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A baseline assessment of emerging organic contaminants in New Zealand groundwater

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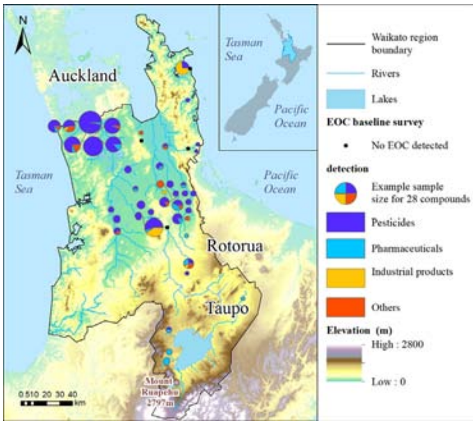
HIGHLIGHTS

- New Zealand first emerging organic contaminants in groundwater survey (regional)
- Novel EOC screen approach and site selection using groundwater mean residence time
- Ubiquitous EOC occurrence with 28 compounds measured above the EU pesticide MAC
- Review and recommendations on current monitoring and laboratory capability

GRAPHICAL ABSTRACT



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ABSTRACT

Emerging organic contaminants (EOCs) are manufactured compounds, used for a range of purposes, that are a rising concern for freshwater quality, human and aquatic health. Their occurrence in groundwater has been demonstrated in several international surveys. We conducted the first baseline survey on EOC occurrence in New Zealand groundwater, using a wide-screening approach (723 compounds) and a novel stratified to mean residence time (MRT) randomised design to inform future monitoring. A total of 61 sites were sampled: 51 baseline sites from the State of the Environment (SOE) network in the Waikato region and 10 targeted sites located in the vicinity of known EOC sources for comparison. EOCs were detected at 91% of the baseline sites at concentrations ranging from 0.1 to 11,000 $\text{ng}\cdot\text{L}^{-1}$. Multiple groups of EOCs were encountered: pesticides (48 compounds), pharmaceuticals (11), industrial (10), preservatives/food additives (3) and personal care products (1). Similar diversity and concentration range of EOCs were observed at the targeted sites, with the addition of drugs of abuse and life-style compounds. EOC detections occurred across young (1–11 yrs. MRT), intermediate (11–50 yrs. MRT) and old (50–250 yrs. MRT) groundwaters with higher concentrations and more types of EOCs detected at sites in the youngest age category. Concentrations of the 73 compounds detected at baseline sites were comparable to those found in overseas groundwaters with 28 compounds measured at concentrations greater than the EU maximum

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admissible concentration for pesticides. We used the survey results to: review current pesticide monitoring; propose complementary monitoring; identify potential EOC groundwater tracers and identify compounds for which cost-effective national laboratory capability is needed. The Waikato survey results demonstrated ubiquitous occurrence of unmonitored, unregulated EOCs in groundwater and limitations in using targeted approaches to establish monitoring.

1. Introduction

Emerging organic contaminants (EOCs) comprise an increasingly wide range of manufactured compounds (>950, NORMAN, 2016) that are mostly unregulated and with unknown toxicity risks (Lapworth et al., 2012; Stewart et al., 2016). EOCs include: pharmaceuticals, personal care and veterinary products, industrial compounds, pesticides, food additives, and nano-materials as well as metabolites and transformation products of these. EOCs are classed as "emerging" owing to their recent detection due to related advances in analytical techniques and better monitoring (Lapworth et al., 2012; Lamastra et al., 2016). There is growing concern that the occurrence of EOCs may have adverse effects human and aquatic health, including in the groundwater receiving environment (Lapworth et al., 2012; Stewart et al., 2016). In response, overseas regulatory organisations are implementing voluntary watchlists to inform drinking-water standards (Lapworth et al., 2018a) or placing an increasing number of restrictions and bans on the use of selected EOCs (Lapworth et al., 2012; Carvalho et al., 2015; Lamastra et al., 2016; Stewart et al., 2016). The watchlists aim to prioritise the collection of scientific information to determine suitable risk reduction measures (Carvalho et al., 2015; Lapworth et al., 2018a).

Several studies have shown that EOCs are present in most groundwaters, sometimes in concentrations above 100 $ng \cdot L^{-1}$ (Loos et al., 2010; Jurado et al., 2012; Lapworth et al., 2012; Lapworth et al., 2015; Manamsa et al., 2016). In a comprehensive literature review of the sources, pathways and fate of EOCs in groundwater, Lapworth et al. (2012 and references therein) identified point and diffuse sources for EOCs and their pathways to the environment (Fig. 1). Point sources of EOCs include waste-water, landfills, septic tanks and animal feeding operations (James et al., 2016). Diffuse sources comprise manure and biosolids from sewage processing application to land, surface water via natural and engineered groundwater-surface water interactions, and diffuse leakage from reticulated sewage. Waste-water contaminated groundwaters exhibit the widest range and highest concentrations of compounds, however, specific sources have also been documented, for instance X-ray compound media and certain therapeutic drugs in hospital-derived waste-waters (Ternes and Hirsch, 2000). EOCs can enter groundwater systems via different pathways. This includes leaching through soil along with rainfall recharge, or via recharge from losing reaches of rivers. Surface waters generally contain a wider range and greater concentrations of EOCs than groundwaters (e.g., White et al., 2019).

Once released to the environment, the presence and persistence of EOCs is dependent on each compound's physico-chemical properties, organic matter content (soil and non-saturated zone), total loading, redox conditions, and groundwater residence time (Estévez et al., 2012; Lapworth et al., 2012; Estévez et al., 2016). Some compounds, such as amide EOCs (e.g., carbamazepine and diethyltoluamide) are resistant to natural attenuation in contrast to phenolic and carboxylic compounds (e.g., ibuprofen, triclosan; Nakada et al., 2008; Stuart et al., 2011). Biodegradation of some EOCs has been clearly demonstrated in the soil zone but may be limited in groundwater due to the lower diversity and abundance of microorganisms. Persistence has been shown to be facilitated by the occurrence of reducing conditions for some emerging substances. The use of key properties, such as molecular properties, to discriminate polluting vs. non-polluting substances remains a priority research area.

The multiple sources, entry pathways and persistence of different EOCs allow them to be used as environmental tracers to understand groundwater flow and processes. For instance, pharmaceuticals and personal care products specifically carbamazepine, galaxolide, and sulfamethozale have been proposed as tracers for organic wastewater contaminants (Lamastra et al., 2016; Lim et al., 2017; White et al., 2019). The use of artificial sweeteners has been successfully tested to distinguish between wastewater and non-wastewater sources (Lapworth et al., 2012; Van Stempvoort et al., 2013). Micro-organic contaminants and hydrochemistry were used to trace recharge pathways and quantify changes in groundwater quality (White et al., 2016).

