Journal of Hydrology (NZ) 55 (2): 73-88 2016


# The 2014 national survey of pesticides in groundwater in New Zealand

**Murray E. Close and Bronwyn Humphries**

*Institute of Environmental Science and Research Limited, PO Box 29 181, Christchurch.*
*Corresponding author: murray.close@esr.cri.nz*

## Abstract

A total of 165 wells were sampled as part of the 2014 national survey of pesticides in groundwater, a survey that is conducted on a four-yearly basis. The survey aims were to update the national overview of pesticides in New Zealand's groundwater systems, to investigate temporal variation in pesticide concentrations, and to identify environmental factors associated with pesticide contamination. Samples were analysed for around 80 pesticides using gas chromatography with mass spectrometry detection. Pesticides were detected in 28 wells (17%), with two or more pesticides detected in 10 wells (6%). Pesticides were detected in wells from six of the 13 regions sampled. One well contained a pesticide (dieldrin) at a concentration greater than the maximum acceptable value (MAV) for drinking water. Twenty-one different pesticides were detected, with most concentrations being less than 0.1 mg $m^{-3}$. Only four of the 51 pesticide detections exceeded a concentration of 1 mg $m^{-3}$. Comparisons with earlier surveys indicate similar levels of pesticide detections in groundwater over the last 12 years, with higher levels of detections before that time. The majority of wells sampled in each national survey have not had pesticides detected; where detected, the concentrations were mostly less than 0.1 mg $m^{-3}$ and, with the exception of dieldrin and terbuthylazine, less than 5% of MAVs.

## Keywords

pesticide; dieldrin; triazines; groundwater; New Zealand

## Introduction

Many pesticides are used in agricultural, horticultural, forestry and industrial applications and some of these pesticides can contaminate groundwater through leaching, spillage, and preferential flow through soils (Close *et al.*, 2001). In many regions of New Zealand groundwater is an important source of drinking water. Ten percent of the volume of groundwater abstracted is used for public water supplies (Ministry for the Environment, 2010) and approximately half of the community drinking water supplies and many rural households rely on groundwater as a sole or partial source of drinking water (Close *et al.*, 2001; Davies, 2001). Groundwater is also used extensively in primary production as a source of water for irrigation and stock, and nationally the volume of groundwater abstracted is increasing (Ministry for the Environment, 2010). Regional and national surveys of groundwater have reported pesticide contamination, predominantly of shallow and unconfined groundwater systems (Close and Skinner, 2012; Hadfield and Smith, 1999; Taranaki Regional Council, 1995). Although pesticides have generally been detected only at low concentrations in groundwater, occasional exceedances of the

corresponding maximum acceptable values (MAVs) for pesticides given in the Drinking-water Standards for New Zealand (Ministry of Health, 2008) have been reported (Close *et al.*, 2001) making ongoing monitoring necessary for regional councils. Regular monitoring is also necessary to assess and demonstrate whether measures to minimise and prevent pesticide contamination of groundwater, such as using more specific and less persistent pesticides and better disposal of pesticide containers, have been successful.

National surveys of pesticides in New Zealand groundwater have been undertaken with the assistance of regional and unitary authorities that have responsibility for management of water resources, every four years since 1990 (Close, 1993; Close, 1996; Close and Rosen, 2001; Close and Flintoft, 2004; Gaw *et al.*, 2008; Close and Skinner, 2012). The seventh national survey of pesticides in groundwater was undertaken in late 2014 and the results are reported here. The aims of this survey were to update the national overview of pesticides in New Zealand's groundwater systems, to investigate temporal variation in pesticide concentrations, and to identify environmental factors associated with pesticide contamination of groundwater.

## Methods

### Well selection

Thirteen regional councils[1] and unitary authorities with responsibility for groundwater management participated in the 2014 survey (Fig. 1). To enable comparison with previous surveys of pesticides in groundwater, similar well selection criteria were applied, including: the regional importance of the aquifer, the known use of pesticides in the area, and the vulnerability of the aquifer to contamination. Where possible, wells sampled in previous surveys were included to provide a direct temporal comparison (64% of wells sampled in 2014 had been sampled in at least one previous survey). For each well sampled the following information was recorded: well location, water level, depth of the well screen, the type of aquifer (confined, semi-confined or unconfined), and the surrounding land use. Most of the wells sampled (82% of the wells for which confinement status was known) were from unconfined aquifers. The selection included wells in most types of aquifers found in New Zealand (alluvial gravel, sand, shell bed and fractured volcanic) with the exception of very deep aquifers that are not expected to show pesticide contamination.

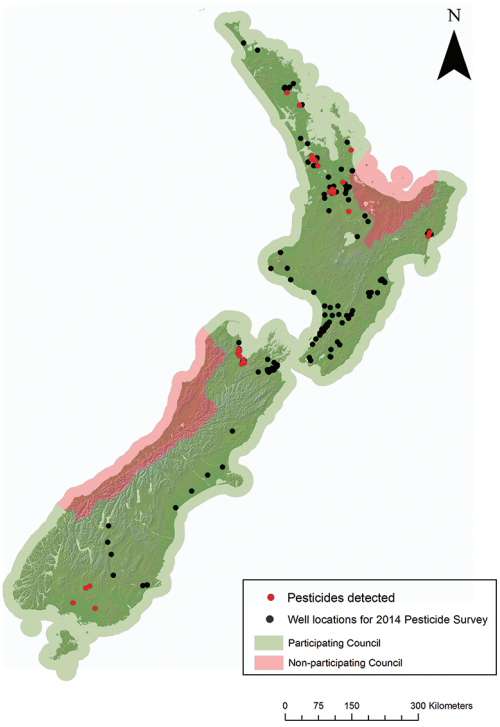


**Figure 1** – Well locations for the 2014 survey; wells with detectable pesticides shown in red

1 West Coast and Bay of Plenty regional councils did not participate in the survey.

### Sampling and analysis

Sampling was undertaken from October 2014 to January 2015 (late spring to summer), with the exception of in the Waikato region. Samples were collected either directly from down-hole pumps or with *in situ* pumps sampling close to the borehead. Wells were purged for three well volumes before samples were collected. Electrical conductivity, dissolved oxygen, temperature, and pH were measured in the field at the time of sampling where possible, and at some sites a sample for testing nitrate-N concentration was taken in conjunction with the pesticide samples. Where these parameters were not measured at the time of sampling, median values of previously collected data were used. Single groundwater samples were collected into solvent-washed 1 litre glass bottles by regional council and unitary authority staff and analysed by AsureQuality, Wellington. The Waikato Regional Council carries out an extensive monitoring of wells in its region which is offset from the national survey by two years. They provided results for 40 wells that had been sampled as part of their regional survey in 2012. These results have been included in this report to give a national perspective.

