0.57 |
| | | Sucralose | 50.5 |
| | 7419009 | Acetominophen | 94.0 |
| | | Bisphenol-A | 3.29 |
| | | Carbamazepine | 59.8 |
| | | Diclofenac | 68 |
| | | 2,4-dihydroxybenzophenone | 2.12 |
| | | Estrone | 1.06 |
| | | 4-hydroxybenzophenone | 2.08 |
| | | Ibuprofen | 63.9 |
| | | Methyl-Triclosan | 1.81 |
| | | Naproxen | 57.3 |
| | 7419126 | Acetominophen | 13.6 |
| | | Bisphenol-A | 2.36 |
| | | Carbamazepine | 5.77 |
| | | Diclofenac | 7.84 |
| | | Ibuprofen | 5.33 |

| Council Region (# detections / # well sampled) | Well ID | EOC Detected | GCMS Concentration (ng $L^{-1}$) |
|---|---|---|---|
| | | Mestranol | 6.78 |
| | | Naproxen | 3.99 |
| | 7419127 | Octinoxate | 7.19 |
| | 7428031 | Bisphenol-A | 9.92 |
| | | Octinoxate | 7.4 |
| | 7428105 | Caffeine | 9.25 |
| | | 17α-estradiol | 5.15 |
| | | Sucralose | 265 |
| Bay of Plenty Regional Council (13/25) | 915 | Bisphenol-A | 5.26 |
| | 1561 | Bisphenol-A | 7.95 |
| | 1670 | Bisphenol-A | 4.44 |
| | | Methyl paraben | 1.43 |
| | | Propyl paraben | 0.5 |
| | 2822 | Bisphenol-A | 4.68 |
| | 3036 | Bisphenol-A | 5.79 |
| | | Caffeine | 2.21 |
| | 100106 | Octinoxate | 11.4 |
| | 170049 | Bisphenol-A | 7.59 |
| | 1001058 | Bisphenol-A | 423 |
| | | Octinoxate | 5.95 |
| | 1001239 | 2,4-dihydroxybenzophenone | 0.65 |
| | | Oxybenzone | 15.6 |
| | 1001241 | Oxybenzone | 7.32 |
| | 1001249 | Bisphenol-A | 4.7 |
| | | Propyl paraben | 0.69 |
| | 1001289 | Caffeine | 2.34 |
| | Waitapu Spring | Caffeine | 1.87 |
| Gisborne District Council (4/5) | GPB099 | Acetominophen | 5.33 |
| | | Bisphenol-A | 56.0 |
| | | 4-methylbenzylidene camphor | 40.1 |
| | | Octinoxate | 13.9 |
| | | Sucralose | 202 |
| | GPF032 | Octinoxate | 25 |
| | GPG019 | Sucralose | 20.3 |
| | R SPRING | Acetominophen | 2.99 |

| **Council Region**<br>**(# detections / # well sampled)** | **Well ID** | **EOC Detected** | **GCMS Concentration (ng $L^{-1}$)** |
|---|---|---|---|
| | | Diclofenac | 1.97 |
| | | Octinoxate | 21.1 |
| | | Oxybenzone | 7.65 |
| Taranaki Regional Council (5/8) | GND0076 | Oxybenzone | 9.06 |
| | | 2,2',4,4'-tetrahydroxybenzophenone | 0.44 |
| | GND0809 | 4-hydroxybenzophenone | 2.08 |
| | GND0827 | Methyl paraben | 1.77 |
| | GND1718 | 2,4-dihydroxybenzophenone | 0.87 |
| | GND2515 | Bisphenol-A | 5.30 |
| | | Caffeine | 5.74 |
| | | Carbamazepine | 72.6 |
| | | Diclofenac | 98 |
| | | 4-methylbenzylidene camphor | 12.3 |
| | | Octinoxate | 9.28 |
| | | o-phenylphenol | 6.12 |
| | | Oxybenzone | 25.4 |
| | | Sucralose | 655 |
| Horizons (6/8) | 338005 | 2,4-dihydroxybenzophenone | 1.77 |
| | | 4-hydroxybenzophenone | 2.00 |
| | | Methyl paraben | 2.2 |
| | | Propyl paraben | 1.26 |
| | | Sucralose | 31.8 |
| | | 2,2',4,4'-tetrahydroxybenzophenone | 5.53 |
| | 342051 | Ibuprofen | 175 |
| | 362397 | Caffeine | 1.81 |
| | | Octinoxate | 6.6 |
| | 362801 | Caffeine | 4.25 |
| | 372034 | Bisphenol-A | 6.49 |
| | | Octinoxate | 14.4 |
| | 421001 | Caffeine | 2.25 |
| | | 2,4-dihydroxybenzophenone | 2.07 |
| | | Estrone | 0.85 |
| | | Methyl paraben | 2.72 |
| | | Methyl-Triclosan | 5.07 |
| | | Octinoxate | 15.6 |
| | | Oxybenzone | 11.0 |