This paper proposes a measurement-driven approach to assess whether EOCs are a concern in New Zealand groundwaters and, if applicable, to recommendations for monitoring including analytical capability development needs. A EOC baseline assessment was performed at

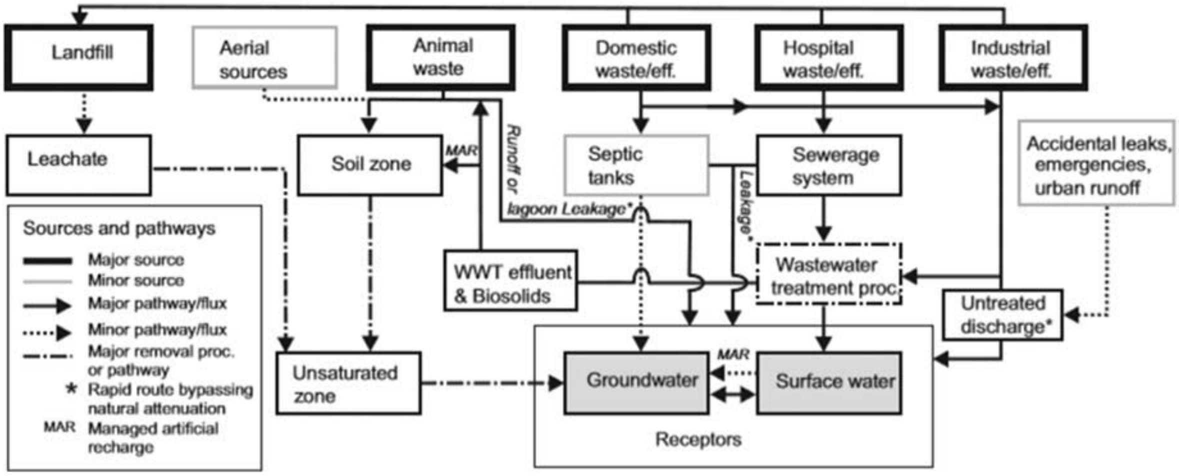

Fig. 1. Schematic diagram using the source-pathway-receptor approach, highlighting potential sources and pathways for groundwater pollution by EOCs (Lapworth et al., 2012). British Geological Survey © UKRI [2012].

the regional scale (Waikato region) using a novel sampling design that combines a randomised stratified site selection with a non-targeted screening approach. Sites from the regional groundwater quality monitoring network were split into equally-distributed mean residence time (MRT) groups, whereby MRT is a key measure of groundwater vulnerability to pollution. Subsequently, an equal number of sampling sites were randomly selected from each MRT group. The wide screening approach (723 compounds) allowed identification, without any source bias, of the different types of EOCs that may be of greatest concern in groundwater. The same analytical suite was also used for samples from selected targeted sites located close to potential EOC sources. This rigorous sampling design will enable the findings from this study to be more generalisable and better suited to inform recommendations for future monitoring, i.e. to help prioritise substances for monitoring and potentially assessing the use of selected EOCs as tracers for contamination from different sources.

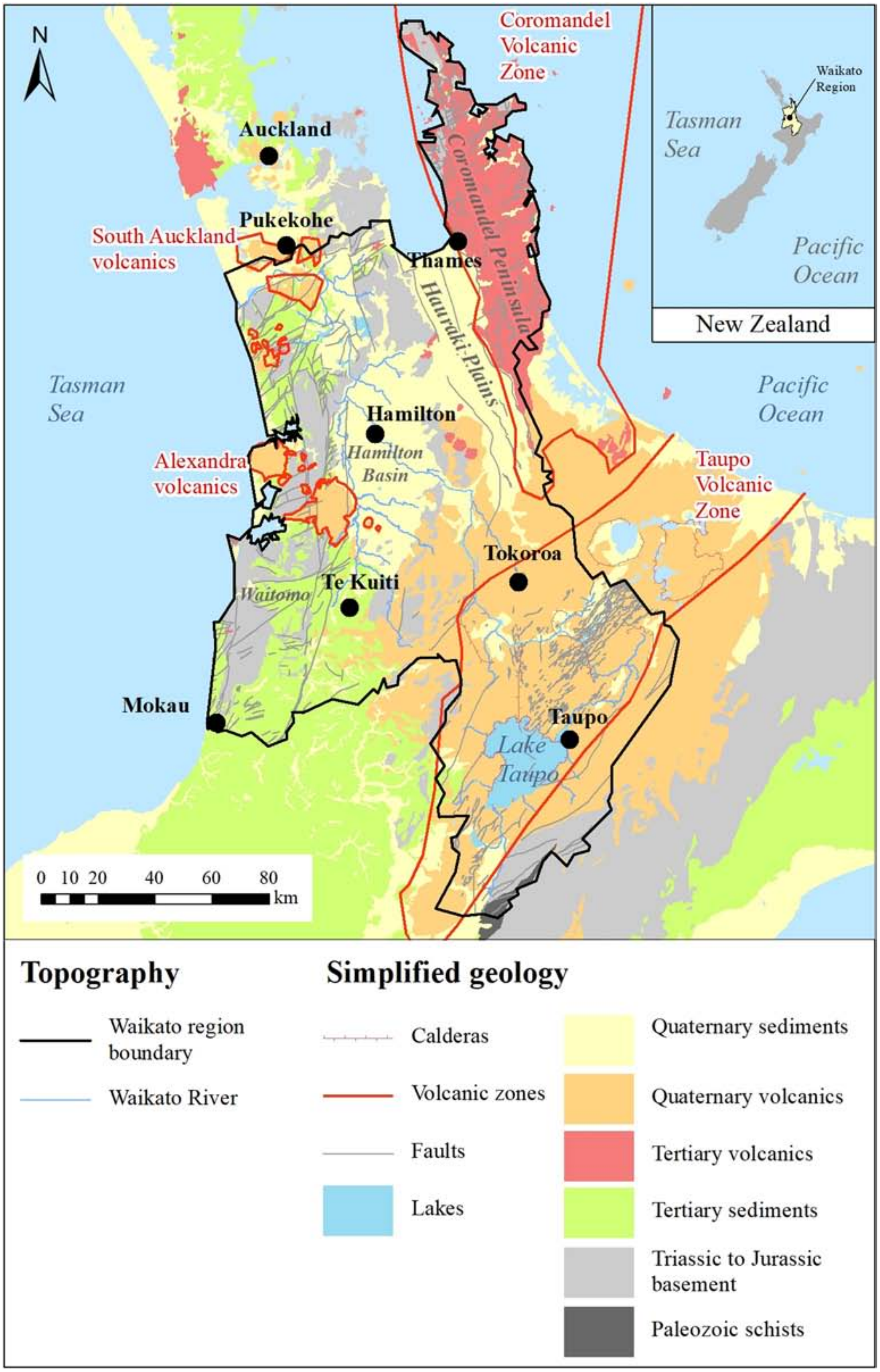

Fig. 2. Simplified geology and main lithology in the Waikato region, New Zealand (Edbrooke, 2001, 2005; Cole and Spinks, 2009).

2. New Zealand context

2.1. Waikato regional hydrogeology

The Waikato region covers a total area of 24,351 km^2 (Fig. 2) and includes the Waikato River, the longest (425 km) river in the country. The region can be divided into five geological units (Fig. 2): Triassic to Jurassic basement, Tertiary volcanics (Coromandel Peninsula), Tertiary sediments (Te Kuiti, Mokau and Pukekohe), Quaternary volcanics (Taupo, Tokoroa and Pukekohe), and Quaternary sediments (Hamilton Basin; Hauraki Plains). Uplift and volcanic activity have strongly shaped the region. Groundwater is a significant resource, comprising about 90% of the region's freshwater volume and is extensively utilised (Hadfield, 2001). The groundwater resource can be characterised by geological units.