A total of 165 wells from 13 regions were sampled. The samples were analysed for around 80 different pesticides including acid and hydrophilic herbicides and a suite of organochlorine, organophosphorus and organonitrogen pesticides (OC/OP/ON) (Appendix 1) using gas chromatography with mass spectrometry detection (GC-MS). There are approximately 700 different pesticides, excluding bacteria and common compounds such calcium chloride, registered for use in New Zealand (Ministry for Primary Industries, 2015). The acid herbicide analysis involved solid phase extraction and derivatisation of the extract with diazomethane followed by GC-MS analysis using single ion monitoring (SIM) and was based on method 6640 (APHA, 2005). The OC/ON/OP pesticide analysis involved extraction with dichloromethane, which is concentrated using a turbovap evaporation system, followed by GC-MS analysis with quantification using the SIM mode (method 8270 – USEPA, 1989). Field blanks and spikes were not collected but samples from ten wells (8%) were collected in duplicate as blind duplicate samples and analysed for quality control purposes. Laboratory blanks and spike recoveries were analysed with each batch of samples by the laboratory as part of the laboratory quality control procedure. There were no pesticides detected in the laboratory blanks. The spike recoveries were required to be in the range of 75–130%. The samples from Waikato Regional Council were analysed by Hill Laboratories in Hamilton using similar methods but with slightly lower detection limits.

### Data analysis

Wells were categorised based on the presence or absence of pesticides and the total concentration of pesticides present in each well was calculated. Results below the detection limit were assigned a value of zero to avoid overestimating the total concentration of pesticides present in each well. *t*-tests were carried out using SYSTAT to explore the association of well parameters and groundwater chemistry, namely well depth, well diameter, temperature, pH, nitrate-N concentration, conductivity and dissolved oxygen, with the pesticide presence/absence data. These well parameters and groundwater chemistry are jointly referred to as groundwater parameters in the remainder of the paper. The *F* statistic was used to determine whether the variances should be pooled or kept separate for the *t*-test analysis (Rothery, 2000). The nitrate, conductivity, well diameter and well depth data were skewed and so were log-transformed before carrying

out the *t*-test analysis. Pearson's correlation coefficient was used to determine correlations between the total pesticide concentration and groundwater parameters for wells with pesticides detected. The wells were also categorised based on the type of aquifer (unconfined, semi-confined or confined) to test the association of aquifer type with detection of pesticides in groundwater. For wells that had been sampled in four or more surveys, a temporal trend assessment was carried out. Pearson's correlation coefficient was used to determine significant correlations between the total pesticide concentration and the year of the survey.

## Results and discussion

Blind duplicate samples from ten wells (8%) were analysed as a quality control measure. There was good agreement for all duplicate analyses (Table 1). Pesticides were not detected in either of the blind duplicate samples from nine wells. Terbuthylazine was detected in both duplicate samples from well WWD8042 with very good agreement.

### Overall survey results

Pesticides were detected in six of the 13 participating regions. Pesticides were not detected in wells from the Hawkes Bay, Taranaki, Horizons (Manawatu-Wanganui), Greater Wellington, Marlborough, Canterbury, and Otago regions. Of the 165 groundwater wells that were sampled, 28 (17%) tested positive for pesticides and in 10 of these wells two or more pesticides were detected (Table 2). The maximum number of pesticides detected in one well was seven.

**Table 1 –** Comparison of blind duplicate samples (ND, not detected)

| Council | Well no. | Pesticide concentration (mg $m^{-3}$) |
|---|---|---|
| Northland Regional Council | 205044 | ND<br>ND |
| Auckland Council | 7428105 | ND<br>ND |
| Hawkes Bay Council | 1558 | ND<br>ND |
| Horizons Regional Council | 312001 | ND<br>ND |
| Horizons Regional Council | 316037 | ND<br>ND |
| Horizons Regional Council | 349012 | ND<br>ND |
| Greater Wellington Regional Council | S25/5322 | ND<br>ND |
| Tasman District Council | WWD8042 | Terbuthylazine 0.014<br>Terbuthylazine 0.014 |
| Marlborough District Council | P28w/3222 | ND<br>ND |
| Otago Regional Council | G41/0103 | ND<br>ND |

**Table 2** – Summary of pesticide concentrations measured in the 2014 groundwater survey. Regions are arranged north to south. DEA = desethyl atrazine; DET = desethyl terbuthylazine