| Council Region (# detections / # well sampled) | Well ID | EOC Detected | GCMS Concentration (ng L$^{-1}$) |
|---|---|---|---|
| | | Propyl paraben | 2.13 |
| | | Sucralose | 39.4 |
| | | 2,2',4,4'-tetrahydroxybenzophenone | 1.69 |
| Greater Wellington Regional Council (7/7) | R26/6587 | Octinoxate | 5.33 |
| | R27/1137 | Bisphenol-A | 1.28 |
| | | Sucralose | 22.5 |
| | R27/1182 | Bisphenol-A | 2.51 |
| | | 2,4-dihydroxybenzophenone | 0.95 |
| | | Estriol | 1.08 |
| | | Sucralose | 88.8 |
| | | 2,2',4,4'-tetrahydroxybenzophenone | 2.85 |
| | S26/0117 | Acetominophen | 96.8 |
| | | Bisphenol-A | 1.97 |
| | | Carbamazepine | 61.4 |
| | | Diclofenac | 63.7 |
| | | Ibuprofen | 63.8 |
| | | Naproxen | 57.1 |
| | | Octinoxate | 25.7 |
| | | Oxybenzone | 2.47 |
| | S26/0457 | Triclosan | 2.03 |
| | S27/0588 | Methyl-Triclosan | 3.03 |
| | | Oxybenzone | 14.3 |
| | | Triclosan | 1.94 |
| | T26/0259 | Acetominophen | 13.3 |
| | | Carbamazepine | 5.91 |
| | | Diclofenac | 7.64 |
| | | Ibuprofen | 5.3 |
| | | Naproxen | 3.98 |
| Tasman District Council (8/10) | 524 | Oxybenzone | 12.3 |
| | | Sucralose | 1.21 |
| | 4096 | 4-methylbenzylidene camphor | 63.8 |
| | | Octinoxate | 63.8 |
| | | Oxybenzone | 19.7 |
| | 6342 | Bisphenol-A | 8.66 |
| | | Methyl-Triclosan | 1.18 |
| | | Octinoxate | 36.2 |

| **Council Region**<br>**(# detections / # well sampled)** | **Well ID** | **EOC Detected** | **GCMS Concentration (ng L$^{-1}$)** |
|---|---|---|---|
| | | Oxybenzone | 10.7 |
| | 23604 | Bisphenol-A | 5.73 |
| | | Caffeine | 5.77 |
| | | 2,4-dihydroxybenzophenone | 4.66 |
| | | 17α-estradiol | 1.50 |
| | | 17α-Ethinylestradiol | 1.48 |
| | | Estriol | 3.10 |
| | | Estrone | 1.49 |
| | | Mestranol | 1.94 |
| | | Methyl paraben | 5.45 |
| | | o-phenylphenol | 4.08 |
| | | Propyl paraben | 5.95 |
| | | Sucralose | 162 |
| | | 2,2',4,4'-tetrahydroxybenzophenone | 8.35 |
| | 23658 | Octinoxate | 31.3 |
| | 23759 | 2,4-dihydroxybenzophenone | 2.76 |
| | 23806 | Estrone | 0.85 |
| | | Methyl-Triclosan | 5.07 |
| | | Sucralose | 1.50 |
| | Pupu springs - Main spring | Octinoxate | 41.2 |
| | | Oxybenzone | 19.6 |
| Marlborough District Council (12/19) | 10542 | Bisphenol-A | 8.46 |
| | | Oxybenzone | 5.51 |
| | O28w/0015 | Methyl paraben | 8.91 |
| | | Propyl paraben | 1.8 |
| | P27w/0448 | Chloroxylenol | 0.50 |
| | | Propyl paraben | 0.77 |
| | P28w/0124 | Methyl paraben | 26.0 |
| | | Propyl paraben | 5.70 |
| | P28w/0610 | Bisphenol-A | 5.05 |
| | | 2,4-dihydroxybenzophenone | 0.81 |
| | | Oxybenzone | 10.8 |
| | P28w/0647 | Octinoxate | 11.5 |
| | P28w/1634 | Bisphenol-A | 9.3 |
| | P28w/2993 | Bisphenol-A | 34.3 |