The Jurassic basement consists of weakly metamorphosed deep marine sedimentary sequences separated into three fault-bounded blocks. These basement terranes are overlain by a succession of Tertiary to Quaternary sediments and volcanic rocks and are regarded as aquicludes and the hydrogeological basement in the region (Edbrooke, 2001; Edbrooke, 2005; White et al., 2015).

The Tertiary volcanics consist of andesitic, dacitic and rhyodacitic volcanoes (Coromandel and Whitianga groups) emplaced as an active convergence margin propagated through northern New Zealand (e.g., Coromandel Volcanic Zone; Edbrooke, 2001). Fractured rhyolites and pocket coastal sands constitute the aquifers in the Coromandel Peninsula. At their seaward extent they are vulnerable to localized seawater intrusion (Hadfield, 2001).

The Tertiary sediments comprise thick, predominantly marine deposits, such as siltstones, sandstones and limestones of the Te Kuiti and Waitemata groups (White et al., 2015). Although often poorly permeable, the Otorohanga and Orahiri karstic limestones, for example, are significant sources of water in the Waitomo area (Fig. 3). These limestones exhibit the highest density polygonal karst landscape in the world and include the iconic Waitomo Caves. Mean discharges from the largest springs from the limestones range from 1 to 3 $m^3 \cdot s^{-1}$ (Scarsbrook et al., 2008). The Kaawa Formation is an important late Tertiary (Pliocene) aquifer in the South Auckland area. It comprises up to 150 m of weak sandstone with notable shell beds, which is mostly confined with high natural groundwater quality (Hadfield, 2001).

The Quaternary volcanics include back-arc intraplate volcanics including volcanic cones, tuffs rings and lava flows of varying thickness such as Alexandra and South Auckland volcanics in the west, and voluminous ignimbrites and tephra deposits from caldera-forming eruptions (Taupo Volcanic Zone) in the east (Edbrooke, 2005). The complex and highly fractured, basalts aquifers of the South Auckland volcanics include both shallow and deeper confined units important to the Pukekohe area and predominantly overlying the Kaawa Formation. Groundwater in the South Auckland volcanics is of naturally high quality, however, where it is unconfined and extensively used, the groundwater quality is impacted by land use (Hadfield, 2001). In the Taupo Volcanic Zone, the most important aquifers are the Pakaumanu, Whakamaru and Waiotapu ignimbrites (Fig. 3; Hadfield, 2001; Tschritter et al., 2014; White et al., 2015). Groundwater from these ignimbrites is also used for geothermal extraction (Hadfield, 2001). Arsenic concentrations can be relatively high in groundwaters with geothermal influence, exceeding the Maximum Admissible Value (MAV) of the New Zealand Drinking-water Standards (NZDWS) (Ministry of Health, 2008; Hadfield, 2011).

The Quaternary sediments include the highly variable, volcanogenic, Tauranga Group which has been deposited in large thicknesses up to 600 m in the Hamilton Basin and Hauraki Plains. This highly variable Group including sands, gravels, silts, peat and clay constitute large leaky, heterogeneous aquifer systems (Fig. 3). Shallow flood deposits of the Pleistocene Hinuera Formation are extensively used for small water supplies. Deeper braided river deposits (Piako Subgroup) and re-worked non-welded ignimbrite (Walton Subgroup) have been developed for larger supplies in the Hauraki Plains and Hamilton Basin (White et al., 2015). Groundwater quality in the Hauraki Plains is spatially distributed with stronger reducing conditions in the north (Hadfield, 2001). There are reported occurrences of nitrate concentrations above the NZDWS MAV (Hadfield, 2001).

The mid-Quaternary Upper Waikato Lake fine-grained lacustrine sediments (Huka Falls Formation) act as aquicludes and a cap rock to several of the Taupo Volcanic Zone geothermal fields.

2.2. Previous EOC studies

In New Zealand, the uptake of findings from international studies on EOCs has been slow, favouring a guidance-driven approach as opposed to a measurement-based approach. This may reflect the growing but limited domestic analytical capability combined with the large number of EOC compounds in use (Stewart et al., 2016). The reason New Zealand is behind in developing analytical capability is due to a combination of a rapid evolution of analytical equipment and techniques, the lack of appropriate and comprehensive compound-matching databases, and cost-effective sample throughput to ensure viability of laboratories.

Pesticides have been nationally monitored four-yearly in groundwaters since 1990 for a suite including 17 acid herbicides, 23 organo nitrogen herbicides, four organo-phosphorous pesticides and 22 organo chlorine pesticides (Close and Humphries, 2016). Wells for the four-yearly pesticide survey are selected based on aquifer importance, vulnerability and pesticide storage and applications. Since the first pesticide survey in the 1990s, the method and detection limit for the selected compounds have improved and continuous refinement was reported in each survey. The number of wells in the pesticide survey has increased with time, often with the addition of regional survey data, ranging from 82 wells in 1990 to 165 wells in 2014 (Close, 1996; Humphries and Close, 2014). In the most recent report, pesticides were detected at 17% of the sites, with multiple compounds detected at 10 wells. The most frequently detected pesticides were: terbuthylazine (16 wells); simazine (5); bentazone (4); acetochlor (3) and hexazinone (3); desethyl terbuthylazine, dieldrin, metolachlor and propazine (2 wells each). Bromacil, propazine and terbuthylazine were measured above 1000 $ng \cdot L^{-1}$, with the highest concentration recorded for the latter, at 1390 $ng \cdot L^{-1}$. Within the Waikato region, glyphosate and aminomethylphosphonic acid (AMPA) were analysed at 40 wells classed as vulnerable to pesticide contamination in 2017 by Waikato Regional Council. There were no detections of glyphosate and only one occurrence of AMPA at a concentration of 1900 $ng \cdot L^{-1}$ (Hadfield, 2017).

Non-pesticide EOCs are currently not analysed in either the National Groundwater Monitoring Programme or regional State of the Environment (SOE) programmes. In 2017, Tearney (2018) undertook a survey in the Wellington region, sampling 16 wells (including production bores and monitoring bores) sourced from the Waiwhetu aquifer and three rivers. The samples were analysed for 73 semi-volatile and 65 volatile compounds, and seven steroid hormones namely bisphenol-A, 17α-estradiol, 17β-estradiol, estriol, estrone, 17α-ethinylestradiol and triclosan. Bisphenol-A was detected in all groundwater samples and at two of the river sites, with concentrations ranging from 4 to 280 $ng \cdot L^{-1}$ (river samples were 21 and 29 $ng \cdot L^{-1}$, respectively). Of the volatile compounds, only trace levels of toluene were detected, occurring in the river samples and nine groundwater sites. Fluorescent whitening agents were also detected at two wells and in two of the river samples. Guidance on non-pesticides EOC monitoring strategies for New Zealand was first drafted in 2005, focussing on endocrine disruptors (Sarmah et al., 2005). EOCs were selected and prioritised based on the monitoring of substances in marine environment sediments, as this is where existing New Zealand regulations specifically include EOCs (Stewart et al., 2016). The scope was broadened to urban-related EOC research in 2008 (Ahrens, 2008). An update was provided in 2016, including a comprehensive review on work to date on waste-