| Region (no. detections/no. wells sampled) | Well No. | Pesticide detected | Pesticide concentration (mg $m^{-3}$) |
|---|---|---|---|
| Northland (2/11) | 7244 | Hexazinone | 0.039 |
| | | Terbuthylazine | 0.012 |
| | 9851 | Terbuthylazine | 0.021 |
| Auckland (4/8) | 43915 | Acetochlor | 0.071 |
| | | Bentazone | 0.15 |
| | | Metolachlor | 0.057 |
| | 7419127 | Bentazone | 0.11 |
| | 7428031 | Acetochlor | 0.043 |
| | | Bentazone | 0.17 |
| | | Metolachlor | 0.027 |
| | 7428105 | Bentazone | 0.11 |
| Waikato (9/40) | 60-348 | Dieldrin | 0.008 |
| | 61-113 | DEA | 0.08 |
| | | Metalaxyl | 0.17 |
| | | Metribuzin | 0.06 |
| | | Procymidone | 0.08 |
| | | Propazine | 3.1 |
| | | Terbuthylazine | 0.08 |
| | 61-230 | Dieldrin | 0.043 |
| | 62-5 | DET | 0.1 |
| | 64-7 | Terbuthylazine | 0.04 |
| | 67-4 | Hexazinone | 0.21 |
| | 69-295 | Bromacil | 3.4 |
| | 69-374 | Simazine | 0.06 |
| | 70-22 | Diuron | 0.21 |
| | | Endosulfan I | 0.01 |
| | | Endosulfan II | 0.022 |
| | | Endosulfan sulphate | 0.075 |
| | | Terbacil | 0.84 |
| | | DET | 0.71 |
| | | Terbuthylazine | 1.39 |
| Gisborne (2/6) | GPF032 | Atrazine | 0.017 |
| | GPM007 | Acetochlor | 0.021 |
| | | Terbuthylazine | 0.024 |
| Hawke's Bay (0/12) | | None detected | |
| Horizons (0/23) | | None detected | |
| Taranaki (0/5) | | None detected | |
| Greater Wellington (0/11) | | None detected | |
| Tasman (5/15) | WWD59 | Terbuthylazine | 0.018 |
| | WWD285 | Simazine | 0.099 |
| | WWD417 | Terbuthylazine | 0.032 |
| | WWD3115 | Terbuthylazine | 0.033 |
| | WWD4096 | Simazine | 0.015 |
| | | Terbuthylazine | 0.022 |
| | WWD8036 | Dinoseb | 0.23 |
| | | Terbuthylazine | 0.019 |
| | WWD8042 | Terbuthylazine | 0.014 |
| Marlborough (0/17) | | None detected | |
| Canterbury (0/5) | | None detected | |
| Otago (0/8) | | None detected | |
| Southland (4/4) | E44/0036 | Terbuthylazine | 0.11 |
| | E46/0093 | Simazine | 0.020 |
| | | Terbuthylazine | 0.046 |
| | F44/0055 | Terbuthylazine | 0.018 |
| | F46/0239 | Hexazinone | 0.076 |
| | | Propazine | 0.17 |
| | | Simazine | 0.089 |
| | | Terbuthylazine | 1.2 |

**Table 3** – Characteristics of detected pesticides for the 2014 groundwater survey

| Pesticide | FAO class | Field half-life (days) | $K_{oc}$ (ml $g^{-1}$) | GUS score | No. of wells | Range (mg $m^{-3}$) | MAV (mg $m^{-3}$)[a] |
|---|---|---|---|---|---|---|---|
| *Herbicides* | | | | | | | |
| Acetochlor | Amide | 20 (13.5-55) | 200 (74-428) | 2.21 T | 3 | 0.021-0.071 | |
| Atrazine | Triazine | 173 (13-402) | 147 (38-288) | 4.10 L | 1 | 0.017 | 2 |
| Bentazone | Other herbicide | 27 (7-98) | 35 | 3.52 L | 4 | 0.11-0.17 | 400 |
| Bromacil | Uracil | 207 (61-349) | 32 (2-72) | 5.78 L | 1 | 3.4 | 400 |
| DEA | Triazine | [b] | [b] | [b] | 1 | 0.08 | |
| DET | Triazine | [b] | [b] | [b] | 2 | 0.1-0.71 | |
| Dinoseb | Dinitrophenol herbicide | 100 | 124 | 3.80 L | 1 | 0.23 | 7[c] |
| Diuron | Urea derivative | 372 | 477 (418-560) | 3.40 L | 1 | 0.21 | 20 |
| Hexazinone | Triazine | 79 (30-180) | 54 (34-74) | 4.3 L | 3 | 0.039-0.21 | 400 |
| Metolachlor | Amide | 141 (12-292) | 70 (22-307) | 4.63 L | 2 | 0.027-0.057 | 10 |
| Metribuzin | Triazine | 47 (23-128) | 52 (3-95) | 3.82 L | 1 | 0.06 | 70 |
| Propazine | Triazine | 123 (35-347) | 161 (100-600) | 3.75 L | 2 | 0.17-3.1 | 70 |
| Simazine | Triazine | 89 (26-186) | 140 (103-230) | 3.61 L | 5 | 0.015-0.099 | 2 |
| Terbacil | Uracil | 200 (50-250) | 63 (41-120) | 5.06 L | 1 | 0.84 | 40 |
| Terbuthylazine[d] | Triazine | 86 (34-193) | 110 (42-575) | 3.79 L | 16 | 0.012-1.39 | 8 |
| *Insecticides* | | | | | | | |
| Dieldrin | Organochlorine | 1000 (225-1260) | 12000 (4000-39000) | -0.24 N | 2 | 0.008-0.043 | 0.04 |
| Endosulfan I | Other insecticide | 60 (4 – 200) | 12,400 | -0.17 N | 1 | 0.01 | 20 |
| Endosulfan II | Other insecticide | [e] | [e] | | 1 | 0.022 | |
| Endosulfan sulphate | Other insecticide | [e] | [e] | | 1 | 0.075 | |
| *Fungicides* | | | | | | | |
| Procymidone[d] | Dicarboximide | 850 (56-950) | 352 (160-724) | 4.26 L | 1 | 0.08 | 700 |
| Metalaxyl | Other fungicide | 77 (27-296) | 171 (30-284) | 3.33 L | 1 | 0.017 | 100 |

Field half-lives and Koc values for topsoil are from the United States National Pesticide Information Center Pesticide Properties Database: selected value with range in parentheses. (FAO = Food and Agriculture Organisation. $K_{oc}$ = soil organic carbon sorption coefficient. Groundwater ubiquity score (GUS) classes: L = leacher; T = transitional; N = non-leacher. DEA = desethyl atrazine; DET = desethyl terbuthylazine). [a]Maximum acceptable value (MAV) from Drinking Water Standards for New Zealand (Ministry of Health 2008); [b]Values for DEA and DET probably similar to atrazine (Ciba-Geigy Corporation, 1993; Close and Rosen, 2001); [c]Health value from the Australian Drinking Water Guidelines (Australian Government, 2004); [d]$K_{oc}$ and half-life values from Close *et al.* (2008); [e]values probably similar to Endosulfan I.

Twenty-one different pesticides and pesticide metabolites were detected in the wells sampled (Table 3). Herbicides were the pesticide group most commonly detected with 15 different herbicides found, followed by insecticides (4), and fungicides (2). There was a total of 51 pesticide detections and of these, 44 (86%) were herbicides with 31 detections of triazine herbicides. Terbuthylazine (16 wells) and simazine (5 wells) were the two most frequently found pesticides (Table 3). Dieldrin, an insecticide, was detected in two wells and three endosulfan-related insecticides were detected in well 70-22 (Table 2), along with multiple herbicides.