| **Council Region**<br>**(# detections / # well sampled)** | **Well ID** | **EOC Detected** | **GCMS Concentration (ng L$^{-1}$)** |
|---|---|---|---|
| | | Oxybenzone | 6.81 |
| | P28w/3222 | Oxybenzone | 6.91 |
| | P28W/3668 | Octinoxate | 9.37 |
| | P28W/3711 | Bisphenol-A | 2.78 |
| | | Octinoxate | 5.13 |
| | | Sucralose | 118 |
| | P28W/6037 | Bisphenol-A | 56.8 |
| Environment Canterbury (5/6) | J40/0256 | Bisphenol-A | 5.71 |
| | K39/0033 | Octinoxate | 14.7 |
| | | Oxybenzone | 14.7 |
| | | Sucralose | 51.3 |
| | L36/0003 | Bisphenol-A | 5.49 |
| | | Octinoxate | 14.4 |
| | M35/5918 | Ibuprofen | 7.71 |
| | M35/8567 | Bisphenol-A | 20.1 |
| | | Octinoxate | 17.9 |
| | | Sucralose | 36.4 |
| Otago Regional Council (11/16) | F40/0045 | Bisphenol-A | 48.9 |
| | F41/0203 | Bisphenol-A | 50.0 |
| | | 2,4-dihydroxybenzophenone | 1.17 |
| | | Methyl paraben | 1.75 |
| | | Methyl-Triclosan | 0.66 |
| | | Octinoxate | 12.8 |
| | | Sucralose | 7.94 |
| | F41/0437 | Bisphenol-A | 9.84 |
| | | 2,4-dihydroxybenzophenone | 0.95 |
| | | Methyl paraben | 2.16 |
| | | Octinoxate | 14.3 |
| | | Oxybenzone | 7.66 |
| | G40/0367 | Oxybenzone | 6.91 |
| | G42/0290 | Bisphenol-A | 34.3 |
| | | Octinoxate | 20.5 |
| | | Oxybenzone | 6.81 |
| | G43/0072 | Bisphenol-A | 5.05 |
| | | 2,4-dihydroxybenzophenone | 0.81 |
| | | Octinoxate | 6.61 |

| **Council Region** **(# detections / # well sampled)** | **Well ID** | **EOC Detected** | **GCMS Concentration (ng $L^{-1}$)** |
|---|---|---|---|
| | | Oxybenzone | 10.8 |
| | G43/0224b | Bisphenol-A | 8.46 |
| | | Octinoxate | 40.3 |
| | | Oxybenzone | 5.51 |
| | H43/0132 | Methyl paraben | 1.49 |
| | | Octinoxate | 35.3 |
| | | Oxybenzone | 10.4 |
| | I44/0821 | Bisphenol-A | 56.8 |
| | | Octinoxate | 7.99 |
| | J41/0008 | Bisphenol-A | 12.4 |
| | | Methyl paraben | 1.59 |
| | J41/0317 | Estrone | 6.24 |
| | | Octinoxate | 30.8 |
| Environment Southland (3/4) | E46/0093 | Octinoxate | 13.4 |
| | F44/0484 | Sucralose | 36.5 |
| | F46/0239 | Methyl-Triclosan | 1.73 |
| | | Sucralose | 11.0 |