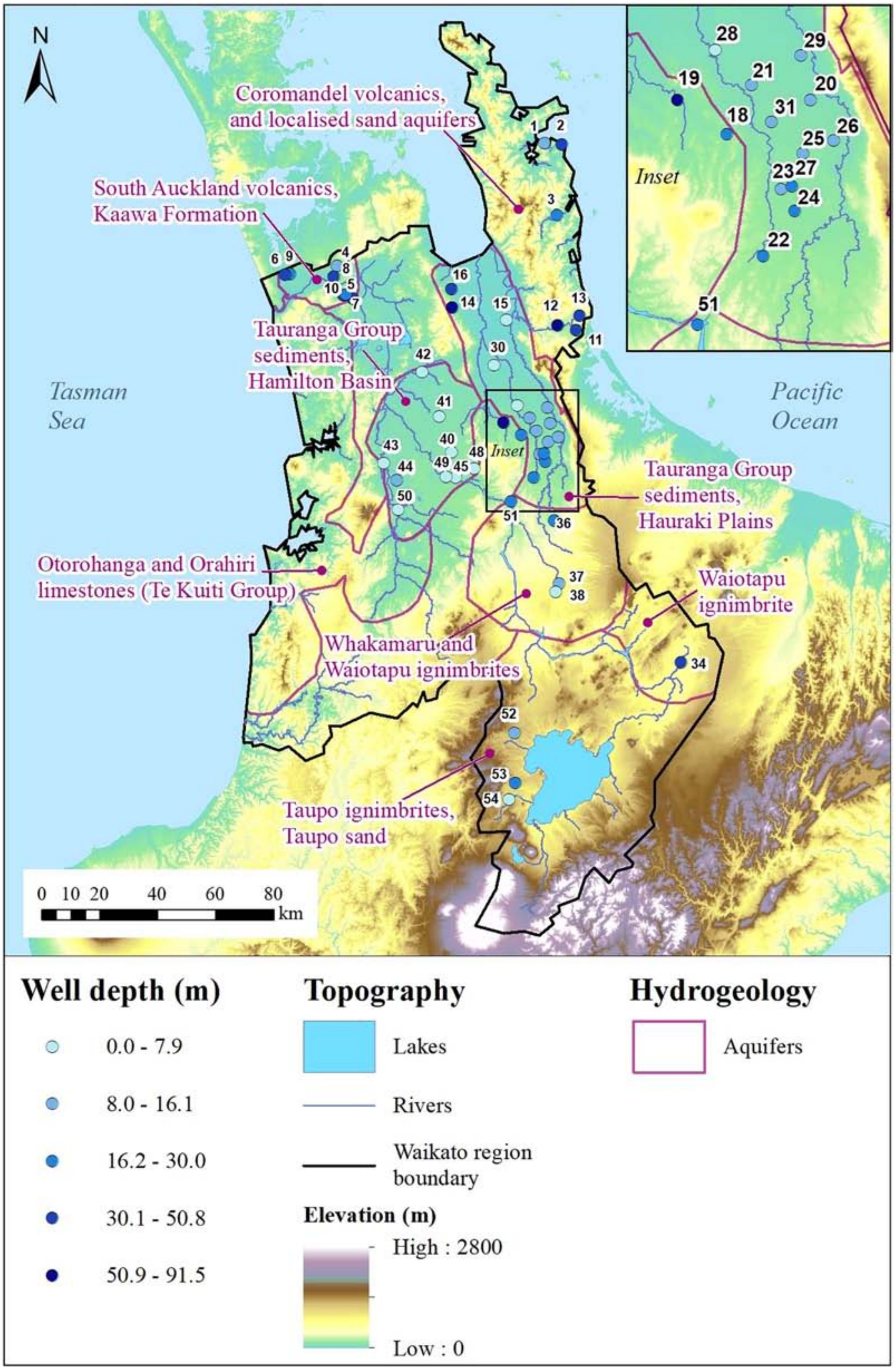

Fig. 3. Locations of sampled SOE sites and mapped aquifers (White, 2001) in the Waikato region.

water treatment effluents, dairy farm effluent, and oestrogen transport through soil (Stewart et al., 2016). In this review, New Zealand-based studies showed that EOC sources and concentrations in receiving environments and biological uptake were similar to those observed globally. A tiered approach was proposed for monitoring, based on source identification first, to reduce possible omission that could occur in targeted surveys of selected compounds (Stewart et al., 2016 and references therein; Northcott et al., 2013; Northcott and Tremblay, 2017). The current New Zealand 5-year programme aims to produce guidelines to manage the risk posed by EOCs, with a strong focus on aquatic system toxicology and aquaculture (Cawthron, 2018). This programme is risk-assessment based, first targeting representative compounds analysed at selected representative locations, then using the results to design a monitoring programme of a refined (presumably shorter) suite of

EOCs at the most impacted sites. However, this strategy will be tailored for a marine sediment contaminant monitoring programme with an urban environment focus (Stewart et al., 2016), and therefore will not be well suited for groundwater environments. Selecting monitoring strategies for EOCs in groundwater has been identified as both a knowledge gap and a research priority regionally and nationally (Tidswell et al., 2012; Moreau and Daughney, 2015; Moreau et al., 2016; Ministry of Business, Innovation, Employment, Science and Innovation, 2017).

3. Data collection and processing

3.1. Sample collection and analysis

Samples from 61 groundwater sites located across the Waikato region (Fig. 3) were collected between April and May 2018. Most (84%) of the sampled sites were randomly selected from the Waikato Regional Council's State of the Environment (SOE) monitoring network to encompass a range of groundwater age and hydrogeological settings (Supplementary Table S1). The remaining samples were from sites with suspected sources of contamination. The age stratification for random site selection consisted of three water age groups: “young” with a mean residence time (MRT) ranging from 1 to 11 years, “intermediate” with MRT ranging from 11 to 50 years, and “old” with MRT ranging from 50 to 250 years. MRTs were derived from tritium and environmental tracer measurements (Stewart and Morgenstern, 2001; Morgenstern and Taylor, 2009; Beyer et al., 2014). The SOE network is designed to characterise groundwater quality state and trends in the region, which makes it a fit-for-purpose and well documented network for baseline characterisation of EOCs.

Samples were also collected at eight groundwater locations close to probable EOC sources e.g., waste-water treatment plant, urban and industrial areas and one site where groundwater was expected to have no contamination. Hereafter these are referred to as targeted sites. Additionally, a treated municipal waste-water sample (further denoted as WWTP) was also collected for comparison. Although the WWTP sample is included in most of the tables, it was excluded from the results and discussion section as it does not represent groundwater. Sampling also included the collection of five blanks (pump tubing, field and laboratory) and three replicates.