The higher number of herbicide detections compared with insecticides and fungicides is consistent with estimates that herbicides comprise at least 60% of the total amount of pesticides sold annually in New Zealand (Manktelow *et al.*, 2005). In addition, although mobility and degradation properties of herbicides vary widely according to their chemical classification (Weber, 1994), they are often more polar and water soluble than insecticides and fungicides, making it more likely that they will leach to groundwater. The higher frequency of herbicide detection (compared with insecticides and fungicides) in New Zealand groundwater is consistent with results of groundwater surveys undertaken in Norway (Haarstad and Ludvigsen, 2007), Spain (Hernandez *et al.*, 2008) and the United States (Kolpin *et al.*, 1998).

The triazine group of herbicides was the most frequently detected, comprising 61% of all the pesticide detections, consistent with the percentage for triazine detections (50–76%) in the previous five surveys (Close *et al.*, 2001; Close and Skinner, 2012) (Table 4). Three pesticide metabolites or transformation products from triazines were detected in this survey (Table 3; see Appendix 1 for list of metabolites

**Table 4 –** Summary statistics for the seven national surveys of pesticides in groundwater in New Zealand

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

analysed for). Pesticide metabolites from triazines have been detected at varying rates in previous surveys. One metabolite was detected in the 2010 survey, no metabolites were detected in the 2006 survey, six metabolites were detected in the 2002 survey (Close and Flintoft, 2004) and 12 metabolites were detected in the 1998 survey (Close and Rosen, 2001). Pesticide metabolites can provide useful information as they have been detected in groundwater at higher concentrations and more frequently than the parent compounds in some studies (Steele *et al.*, 2008; Hernandez *et al.*, 2008).

The infrequent detection of insecticides is consistent with the previous national surveys of pesticides in groundwater (Gaw *et al.*, 2008; Close and Rosen, 2001; Close and Flintoft, 2004). All the insecticide detections were from wells in the Waikato region in this survey, although previous surveys have detected insecticides in groundwater from other regions. The Waikato region has had an extensive monitoring programme for pesticides in groundwater over many years and dieldrin has been detected and investigated in the past (Hadfield and Smith, 1999). The detected insecticides all have very high soil organic carbon sorption coefficient ($K_{oc}$) values corresponding to low mobility (Table 3) but have very long half-lives and dieldrin was used extensively in the past all over New Zealand (Boul, 1995; Close *et al.*, 2001). The pesticide half-lives listed in Table 3 are for the topsoil and persistence of pesticides can be ten times those values in the vadose and groundwater environments (Levy and Chesters, 1995).

The MAVs for the detected pesticides in drinking water range from 0.04–700 mg $m^{-3}$ (Table 3) and most of the pesticides detected were at concentrations of less than 1% of the MAV, consistent with previous surveys (Close, 1993; 1996; Close and Rosen, 2001; Close and Flintoft, 2004). Concentrations of only four of the 51 pesticide detections exceeded 1 mg $m^{-3}$, and only one of the positive pesticide detections, dieldrin, exceeded its corresponding MAV. Dieldrin was detected in one well at a concentration of 0.043 mg $m^{-3}$, just above the MAV of 0.04 mg $m^{-3}$ for drinking water. Dieldrin was used in New Zealand primarily for the government-required control of ectoparasites on sheep in the 1960s. 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-1960s, 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 and Smith (1999) carried out an investigation into dieldrin in groundwater in the Waikato region. Their results indicated that dieldrin contamination could be widespread and that concentrations in shallow groundwater (about 5 m below ground level) could be expected to increase, even though usage had ceased 30-40 years previously. The low MAV for dieldrin (0.04 mg $m^{-3}$, which is actually for the sum of dieldrin and aldrin) based on its toxicity means that concentrations in groundwater just above the detection limit can exceed the MAV for drinking water.

Terbuthylazine was the most commonly detected pesticide, being detected in 16 wells from five regions at concentrations ranging from 0.012 to 1.39 mg $m^{-3}$. The highest level detected, 1.39 mg $m^{-3}$, was 17% of the MAV (Table 3). This well had been sampled previously in 2002 with no pesticides detected on that occasion. Another well had terbuthylazine detected at 1.2 mg $m^{-3}$, but all other detections of terbuthylazine in the 2014 survey were at concentrations less than 0.2 mg $m^{-3}$. Bromacil and propazine were detected at levels above 1 mg $m^{-3}$ (Tables 2 and 3) but these were only 0.9% and 4.4% of their MAVs, respectively, as their MAVs are much higher than the MAV for terbuthylazine.

The detection limits for the surveys undertaken since 1998 have been lower than the limits for the 1994 and 1990 national surveys by a factor of between 5 and 10, making direct comparison among the seven surveys difficult. If the detection limits for the 1990 and 1994 surveys are applied to the 2014 survey, then pesticides would have been detected in 16 out of the 165 wells sampled (10%), rather than 28 wells (17%). In comparison, 7% of the 162 wells in 2010 would have contained detectable pesticides, 8% of the 163 wells in 2006, 9% of the 133 wells in 2002, 11% of the 95 wells in 1998, 14% of the 118 wells in 1994, and 7% of the 82 wells in 1990, when results are adjusted for higher detection limits (Table 4). These values indicate that a similar percentage of wells had detectable pesticides in each survey once the results were corrected for variable detection limits.

The mobility and degradation characteristics, groundwater ubiquity scores (GUS) and FAO class (FAO, 1996) for each pesticide are also given in Table 3. A review and collation of mobility and degradation values for pesticides has been carried out by the United States National Pesticide Information Center (US NPIC, 2011) and the mobility and degradation values are from this source unless otherwise noted. The selected values listed in this database, plus the range of values in the literature, are given in Table 3. The mobility is represented by the soil organic carbon sorption coefficient ($K_{oc}$). $K_{oc}$ is calculated by measuring the ratio, $K_d$, of sorbed to solution pesticide concentrations after equilibration of a pesticide in a water/soil slurry and then dividing by the weight fraction of organic carbon present in the soil. This assumes that the pesticides are sorbed to the organic matter and not to the clay or mineral content in the soil. High $K_{oc}$ values indicate compounds with high adsorption to soils and low mobility. The soil half-life is the time it would take for half the amount of pesticide to degrade in soil, assuming a first order degradation process. The GUS scores are a simplified assessment of whether a pesticide is likely to leach or not (Gustafson, 1989) and are calculated as:

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

Gustafson (1989) used GUS values greater than 2.8 to indicate that the compound would leach relatively readily and a GUS score of less than 1.8 to indicate a 'non-leacher'. There was a transitional zone between 1.8 and 2.8 where pesticides could leach under favourable conditions. Primi *et al.* (1994) suggested a wider transitional zone with GUS criteria of 1.5 and 3.0 to differentiate leachers and non-leachers and these criteria were used in this study. In the past 20 years there have been a number of more complex indicators to assess whether pesticide leaching is likely under different scenarios. Lindahl and Bockstaller (2012) describe the development of an indicator (I-Phy) that includes the assessment of the likelihood of pesticide movement via preferential flow. It does this by data-mining a comprehensive set of pesticide transport simulations using the MACRO model (Jarvis 1994), which considers a range of weather and soil profile scenarios. These types of indicators provide a much more complete assessment of pesticide transport but also require a substantial increase in resources and the indicator will be relevant to the weather and soil scenarios that have been simulated. For interpretation of the detections of different pesticides in this survey, we have used the simple GUS indicator which depends solely of two pesticide properties but acknowledge that the actual leaching observed depends on many factors, including the soil type, timing and method of application, weather, and crop characteristics.

GUS values could be calculated for 17 of the pesticides detected (Table 3), and indicated that 12 were leachers, three

were transitional, and two were non-leachers. The two non-leacher pesticides were insecticides, namely dieldrin, which was widely used and is very persistent, as discussed above, and endosulfan (and related compounds). Endosulfan is an organochlorine but not nearly as persistent as dieldrin. It was used in New Zealand from the 1960s onwards to control insects in crops such as potatoes, citrus and berry fruit, and on turf for earthworm control. Its use declined from the mid-1990s to mid-2000s and it was de-registered by ERMA in December 2008.

Procymidone, a fungicide, has been detected in one or two wells in six of the seven national surveys, including this survey, and has also been detected in some regional investigations of pesticides in groundwater (Hadfield and Smith, 1999). Procymidone, reported to have a $K_{oc}$ value of 1500 ml $g^{-1}$ and a soil half-life of 15 days (USDA, 2005) and therefore is not expected to leach to groundwater, was included in a series of field trials (Close *et al.*, 2008) after its detection in the 1990 survey. The field trials for three New Zealand soils gave a median $K_{oc}$ value of 352 ml $g^{-1}$ and a median soil half-life of 850 days. Thus procymidone is much more likely to leach from New Zealand soils than would have been expected from previous literature values. The GUS score calculated using the new leaching parameters (Table 3) indicates that procymidone is likely to leach in New Zealand conditions.

There is only one well that has been sampled in all seven surveys, 11 wells have been sampled in six surveys, 36 wells have been sampled in five surveys and 52 wells have been sampled in four surveys. Of the 100 wells that have been sampled on four or more surveys, using the sum of all pesticides detected as the comparison measure, 56 wells had no pesticides detected for any of the surveys. There were no wells that showed a significant ($p < 0.05$) increasing trend in total pesticide concentrations and there were two wells (2%) that showed a significant ($p < 0.05$) decreasing trend in total pesticide concentrations. One of these wells (F46/0239) is associated with long-term contamination around Edendale, Southland that was further investigated by Hughes (2000). He found a number of sources were likely involved in the groundwater contamination including a nursery, horticultural activities and spraying for weed control around the railway yards. The other well (P28w/2600) was a very shallow, large diameter well that had high levels of simazine (1.6 mg $m^{-3}$) detected in 1994. These levels have steadily decreased in subsequent surveys and the well was not sampled in 2014. There were a further four wells that showed increasing levels, and a further six wells that showed decreasing total pesticide concentrations at lower significance levels ($0.05 < p < 0.20$). Eight wells (8%) had positive detections of pesticides for each survey sampled but with no trend. Overall, this indicates that the detections of pesticides is similar to previous surveys with no overall increasing or decreasing trend in total levels of pesticides detected.

The small number of wells showing significant trends in total pesticide concentrations over time is explained, at least partially, by the small number of surveys (7) even though these have taken place over a 24-year period. There are slightly more wells showing decreases in total pesticide concentrations compared to those showing increases, but the majority of wells show no change in total pesticide concentrations with time. About half of all wells that had been sampled in at least four surveys had no pesticides detected in any survey. 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 used then the 1994 survey had the highest frequency of pesticide detections (Table 4). However,

detection frequencies of pesticides have been fairly constant over the last four surveys, ranging between 17% and 24% for the unadjusted detection limits and between 7% and 10% for the higher detection limits. The timing of the sampling of wells for the surveys has been focussed on the October to December (late spring to early summer) period and has been similar for all surveys. Although seasonal patterns in pesticide concentrations are often observed for particular wells (e.g., Hadfield and Smith, 1999; Close *et al.*, 2001), variability for different wells with respect to the travel times through the vadose (unsaturated) zone and groundwater systems, together with the difference in pesticide mobility and persistence characteristics, means that maximum concentrations in different wells could be observed throughout the year. The data comparing wells sampled in multiple surveys indicate that there have been fairly constant levels and detection frequencies for pesticides in groundwater over the past 16 years for the assayed pesticides.

Some wells have shown detections of the same pesticide over multiple surveys. Figure 2 shows selected wells where the same