**Table 7: Summary of EOC detections, method detection limits (MDL), and concentrations (ng/L).**

| EOC | # detects | Mean | Min | Max | MDL | Detailed type |
|---|---|---|---|---|---|---|
| ***Anti microbial/Preservative*** | | | | | | |
| Chloroxylenol | 1 | 0.5 | 0.5 | 0.5 | 0.05 | |
| Methyl paraben | 11 | 5.0 | 1.43 | 26 | 0.05 | preservative |
| Methyl-Triclosan | 7 | 2.7 | 0.66 | 5.07 | 0.05 | Triclosan metabolite |
| o-phenylphenol | 2 | 5.1 | 4.08 | 6.12 | 0.10 | |
| Propyl paraben | 8 | 2.4 | 0.5 | 5.95 | 0.05 | preservative |
| Triclosan | 2 | 2.0 | 1.94 | 2.03 | 0.10 | Antimicrobial |
| ***Estrogenic steroid hormones*** | | | | | | |
| 17α-estradiol (17αE2) | 3 | 2.5 | 0.95 | 5.15 | 0.05 | All but mainly dairy |
| 17β-estradiol (17βE2) | 0 | | | | 0.05 | All but mainly human |
| Estriol (E3) | 2 | 2.1 | 1.08 | 3.1 | 0.05 | pregnant women |
| Estrone (E1) | 6 | 1.8 | 0.57 | 6.24 | 0.05 | dairy and swine effluent |
| 17α-Ethinylestradiol (EE2) | 1 | 1.5 | 1.48 | 1.48 | 0.05 | contraceptive pill |
| Mestranol (17α-Ethinylestradiol 3-methyl ether) | 2 | 4.4 | 1.94 | 6.78 | 0.05 | contraceptive pill |
| ***Human Wastewater tracer*** | | | | | | |
| Caffeine | 10 | 8.1 | 1.81 | 45 | 5.0 | stimulant |
| Cotinene | 0 | | | | 5.0 | Stimulant – nicotine metabolite |
| 1,7-dimethylxanthine | 0 | | | | 5.0 | stimulant -caffeine metabolite |
| Nicotine | 0 | | | | 5.0 | stimulant |
| Sucralose | 18 | 100.1 | 1.21 | 655 | 1.0 | Artificial sweetener |
| ***Industrial*** | | | | | | |
| Bisphenol-A (BPA) | 40 | 26.1 | 1.28 | 423 | 0.62 | Plasticiser |

| EOC | # detects | Mean | Min | Max | MDL | Detailed type |
|---|---|---|---|---|---|---|
| ***Pharmaceuticals*** | | | | | | |
| Acetominophen | 7 | 32.5 | 1.18 | 96.8 | 0.10 | NSAID |
| Carbamazepine | 6 | 35.12 | 5.49 | 72.6 | 0.10 | Epilepsy & mental health treatment |
| Diclofenac | 7 | 37.1 | 1.97 | 98 | 0.10 | NSAID |
| Ibuprofen | 8 | 44.7 | 5.3 | 175 | 0.10 | NSAID |
| Naproxen | 5 | 25.4 | 3.98 | 57.3 | 0.10 | NSAID -Aleve, Naprosyn |
| ***UV filter/stabiliser*** | | | | | | |
| 2,4-dihydroxybenzophenone (BP1) | 13 | 1.78 | 0.65 | 4.66 | 0.10 | |
| 4-hydroxybenzophenone | 3 | 2.1 | 2 | 2.08 | 0.10 | |
| 4-methylbenzylidene camphor (4-MBC) | 3 | 38.7 | 12.3 | 63.8 | 0.10 | |
| Octinoxate (OMC) | 33 | 19.0 | 5.13 | 63.8 | 2.15 | |
| Oxybenzone (BP3) | 24 | 10.8 | 2.47 | 25.4 | 1.21 | |
| 2,2',4,4'-tetrahydroxybenzophenone (BP2) | 5 | 3.8 | 0.44 | 8.35 | 0.10 | |

# 4. DISCUSSION

## 4.1 PESTICIDES

There were three pesticide detections exceeding 1 μg/L with none of the sampled wells exceeding the MAV for drinking water. The highest detection as a percentage of the MAV was dieldrin which was detected at a concentration of 0.025 μg/L which was 62.5% of the MAV of 0.04 μg/L (Ministry of Health 2018). The next highest detections relative to the MAV were for total atrazine and metabolites at 16.5% of the MAV, hydroxyatrazine (another atrazine metabolite) at 11% of MAV assuming the same MAV as for atrazine, then terbacil at 9.5% of the MAV (Table 6). The remainder of pesticide detections were less than 5% of the MAV with the median of the pesticide detections being below 0.5% 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 has been detected occasionally in previous surveys at concentrations above the MAV (Close & Humphries 2016; Close & Skinner 2012). 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 μg/L) 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 36 wells (16%) at levels ranging from 0.005 – 0.35 μg/L (Table 6), with the next most common pesticide being desethyl terbuthylazine (a metabolite of terbuthylazine) with 15 detections. Simazine was detected in 10 wells.