Samples were collected following the New Zealand national protocol for SOE groundwater sampling (Daughney et al., 2006). Wells were purged prior to sampling using in-situ pumps (46% of sites), a portable submersible pump (34% of the sites) or a peristaltic pump (2 sites). Following purging of the wells, unfiltered, unpreserved samples were collected in 1 L acetone-rinsed glass bottles that were kept sealed until sampling. The sampler wore nitrile gloves to prevent cross-contamination where applicable, typically at sites located close to EOC source or when the sampler was under medication or had applied personal care products, e.g., sunscreen.

Samples were transported in cold (<4 °C) and dark conditions to the New Zealand Geothermal Analytical Laboratory at GNS Science for solid phase micro-extraction onto pre-conditioned sorbent OASIS ® HLB cartridges provided by the National Laboratory Services (NLS, Starcross, England). Micro-extraction involved running the samples through the cartridges using a multi-channel peristaltic pump and high grade Tygon tubing to minimise plasticizer contamination following the method from White et al. (2017), field-tested by Lapworth et al. (2018b). Micro-extraction was executed under a fume cupboard outside of normal laboratory operation times to minimise cross-contamination. Samples were processed in batches (5 to 6 samples), except for samples expected to have high concentrations of EOCs, which were processed individually to avoid cross-sample contamination.

Processed cartridges were refrigerated until transport and shipped in cold and dark conditions within three days to the NLS where they were analysed using a semi-quantitative target based screen of 723 EOC compounds (list provided in supplementary material, Table S2) by an Agilent Liquid Chromatography/Quadrupole-Time-of-Flight Mass Spectrometry (LC/Q-TOF-MS). This method provides both compound identification and concentrations; however, for a limited number of compounds, only positive detections can be reported. This analytical suite includes compounds currently approved by the New Zealand Inventory of Chemicals (e.g., atrazine, imidacloprid; Environmental Protection Agency, 2018) and non-approved substances (e.g., cotinine, mepronil), some of which are variations of approved compounds (e.g., mecoprop approved form CAS93-65-2, unapproved form CAS 7085-19-0). At the time of writing, this analytical capability both in breadth and detection limit (compound-specific, ranging from 1 to 100 $ng \cdot L^{-1}$) is unmatched by New Zealand laboratories because it relies on an extensive compound database which was developed by NLS through more than ten years of national EOC monitoring by the UK Environment Agency (Civil, 2017).

3.2. Quality assurance

At the beginning and end of each day of sampling, the dedicated pumps (tubing and intake) were thoroughly disinfected with Virkon® and rinsed with Ultrapure water. Two tubing blanks were collected after each rinse. No EOCs were detected in these blanks. A third tubing blank was collected from the peristaltic pump at the end of one sampling day. In this blank, two pesticides were detected, one with a concentration of 100 $ng \cdot L^{-1}$. These pesticides were detected at similar concentrations at the last site that was sampled that day, suggesting a need for a longer period of flushing. In the field blank collected at Site 23, two pesticides were detected that do not match the corresponding groundwater sample. One of these compounds was detected at one other site (Site 49) at a similar concentration, sampled earlier that day (in-situ pump). The sample and the field blank were processed with four other samples, none of the which containing any trace of the pesticide found in the blank. It is therefore unclear how this field blank was contaminated.

A laboratory blank collected during laboratory processing indicated detection of surfactants that are not used in the laboratory. This sample was processed with another four samples, three of which did not have any detectable EOCs, which may indicate a mislabelling error. This is consistent with laboratory notes recording interruption of processing to repair tubing due to a cartridge overfill, which only happened once throughout the entire processing of the survey. The corresponding analyses, as well as blank and duplicates, were removed from the dataset.

Graphical analysis of EOC detections against processing batch, collection date and time and sampler did not show any evidence of cross-contamination for these variables.

3.3. EOC categories assignment

In this study, the term EOC refers to the suites of tested compounds which includes both regulated (e.g., pesticides) and unregulated compounds. For interpretation purposes, the EOCs were categorised into seven groups based on their uses, in accord with published references (Jurado et al., 2012; Lapworth et al., 2012). These are drugs of abuse (8 EOCs), industrial compounds (23), life-style compounds (1), personal care products (3), pesticides (362), pharmaceuticals (307), and preservatives and food additives (4). Some groups comprise only a limited number of compounds, as the LCMS technique used in this study is suited for polar, non-volatile compounds. EOCs with multiple uses, e.g., albendazole (pesticide, veterinary drug and anthelmintic), were nonetheless assigned to just one category for ease of interpretation. The full categorisation is provided in Table S2 for future reference, as there is currently no single database available to consistently categorise EOC compounds. Duplicate and blank analyses were removed from the dataset. Analytical results for each sample are provided in the Table S3, these include blanks and replicate analyses.