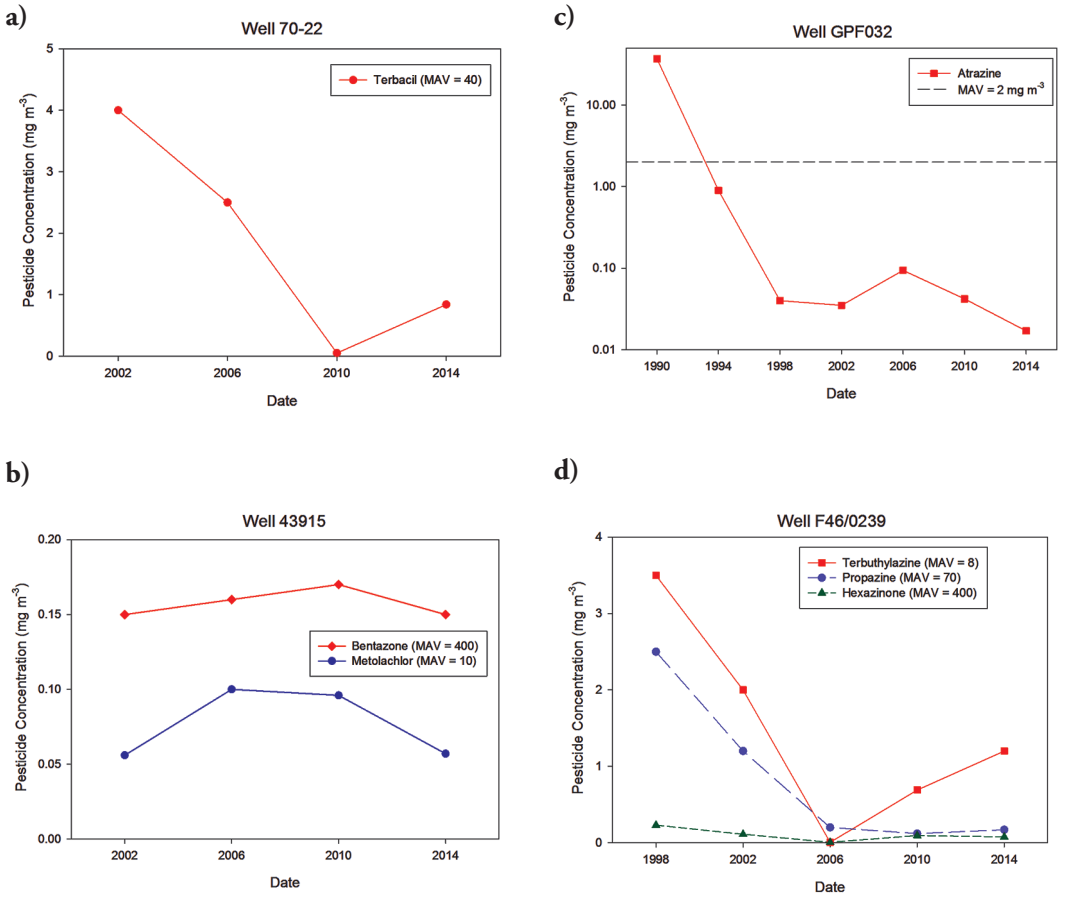


**Figure 2** - Time series plots for selected wells and pesticides. Two values less than detection limit for well F46/0239 in 2006 were set to zero for plotting. Note that the y-axis is a log scale for well GPF032 (atrazine). The MAV for each pesticide is inserted in the legend

pesticide has been detected in the well over four or more surveys. The wells were selected to demonstrate this for seven different pesticides, with between one and three pesticides for each well. The longevity for these pesticide detections is probably related to both the length of pesticide application (with consistent land use and management taking place in the capture zone of each well), and the increased persistence of pesticides once they leach from the soil zone into the vadose zone and groundwater system, as shown by Pang and Close (1999) and Levy and Chesters (1995).

A limitation of these types of pesticide surveys are the budgetary constraints and the availability of analytical tests, meaning that every pesticide that is registered for use in New Zealand could not be included in this survey. For example, the non-selective herbicide glyphosate is widely used in New Zealand (Manktelow *et al.*, 2005) but was not included in the current survey as it requires a separate extraction method that put it beyond the budget for this survey.

### Effects of groundwater parameters and aquifer confinement status

A range of groundwater factors, including well design and depth, land use, aquifer type, and climate, can make groundwater more or less vulnerable to pesticide contamination (Worrall and Kolpin, 2004; Close *et al.*, 2001). The relationships between groundwater parameters and the presence/absence of pesticides were investigated using *t*-tests (Table 5). Table 5 also summarises the means and standard deviations for the groundwater parameters. There were significant differences for nitrate concentrations, pH, well depth and well diameter between wells with and wells without detected pesticides. Wells with pesticide detections had higher nitrate concentrations, lower pH values, shallower well depths and larger well diameters compared to wells with no pesticides detected. As most pesticide contamination results from land surface recharge, shallow groundwaters are expected to be more contaminated and wells screened at greater depth will tend to be much less contaminated. There was a bimodal distribution in well diameters with most wells (80%) being less than 250 mm in diameter but there was also a group of larger diameter (800–1500 mm) wells which were shallow (maximum depth = 24.4 m) and had a higher frequency of pesticide detections. The wells with diameters less than 250 mm had no significant correlation with well depth.

**Table 5 –** Summary of *t*-test results between groundwater parameters and the presence/absence of pesticides (* significant at $p < 0.05$; # data were log-transformed before analysis; untransformed mean and SD are shown in the table.)

| Variable | Pesticide absent | | | Pesticide detected | | | *t* | *P* |
|---|---|---|---|---|---|---|---|---|
| | *n* | Mean | SD | *n* | Mean | SD | | |
| Conductivity (mS $m^{-1}$)# | 136 | 25.7 | 15.8 | 28 | 28.2 | 28.0 | -0.31 | 0.76 |
| Dissolved oxygen (g $m^{-3}$) | 116 | 5.34 | 3.55 | 23 | 5.92 | 2.40 | -0.98 | 0.33 |
| Nitrate-N (g $m^{-3}$)# | 111 | 5.33 | 6.35 | 19 | 7.33 | 4.94 | -4.70 | 0.000* |
| pH | 132 | 6.56 | 0.56 | 28 | 6.20 | 0.53 | 3.09 | 0.002* |
| Temperature (°C) | 136 | 14.9 | 1.46 | 28 | 14.7 | 2.29 | 0.57 | 0.58 |
| Well depth (m)# | 135 | 19.6 | 15.5 | 26 | 15.5 | 17.8 | 2.45 | 0.015* |
| Well diameter (mm)# | 129 | 234 | 291 | 26 | 502 | 482 | -2.13 | 0.042* |

Pesticides and nitrogen fertiliser (which then leaches as nitrate) are often used concurrently on horticultural and agricultural land. Nitrate has been proposed as a possible indicator of likely pesticide contamination (Close *et al.*, 2001). The pattern of higher nitrate concentrations being associated with pesticide detections was also observed in the 1998, 2002 and 2010 surveys (Close and Rosen, 2001; Close and Flintoft, 2004; Close and Skinner, 2012).