Herbicides were the most frequently detected pesticide group with seven insecticides and only one fungicide detected in the sampled wells. There were 80 out of the total of 112 detections (71%) of triazine herbicides. 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 8).

Of the 25 pesticides detected that had data available for soil half-life and Koc, GUS values indicated that 13 were leachers, 2 were transitional, and 6 were non-leachers (Table 5). Most of the detections were for pesticides classed as leachers (Table 5). One of the non-leacher pesticides was the glyphosate detection that was probably the results of poor well-head protection and ingress of contamination directly from the surface into the well, as discussed above. DDT and DDE are non-leacher pesticides that are extremely persistent and were detected in samples from Waikato and Canterbury by Hill laboratories using lower detection limits. Two other non-leacher pesticides were dieldrin, which was widely used and very persistent as discussed above, and endosulfan. Endosulfan is an organochlorine but not nearly as persistent as dieldrin (Table 5). 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 mix of leaching properties indicates that normal leaching processes are mostly responsible for the presence of the detected pesticides in the groundwater but other pathways, such as spills, ingress from the surface via poor well-head protection or preferential flow, may also occur. Leaching of extremely persistent pesticides, such as DDT and its metabolites and dieldrin, can also occur over long time periods to shallow groundwater.

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 2018 survey then there would only be a total of 21 wells (8%) with detectable pesticides instead of 68 wells (Table 8). Table 8 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 2018 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 eight surveys from 1990 to 2018. 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 μg/L. There has been a maximum of one pesticide detected at a concentration greater than the MAV in five out of the eight surveys, with the other three surveys having no pesticides detected at a concentration greater than the MAV (Table 8). 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.

## 4.2 GLYPHOSATE

Reviews of the mobility and likely leaching of glyphosate to groundwater have been carried out (Vereecken 2005; Borggaard & Gimsing 2008) and indicate that under normal conditions leaching of glyphosate through the soil to groundwater should be very limited due to strong sorption to soil and relatively fast degradation (Borggaard & Gimsing 2008). There is the possibility that transport processes with high recharge (intense rainfall or heavy irrigation) combined with structured soils containing macropores or cracks may bypass much of the soil profile and enable even strongly sorbing pesticides to leach into groundwater (Vereecken 2005).

There has been little monitoring of glyphosate and its metabolites (principally AMPA) in groundwater until the last 5 years. Battaglin et al., (2014) developed an extremely sensitive method for the measurement of glyphosate and AMPA (DL = 0.02 μg/L) and analysed 1171 groundwater samples as well as a further 2500 samples from surface waters, drains and rainfall. They found extensive contamination of surface waters by glyphosate (30 – 70% of samples) and 5.8% of groundwater samples having detectable glyphosate. The median and maximum concentrations of glyphosate found in groundwater were < 0.02 and 2.03 μg/L, respectively. AMPA was found in 14.3% of groundwater samples with median and maximum concentrations of < 0.02 and 4.88 μg/L, respectively.

In New Zealand John Hadfield collected samples from 40 wells in the Waikato region that were selected as having higher potential for pesticide contamination and had the samples analysed for glyphosate and AMPA by AsureQuality (Hadfield, 2017). The detection limit was 1 μg/L which was the same as for this study. He found one detection of AMPA at a concentration of 1.9 μg/L. The landowners indicated that a herbicide, and most likely roundup, had been used on the property in the months before sampling took place.

The investigations on the well in this study where glyphosate was detected indicated that this detection was likely caused by poor well head protection and contamination from the containers and activities occurring around the well. The detection of other pesticides such as DDT, diazinon and atrazine, which have very different leaching characteristics (Table 6) support contamination of the well from surface sources rather than widespread groundwater contamination. The very low frequency of glyphosate and AMPA detections in both the national and Waikato surveys imply that there is little risk of glyphosate reaching groundwaters in New Zealand. The detected levels of 2.1 μg/L for glyphosate in this survey (probably from surface contamination) and 1.9 μg/L for AMPA found in the Waikato survey, are far below the WHO Health Based Value for glyphosate of 900 μg/L (WHO 2017) indicating a very low risk from glyphosate for drinking water purposes in New Zealand.