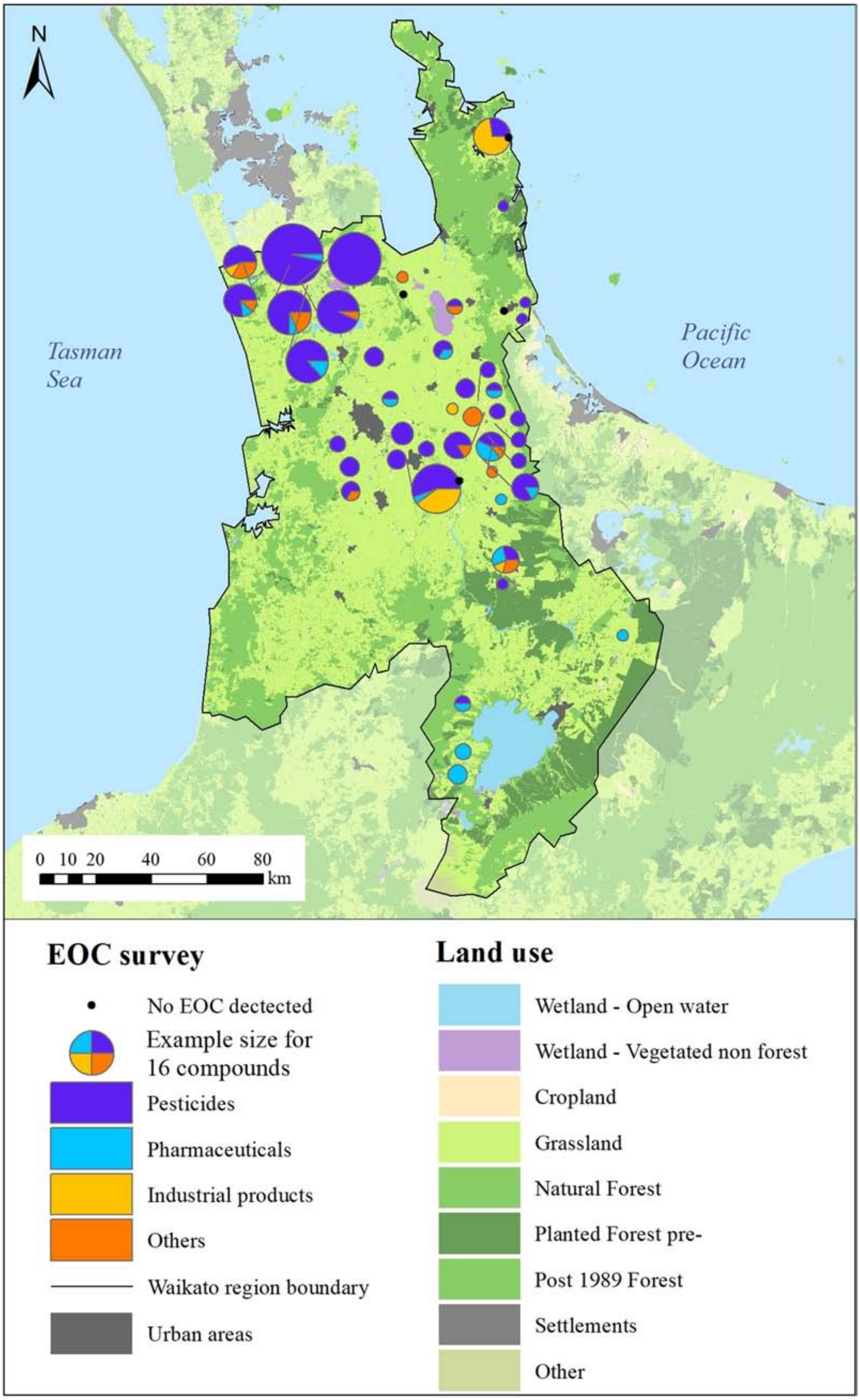

Fig. 4. Spatial distribution of EOC detections at SOE groundwater sites in the Waikato region. The size of the circle is proportional to the number of detected compounds, a scaled example displaying 16 compounds is shown in the legend for reference.

4. Results and discussion

4.1. Frequency of detection

At least one EOC was detected at 91% of the SOE sites ($n = 47$), with a maximum of 31 compounds detected at Site 4 (Fig. 4). There were only four sites, all SOE sites, at which no EOCs were detected. In total, 73 EOC compounds were detected in this survey, mostly pesticides and pharmaceuticals, the majority of which (60%) are listed as approved hazardous substances (NZ Environment Protection Agency, 2018). Drugs of abuse and lifestyle compounds were not detected at SOE sites (Fig. 5). The three highest detections were for pesticides (74%), followed by pharmaceuticals (30%) and preservatives and food additives (26%). Pesticide degradates were the most frequently detected: chloridazon-desphenyl-methyl was detected at 47% of the sites, atrazine-desethyl and atrazine-desisopropyl at 30% and 26% of the sites respectively. Other frequently detected EOCs were clothianidin (pesticide, 26% of the sites) and acesulfame (food additive, 17% of the sites). The most detected pharmaceutical was thiabendazole (11% of the sites). A total of 68 compounds were detected at the targeted sites, with a minimum of 1 detection (Site 58) to a maximum of 48 detections (Site 61). All EOC categories except lifestyle compounds were detected at the targeted sites with a 48% compound overlap with SOE sites (Fig. 5). Detection frequencies in Waikato groundwaters were lower than those recorded in a recent pan-European survey (Loos et al., 2010) and exhibited similar patterns, for instance the highest detection frequencies occurred for chloridazon and atrazine degradates (Table 1). It was not possible to use published surveys to identify EOCs specific to New Zealand groundwaters because non-detected compounds are generally not reported. At the WWTP site, 68 compounds encompassing all seven tested EOC categories were detected, with a 51% compound overlap with SOE sites and 50% overlap with targeted sites (less pesticides, more pharmaceuticals). Summary statistics on concentrations and frequency of EOCs at the Waikato sites for all EOC categories are provided in Table S4.

4.2. Concentrations of detected compounds

At SOE sites, 28 compounds (75% pesticides) were detected above 100 $\text{ng}\cdot\text{L}^{-1}$ at one or more location (Fig. 6), which corresponds to the EU maximum admissible concentration for pesticides (European Commission, 2015). The highest four concentrations were: the pesticide chloridazon-desphenyl at two different sites (7800 $\text{ng}\cdot\text{L}^{-1}$ and 4100 $\text{ng}\cdot\text{L}^{-1}$), the herbicide bentazone (6000 $\text{ng}\cdot\text{L}^{-1}$), and the

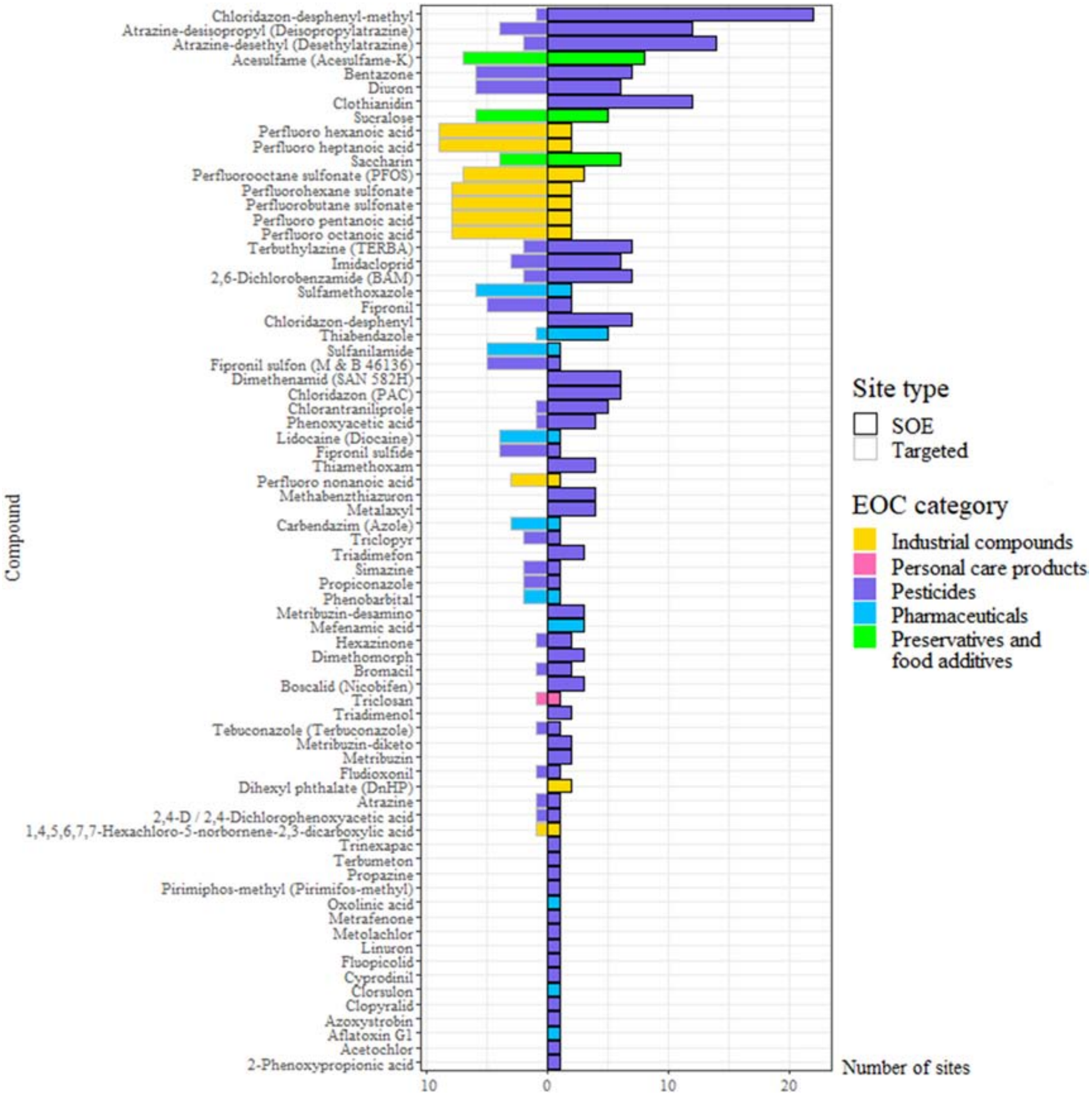

Fig. 5. Number of SOE sites ($n = 47$) and targeted sites ($n = 9$) in the Waikato region at which each of the 73 detectable EOCs in SOE wells was found, ordered by decreasing total detection. SOE and targeted sites were separated to allow visualisation of compounds ubiquitous to both site types.