The aquifer confinement status was known for 138 out of 165 wells. Pesticides were detected in 24 wells from unconfined aquifers (out of a total 86 unconfined wells), in one well from a semi-confined aquifer (18 wells in total) and in three wells from aquifers with unknown status (34 wells in total with unknown status). No pesticides were detected in the nine wells sampled from confined aquifers. There were more pesticide detections in the unconfined aquifers than would be expected on the basis of the numbers of wells sampled from these aquifers, as compared with the semi-confined and confined aquifers, although the differences were not statistically significant ($\chi^2 = 5.12$, $p = 0.08$, likelihood ratio chi-square test). Unconfined aquifers by definition are more likely to become contaminated by pesticides because they do not have an overlying impermeable layer that prevents contaminants from infiltrating into the aquifer, which results in less protection.

## Summary and conclusions

A total of 165 wells were sampled as part of the 2014 national survey of pesticides in groundwater. Pesticides were detected in 28 wells (17%), with 10 of these wells (6%) having two or more pesticides detected. The maximum number of pesticides detected in one well was seven. There were one or more wells with pesticides detected in 6 of the 13 participating regions. Pesticides were not detected in sampled wells from Hawkes Bay (12 wells), Taranaki (5 wells), Horizons (Manawatu-Wanganui) (23 wells), Wellington (11 wells), Marlborough (17 wells), Canterbury (5 wells), and Otago (8 wells). A total of 21 different pesticides were detected, with most concentrations being less than 0.1 mg $m^{-3}$. Herbicides were the most frequently detected pesticide group with four insecticides and two fungicides also detected. Levels of only four of the 51 pesticide detections exceeded 1 mg $m^{-3}$. Only one well contained a pesticide (dieldrin) at a concentration greater than the MAV for drinking water. The next highest detection relative to the MAV was for terbuthylazine, at 17% of the MAV, with the remainder of detections being less than 5% of the MAV.

There were significant differences for nitrate concentrations, pH, well depth and well diameter between wells with and wells without detected pesticides. Wells with pesticide detections had higher nitrate concentrations, lower pH values, shallower well depths and larger well diameters compared to wells with no pesticides detected. There were more pesticide detections in the unconfined aquifers than would be expected on the basis of the numbers of wells sampled from these aquifers, as compared with the semi-confined and confined aquifers, although the differences were not statistically significant.

Comparisons with earlier surveys indicate similar levels of pesticide detections in groundwater over the last 12 years, with higher levels of detections before that time. The majority of wells sampled in each national survey have not had pesticides detected but where detected, the concentrations of pesticides are mostly very low.

## Acknowledgements

This study was funded by the regional and unitary authorities that manage groundwater resources in New Zealand. We are grateful

for the comments by Liping Pang and Chris Nokes (ESR) and two anonymous reviewers who improved the quality of this paper.

## References

APHA. 2005: *Standard methods for the examination of water and wastewater*. 21st ed. American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, D.C.

Australian Government. 2004: *Australian Drinking Water Guidelines*. National Health and Medical Research Council and Natural Resource Management Ministerial Council, Australia.

Boul, H.L. 1995: DDT residues in the environment – a review with a New Zealand perspective. *New Zealand Journal of Agricultural Research 38*: 257-277.

Ciba-Geigy Corporation. 1993: *Summary of toxilogical data on atrazine and its chlorotriazine metabolites*. Attachment 12, 56 FR 3526.

Close, M.E. 1993: Assessment of pesticide contamination of groundwater in New Zealand. II. Results of groundwater sampling. *New Zealand Journal of Marine and Freshwater Research 27(2)*: 267-273.

Close, M.E. 1996: Survey of pesticides in New Zealand groundwaters 1994. *New Zealand Journal of Marine and Freshwater Research 30(4)*: 455-461.

Close, M.; Flintoft, M. 2004: National Survey of Pesticides in Groundwater 2002. *New Zealand Journal of Marine and Freshwater Research 38(2)*: 289-299.

Close, M.E.; Lee, R.; Sarmah, A.K.; Pang, L.; Dann, R.L.; Magesan, G.N.; Watt, J.P.C.; Vincent, K.W. 2008: Pesticide sorption and degradation characteristics in New Zealand soils – a synthesis from seven field trials. *New Zealand Journal of Crop and Horticultural Science 36*: 9-30.

Close, M.E.; Rosen, M.R. 2001: 1998/99 National Survey of Pesticides in Groundwater using GCMS and ELISA. *New Zealand Journal of Marine and Freshwater Research 35(2)*: 205-219.

Close, M.E.; Rosen, M.R.; Smith, V.R. 2001: Fate and transport of nitrates and pesticides in New Zealand's aquifers. *In:* Rosen, M.R.; White, P.A. (*eds.*) *Groundwaters of New Zealand.* New Zealand Hydrological Society, Wellington, New Zealand.

Close, M.E.; Skinner, A. 2012: Sixth national survey of pesticides in groundwater in New Zealand. *New Zealand Journal of Marine and Freshwater Research 46*: 443-457.

Davies, H. 2001: Groundwater and Health. *In:* Rosen, M.R.; White, P.A. (*eds.*) *Groundwaters of New Zealand.* New Zealand Hydrological Society, Wellington, New Zealand.

FAO. 1996: Disaggregated data sets for pesticides. FAO Pesticides Database. UN Food and Agricultural Organisation, Rome.

Gaw, S.; Close, M.E.; Flintoft, M.J. 2008: Fifth national survey of pesticides in groundwater in New Zealand. *New Zealand Journal of Marine and Freshwater Research 42*: 397-407.

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

Hadfield, J.; Smith, D. 1999: *Pesticide contamination of groundwater in the Waikato region*. Environment Waikato Technical Report 1999/9. Environment Waikato, Hamilton.

Haarstad, K.; Ludvigsen, G.H. 2007: Ten years of pesticide monitoring in Norwegian Groundwater. *Ground Water Monitoring and Remediation 27(3)*: 75-89.

Hernandez, F.; Marin, J.M.; Pozo, O.J.; Sancho, J.V.; Lopez, F.J.; Morell, I. 2008: Pesticide residues and transformation products in groundwater from a Spanish agricultural region on the Mediterranean Coast. *International Journal of Environmental Analytical Chemistry 88(6)*: 409-424.