## 4.3 EMERGING ORGANIC CONTAMINANTS

EOCs can arise from sewage treatment plants, industrial effluents, leaking sewage networks, runoff from agricultural, storm-water and urban sources, application of effluents to land and septic tanks. Many of these sources are associated with urban environments. In New Zealand, where most of the large cities are located on the coast, there should be limited opportunity for these municipal discharges to impact groundwater. Some compounds can arise from farming activities such as dairy shed effluent and animal manures (estrogens associated with dairy cows: E1, 17α-E2 – Table 7). Many EOC detections are likely to be associated with the widespread use of septic tank systems in the rural environment from which the majority of the groundwater samples in this study originated. The high rate of EOC detections, albeit at low concentrations, indicates that effluents from small towns, septic tank systems and farming activities are probably the sources for the detections of EOCs in groundwater in this study.

Schaider et al., (2016) evaluated whether septic tanks are a likely source of EOCs in groundwater. They tested 20 domestic drinking water wells in a sand and gravel aquifer on Cape Cod, Massachusetts, USA, for 117 EOCs and detected 27 compounds, including 12 pharmaceuticals, four organophosphate flame retardants, and an artificial sweetener (acesulfame). These wells were all located in areas served exclusively by onsite wastewater treatment systems, which are likely the main source of the EOCs in these wells, although landfill leachate may also be a source. Their results suggest that current regulations to protect domestic wells from pathogens in septic system discharges do not prevent EOCs from reaching domestic wells.

Overall detection frequencies are often difficult to compare between studies as different combinations of EOCs are measured, sometimes with differing detection limits. Nevertheless, the detection frequencies and levels of EOCs found in this national survey are broadly similar to studies in other countries. Focazio et al., (2008) carried out a national study in the USA in untreated drinking water sources, which included 25 groundwater wells and analysed the samples for 100 EOCs. The most commonly detected compounds in their study were tetrachloroethylene (24%, solvent), carbamazepine (20%, pharmaceutical), bisphenol-A (20%, plasticizer), and 1,7-dimethylxanthine (16%, caffeine metabolite). Of these compounds we didn't analyse for tetrachloroethylene but detected carbamazepine and bisphenol-A in 5% and 33% of samples, respectively. Loos et al., (2010) carried out a study of EOCs in European groundwater and analysed 164 samples from 23 countries for 59 selected EOCs. The non-pesticide compounds that were common to the New Zealand national survey, in terms of frequency of detection and maximum concentrations detected, were caffeine (83%; 189 ng/L), carbamazepine (42%; 390 ng/L), and bisphenol A (40%; 2.3 mg/L). Jurado et al., (2012) reviewed the detection of EOCs in groundwater in Spain and found a wide range of compounds had been detected with maximum concentrations generally above the levels in the rest of Europe found by Loos et al., (2010). They noted that none of the studied estrogens have been found in Spanish aquifers but some of them have been detected in groundwater from the rest of Europe at low concentrations (up to 10 ng/L). They concluded that most EOCs are usually detected at low ng/L concentrations or not detected at all in groundwater throughout Europe. Lapworth et al., (2012) has carried out a comprehensive review of the sources and occurrence of EOCs in groundwater and noted the occurrence and detected concentrations for 10 of the 29 EOCs analysed for in the New Zealand survey, namely carbamazepine, ibuprofen, diclofenac, paracetamol, triclosan, caffeine, cotinine, bisphenol A, estrone, and 17β-estradiol.

The regional study of EOCs in Waikato groundwater detected EOCs in 91% of the sites (Moreau et al., 2019) although this included a large number of pesticides that were the most frequently detected category of EOC in that study. Of the non-pesticide EOCs, they detected BPA, triclosan, diclofenac, and sucralose in common with this national survey. The Canterbury groundwater study detected BPA, various paraben compounds (preservatives), Estriol (E3), and 4 UV filter compounds – BP1, BP2, BP3 and OMC in common with this national study (van der Krogt et al., 2018).

Most of the EOCs detected in this study originate through human body metabolisms such as caffeine, sucralose, ibuprofen, or steroidal hormones, or are applied to our skin to protect us from the UV from the sun. Other EOCs such as BPA are used widely in packaging and plastic products or in the case of parabens, as food preservatives. The compounds tend to be used in milligram and gram quantities in such applications and most compounds are likely to exhibit low toxicity to humans. There are no MAVs for drinking water for these non-pesticide EOCs in New Zealand. However, the environmental or ecological impacts of most EOCs are largely unknown or the concentration at which effects begin to exhibit are unknown (Tremblay et al., 2018). Some compounds such as BPA are known to have endocrine disrupting properties (Rochester 2013).