Table 1
Detection frequency (%) and maximum concentration in (ng·L^{-1}) for selected EOCs tested in Waikato groundwaters compared to published European studies (* Loos et al., 2010; ** Lapworth et al., 2015). Waikato region concentrations at SOE sites are shown first, and concentrations at targeted sites are shown in square brackets.

EOC category Compound name	Waikato (n = 47)	EU countries* (*n* = 164)	English Chalk** (*n* = 300)	French Chalk** (*n* = 45)	Max concentration	
					Waikato	EU countries*
Industrial compounds–surfactants						
Perfluoro decanoic acid	0.0	23.8			[3.8]	11
Perfluoro heptanoic acid	4.3	29.9			10 [160]	21
Perfluoro nonanoic acid	2.1	15.2			6 [4.8]	10
Perfluoro octanoic acid	4.3	65.9			12 [340]	39
Perfluorobutane sulfonate	4.3	15.2			31 [300]	25
Perfluorohexane sulfonate	0.0	34.8			570 [820]	19
Perfluorooctane sulfonate (PFOS)	6.4	48.2			110 [34]	135
Life-style compounds						
Estrone	0.0	0.6				4
Cotinine	0.0		0	2.2		
Personal care products						
Triclosan	2.1	1.8	0	0	3	9
Pesticides - degradates						
2,6-Dichlorobenzamide (BAM)	14.9		6.3	4.4	22 [67]	
Atrazine-desethyl (Desethylatrazine)	29.8	54.9	12.3	60	21 [470]	487
Atrazine-desisopropyl (DIA)	25.5		2	6.7	420 [86]	
Chloridazon-desphenyl	14.9	16.5			7800	13,000
Pesticides - fungicides						
Oxadixyl	0.0		4.7	4		
Propiconazole	2.1		0.7	0	2 [1.3]	
Pesticides - herbicides						
2,4,5-T/2,4,5-Trichlorophenoxyacetic acid	0.0	3.7				3
2,4-D/2,4-Dichlorophenoxyacetic acid	0.0	3.7			29	12
Alachlor	0.0	4.9				27
Atrazine	2.1	56.1	7.3	47	37 [1.3]	253
Bentazone	14.9	31.7	0.7	11	6000 [2700]	10,550
Boscalid	6.4		0.7	0	220	
Chloridazon-desphenyl-methyl	46.8	6.1			1700 [0.2]	1200
Chlortoluron (Chlorotoluron)	0.0	7.9				91
Dichlorprop	0.0	4.9				3199
Dimethenamid	12.8		0	0	1400	
Diuron	12.8	28.7	0.3	6.7	54 [150]	279
Hexazinone	4.3	17.7			230	589
Isoproturon	0.0	20.1	0.7	0		22
Linuron	2.1	2.4			4.3	293
2-Methyl-4-chlorophenoxyacetic acid (MCPA /MCP)	0.0	7.9				36
Mecoprop (MCPP)	0.0	13.4				785
Methabenzthiazuron	8.5	5.5			180	104
Metolachlor	2.1	20.7			62	209
Propazine	2.1	31.7			71	25
Simazine	2.1	43.3	2	6.7	15 [110]	127
Terbuthylazine (TERBA)	14.9	33.5			39 [40]	716
Pesticides–insecticides						
Diazinon (Dimpylate)	0.0	9.1				1
Pharmaceuticals						
Carbamazepine	0.0	42.1	2.3	13	[620]	390
Diclofenac	0.0	4.9			[1000]	24
Ibuprofen	0.0	6.7	0	0	[1000]	395
Ketoprofen	0.0	10.4				2886
Sulfamethoxazole	4.3	24.4			8 [260]	38
Metronidazole	0.0		0	4.4		
Propyzamide	0.0		0	0		
Oxazepam	0.0		0	2.2	[11]	

preservative acesulfame (5700 ng.L^{-1}). Mefenamic acid was the pharmaceutical measured at the highest concentration (120 ng·L^{-1}). Imidachloprid, currently listed on the EU surface water watchlist, was detected at six SOE sites in concentrations ranging from 6 to 330 ng·L^{-1}. Where compound matched, EOC concentrations at Waikato SOE sites were generally below those reported in European studies, with the notable exceptions of acesulfame, sucralose, and perfluorohezane sulfonate (Fig. 7; Lapworth et al., 2012). It should be noted that site selection criteria differed between these European studies.

At targeted sites, pesticide concentrations were consistently lower than SOE sites, but higher for all other EOC categories (Fig. 6, Table S4). Similary to SOE sites, most EOC concentrations were below those reported in European studies, except for acesulfame, sucralose and perfluorohezane sulfonate (Fig. 7; Lapworth et al., 2012). Forty EOCs reported overseas were tested but without detections at any