Hughes, B. 2000: *Edendale pesticide investigation report 2000*. Southland Regional Council Report 2000-14. Southland Regional Council, Invercargill.

Jarvis, N. 1994: The MACRO model (version 3.1): Technical description and sample simulations. *Reports and Dissertations 19*, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Kolpin, D.W.; Barbash, J.E.; Gilliom, R.J. 1998: Occurrence of pesticides in shallow ground water of the United States: initial results from the National Water-Quality assessment programme. *Environmental Science and Technology 32(2)*: 558-566.

Lindahl, A.; Bockstaller, C. 2012: An indicator of pesticide leaching risk to groundwater. *Ecological Indicators 23*: 95-108.

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

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

Ministry for Primary Industries. 2015: ACVM register of agricultural chemicals. https://eatsafe.nzfsa.govt.nz/web/public/acvm-register. Accessed May 2015.

Ministry for the Environment. 2010: *Update of water allocation data and estimate of actual water use of consented takes 2009-10*. Ministry for the Environment Report CR 100. Prepared by AquaLinc Research Ltd.

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

NATA. 2012: Guidelines for the validation and verification of quantitative and qualitative test methods. *NATA Technical Note 17*. August 2004, amended and reissued March 2012. National Association of Testing Authorities, Australia.

Pang, L.; Close, M.E. 1999: Attenuation and transport of atrazine and picloram in an alluvial gravel aquifer: a tracer test and batch study. *New Zealand Journal of Marine and Freshwater Research 33:* 279-291

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

Rothery, P. 2000: Basic Concepts. *In:* Sparks, T. (*ed.*) *Statistics in Ecotoxicology.* John Wiley & Sons Ltd., Chichester.

Steele, G.V.; Johnson, H.M.; Sandstrom, M.W.; Capel, P.D.; Barbash, J.E. 2008: Occurrence and fate of pesticides in four contrasting agricultural settings in the United States. *Journal of Environmental Quality 37(3)*: 1116-1132.

Taranaki Regional Council. 1995: *Report on an investigation of pesticides in shallow groundwater in Taranaki*. Technical Report 95-14.

USDA. 2005: The ARS pesticide properties database. www.arsusda.gov/acsl/ppdb.html accessed March 2005. Currently available (2016) at: https://www.ars.usda.gov/docs/pesticide-properties-database/

USEPA. 1989: *Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)*. EPA 600/S 4-89/010. United States Environmental Protection Agency.

US NPIC. 2011: United States National Pesticide Information Center pesticide properties databases. http://npic.orst.edu, accessed in May 2015.

Weber, J.B. 1994: Properties and behaviour of pesticides in soil. *In:* Honeycutt, R.C.; Schabacker, D.J. (*eds.*) *Mechanisms of pesticide movement into ground water.* Lewis Publishers.

Worrall, F.; Kolpin, D.W. 2004: Aquifer vulnerability to pesticide pollution – combining soil, land-use and aquifer properties with molecular descriptors. *Journal of Hydrology 293(1-4)*: 191-204.

# Appendix 1

List of pesticides and limits of detection (LD). LD is calculated based on the standard deviation of the blank (NATA, 2012). Units are mg $m^{-3}$ (ppb). Note that the samples from Waikato Regional Council were analysed at Hill Laboratories with slightly lower LDs.

* indicates pesticides only analysed by Hill Laboratories

| Pesticide screen | LD | Pesticide screen | LD |
|---|---|---|---|
| *Organochlorine pesticides* | | desethyl terbuthylazine | 0.04* |
| aldrin | 0.02 | desisopropyl atrazine | 1.0 |
| BHC-α | 0.01 | diuron | 0.04* |
| BHC-β | 0.01 | hexazinone | 0.02 |
| BHC-γ (lindane) | 0.01 | linuron | 1.0 |
| BHC-δ | 0.01 | metolachlor | 0.02 |
| α-chlordane | 0.02 | molinate | 0.02 |
| γ-chlordane | 0.02 | metribuzin | 0.02 |
| *p,p'*-DDE | 0.01 | metalaxyl | 0.01 |
| *p,p'*-DDD | 0.01 | norflurazon | 0.02 |
| *p,p'*-DDT | 0.01 | oryzalin | 2.0 |
| dieldrin | 0.01 | oxadiazon | 0.01 |
| endosulfan I | 0.02 | pendimethalin | 0.02 |
| endosulfan II | 0.04 | propanil | 0.02 |
| endosulfan sulphate | 0.02 | propazine | 0.01 |
| endrin | 0.02 | pyriproxyfen | 0.5 |
| endrin aldehyde | 0.04 | simazine | 0.01 |
| endrin ketone | 0.04 | terbacil | 0.02 |
| heptachlor | 0.02 | terbuthylazine | 0.01 |
| heptachlor epoxide | 0.03 | trifluralin | 0.02 |
| hexachlorobenzene | 0.1 | *Acid herbicides* | |
| methoxychlor | 0.02 | 2,4-D | 0.1 |
| *cis* permethrin | 0.01 | 2,4-DB | 0.1 |
| *trans* permethrin | 0.01 | 2,4,5-T | 0.1 |
| procymidone | 0.02 | 2,4,6-trichlorophenol | 0.5 |
| vinclozin | 0.02 | 3,5-dichlorobenzoic acid | 0.1 |
| *Organophosphorus pesticides* | | acifluorfen | 0.1 |
| azinphos methyl | 0.4 | bentazone | 0.1 |
| diazinon | 0.01 | bromoxynil | 0.1 |
| chlorpyrifos | 0.02 | dicamba | 0.1 |
| dimethoate | 0.4 | dichlorprop | 0.1 |
| pirimiphos methyl | 0.02 | dinoseb | 0.1 |
| *Organonitrogen herbicides* | | fenoprop | 0.1 |
| acetochlor | 0.02 | MCPA | 0.1 |
| alachlor | 0.02 | MCPB | 0.1 |
| atrazine | 0.01 | mecoprop | 0.1 |
| bromacil | 0.03 | triclopyr | 0.1 |
| carbofuran | 0.9 | picloram | 0.1 |
| cyanazine | 0.02 | pentachlorophenol | 0.1 |
| desethyl atrazine | 1.0 | triclopyr | 0.1 |

Manuscript received ?????; accepted for publication ?????