These results indicate that EOCs, sourced from either animal or human effluents or activities, are making their way into shallow groundwater systems and can be detected at low concentrations in groundwater. Currently there is a lack of knowledge of the fate and effects of many EOCs and whether the concentrations measured in this study are likely to have impacts for ecological systems. We recommend that monitoring of EOCs in groundwater resources is extended and that research is carried out to quantify the potential risks to ecosystems for the EOCs most frequently detected in this study.

**Table 8: Summary statistics for the eight national surveys of pesticides in groundwater in New Zealand.**

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

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# APPENDIX A: ESR 2018 PROCEDURES FOR SAMPLING PESTICIDES AND EOCS

Science for Communities

## National Survey of Pesticides in Groundwater 2018 - Sampling Procedures

**To:** The Regional or Unitary Authority

Thank you for participating in the National Survey of Pesticides in Groundwater 2018. The survey has occurred every four years since 1990 with this year being the 8th survey.

This document contains details of the required sampling procedures for this year's survey. Three organisations are involved in the survey, ESR, AsureQuality and Northcott Research Consultants Ltd, 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

**AsureQuality** *(Pesticide and Glyphosate analysis laboratory)*

- x1 1L amber glass bottle which has been preserved with sodium thiosulphate
- x1 500ml amber glass sample bottle which has been preserved with sodium thiosulphate
- x1 250mL amber glass bottle (no preservative)
- x1 250ml plastic (HDPE, no preservative) sample bottle for Glyphosate analysis if chosen.
- **NOTE: For all Assure Quality (AQ) samples, there are holding time requirements that must be met. Samples must be refrigerated after collection and received at AQ-Wellington 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)

## 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
- Courier tickets and address information for AsureQuality and Northcott Research Consultants Ltd.

## 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 AsureQuality and Northcott Research Consultants immediately via courier.
2. **NOTE: For all AQ samples, there are holding time requirements that must be met. Samples must be refrigerated after collection and received at AQ-Wellington within 3 calendar days of collection.**
3. Field staff please strictly avoid the following on the day of sampling if sampling for EOCs :

- 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)

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

## WELL SAMPLING PROCEDURE

1) Collect the **static water level** within the well, this information can be very important during the process of 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).

2) 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.

3) 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**).

4) If you are using your own pump for sampling (i.e. Grundfos MP1 or SuperTwister pump) while you are purging the well (x3 well volumes) ensure that any water within the entire length of the hosing is purged between wells. This will also ensure that the pump itself is adequately rinsed between wells.

5) If you have a multi-parameter water meter (i.e. pH, temperature, conductivity, dissolved oxygen etc) make sure that these **readings have stabilised** before taking the sample.

6) Clearly label the bottles before you get your hands or the bottles wet with the date, time and well ID number.

7) 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.

8) **AsureQuality bottles:** The 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. **DO NOT RINSE THE BOTTLES AS THERE ARE PRESERVATIVES INSIDE EACH BOTTLE.**

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.

9) **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.

10) Make sure that you fill the correct number of bottles for each well that is sampled. If your council has opted to sample everything (i.e. Pesticides, Glyphosate and Emerging Organic Contaminants) there will be a total of x5 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 AsureQuality chain of custody form do not indicate which sample is the blind duplicate sample.**

- For example, if you are sampling 8 wells then only 1 blind duplicate sample is required. If you are sampling 15 wells then 2 blind duplicate samples are required. If you are sampling 22 wells then 3 blind duplicate samples are required and so on.
- 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.

  - 1st 1L glass bottle for the well sample
  - 1st 1L glass bottle for the Blind Duplicate
  - 2nd 500mL glass bottle for the well sample
  - 2nd 500 mL glass bottle for the Blind Duplicate
  - 3rd 250ml glass bottle for the well sample
  - 3rd 250ml glass bottle for the Blind Duplicate
  - 4th 250ml plastic for the well sample
  - 4th 250ml plastic for the Blind Duplicate
  - 5th 4L bottle for the well sample
  - 5th 4L 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 what well the blind duplicate belongs to.

- **AsureQuality 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)

**Scan and email copies of the ESR Field Sampling forms to Bronwyn Humphries: bronwyn.humphries@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 AsureQuality and Northcott Research Consultants Ltd (addresses are provided at the end of this document).

Please advise AsureQuality of any breakages at GracefieldSR@asurequality.com and Environmental.wgtn@asurequality.com 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 PESTICIDE SAMPLING FIELD SHEET

## Field Sampling Form: 2018 National Survey of Pesticides in Groundwater

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***(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

Units are µg/L (ppb).

| **(1) Pesticide Screen** | | |
|---|---|---|
| *(i)* | *Organochlorine pesticides:* | |
| | aldrin | 0.01 |
| | α-chlordane | 0.01 |
| | γ-chlordane | 0.01 |
| | *p,p′*-DDE (also *o, p′*) | 0.01 |
| | *p,p′*-DDD (also *o, p′*) | 0.01 |
| | *p,p′*-DDT (also *o, p′*) | 0.01 |
| | dieldrin | 0.01 |
| | endosulfan I | 0.02 |
| | endosulfan II | 0.04 |
| | endosulfan sulphate | 0.02 |
| | endrin | 0.02 |
| | endrin aldehyde | 0.04 |
| | endrin ketone | 0.04 |
| | α-HCH | 0.01 |
| | β-HCH | 0.01 |
| | γ-HCH (Lindane) | 0.01 |
| | heptachlor | 0.01 |
| | heptachlor epoxide | 0.03 |
| | hexachlorobenzene | 0.1 |
| | methoxychlor | 0.02 |
| | *cis* permethrin | 0.01 |
| | *trans* permethrin | 0.01 |
| | procymidone | 0.02 |
| | vinclozin | 0.02 |
| *(ii)* | *Organophosphorus pesticides:* | |
| | azinphos methyl | 0.6 |
| | chlorpyrifos | 0.02 |
| | diazinon | 0.01 |
| | dimethoate | 0.4 |
| | pirimiphos methyl | 0.02 |
| *(iii)* | *Organonitrogen herbicides:* | |
| | acetochlor | 0.02 |
| | alachlor | 0.02 |
| | aldicarb | 0.1 |
| | atrazine | 0.02 |
| | bromacil | 0.03 |
| | carbofuran | 0.9 |
| | chlorotoluron | 0.04 |
| | cyanazine | 0.02 |
| | desethyl atrazine | 0.01 |
| | desethyl terbuthylazine | 0.01 |
| | desisopropyl atrazine | 0.1 |
| | diuron | 0.04 |
| | hexazinone | 0.01 |
| | 2-hydroxyatrazine | 0.1 |
| | isoproturon | 0.04 |
| | linuron | 0.1 |
| | metalaxyl | 0.02 |
| | metolachlor | 0.02 |
| | metribuzin | 0.02 |
| | molinate | 0.01 |
| | norflurazon | 0.1 |
| | oryzalin | 2.0 |
| | oxadiazon | 0.01 |
| | pendimethalin | 0.02 |
| | primisulfuron-methyl | 0.1 |
| | propanil | 0.06 |
| | propazine | 0.01 |
| | pyriproxyfen | 0.5 |
| | simazine | 0.01 |
| | terbacil | 0.02 |
| | terbuthylazine | 0.01 |
| | thiabendazole | 0.1 |
| | trifluralin | 0.02 |
| | total atrazine & metabolites | 0.32 |
| *(iv)* | *Acid herbicides* | |
| | 2,4-D | 0.1 |
| | 2,4-DB | 0.1 |
| | 2,4,5-T | 0.1 |
| | 2,4,6-trichlorophenol | 0.12 |
| | 3,5-dichlorobenzoic acid | 0.1 |
| | acifluorfen | 0.4 |
| | bentazone | 0.1 |
| | bromoxynil | 0.1 |
| | dicamba | 0.1 |
| | dichlorprop | 0.1 |
| | dinoseb | 0.1 |
| | fenoprop | 0.1 |
| | MCPA | 0.1 |
| | MCPB | 0.1 |
| | mecoprop | 0.1 |
| | pentachlorophenol | 0.1 |
| | picloram | 0.1 |
| | triclopyr | 0.1 |
| **2/ Glyphosate suite** | | |
| | AMPA | 1 |
| | glyphosate | 1 |
| | glufosinate | 5 |
| | MPPA | 5 |

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