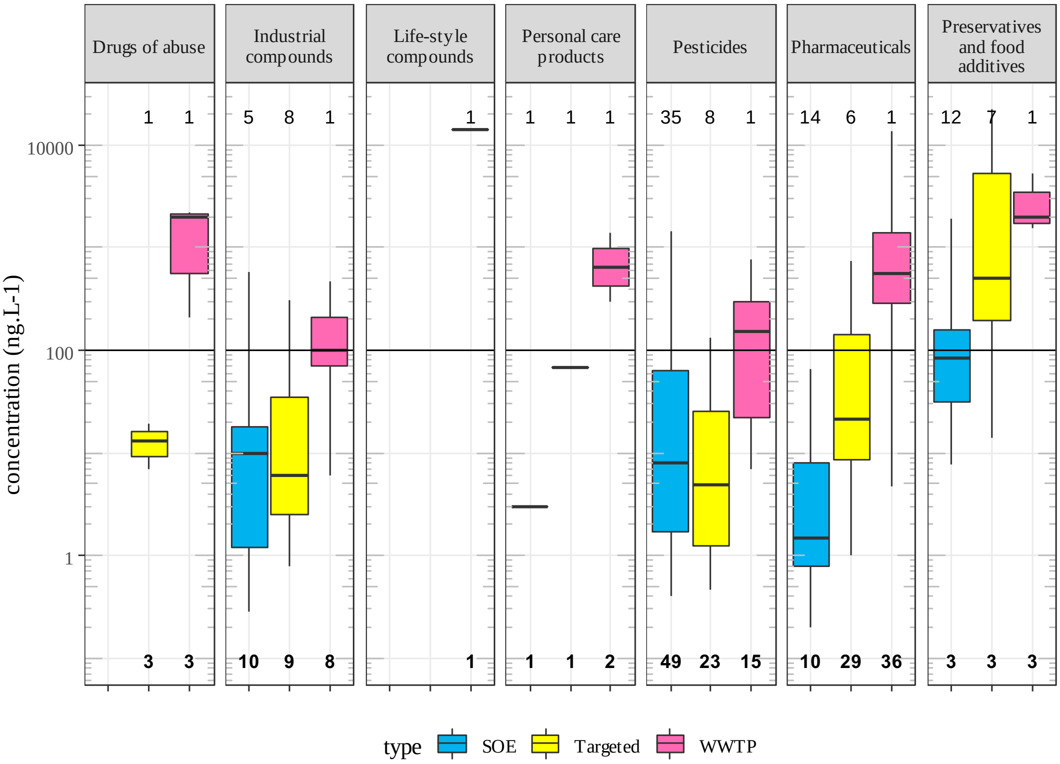

Fig. 6. Boxplot of EOC concentrations measured at SOE sites in the Waikato region, per site type. The number of site is shown at the top, whereas the number of compound is displayed at the bottom. The horizontal lines in the middle of each box are median values and the upper and lower limit of the box are the 75th and 25th percentiles, respectively. The vertical lines extend from the 95th to the 5th percentiles.

targeted sites, including prozac, paracetamol, estrone and cocaine (Loos et al., 2010; Lapworth et al., 2015). The maximum EOC concentration was 24,000 ng·L^{-1} for the preservative acesulfame, followed by the pharmaceutical levamisole (1200 ng·L^{-1}). At the WWTP sites, EOC concentrations were unsurprisingly higher than those found in Waikato and European groundwaters (Fig. 7). Preliminary New Zealand data

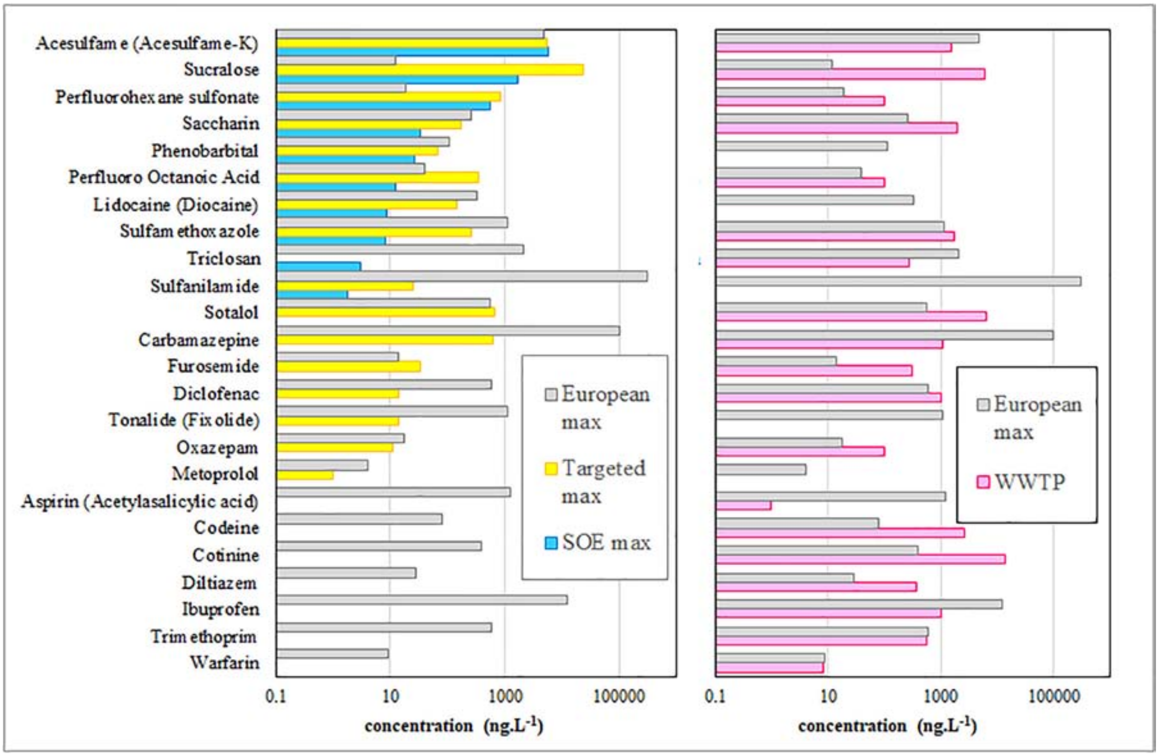

Fig. 7. Left, maximum concentration of selected EOCs in the Waikato region (this study) and European groundwaters (Lapworth et al., 2012). Right, maximum concentration of selected EOCs detected in the WWTP samples (this study) and European groundwaters (Lapworth et al., 2012). Forty compounds detected elsewhere globally are not shown as these were not detected in the Waikato region. It should be noted that site selection criteria differed between these European studies.

suggests that waste-water treatment plant effluents, EOC concentrations are comparable to those measured overseas (Gaw et al., 2014; Stewart et al., 2016).

4.3. Relationship with land use, well depth, aquifer lithology and confinement

Samples from SOE sites were collected in areas where the following activities were undertaken: horticulture (12 sites), dairy farming (20), agriculture (7), urban areas (7) and forestry (1). Pesticides were ubiquitous and exhibited the largest overlap of compounds (18) between land uses, with a wider range and higher concentrations found in horticultural areas (Table 2). Intensive use of pesticides in horticulture areas has been reported previously (Hadfield and Smith, 1999; Close and Humphries, 2016). The dihexhyl phthalate (DnHP) plasticizer was only detected at dairy sites (two occurrences, maximum concentration 20 ng·L^{-1}). Eight other industrial compounds (e.g., PFOS) were detected at horticultural (maximum concentration of 590 ng·L^{-1} for 1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dicarboxylic acid) and urban sites (maximum concentration of 570 ng·L^{-1} for perfluorohexane sulfonate). The single trace (<5 ng·L^{-1}) detection of disinfectant triclosan (personal care product) occurred at a shallow (<5 m) site located in an urban setting. At targeted sites, industrial compounds (mostly surfactants) and pesticides were detected at variable quantities under a range of land uses (e.g., waste-water treatment sites, urban). Pharmaceuticals and personal care products were only detected at urban and waste-water treatment sites.

Lithological information was only available for the SOE sites. The most represented aquifer lithologies were: sand (15 sites), pumice (9), ignimbrite (8), and basalt (7). Industrial compounds were mostly detected in sands, whereas pesticides, pharmaceuticals and preservatives and food additives occurred in all lithologies (Table 2). Basalt aquifers exhibited by far the widest range of pesticides (39 compounds), followed by sand (20 compounds) and pumice (9 compounds) aquifers. Most wells drawing from basalt aquifers are located in horticulture areas (5 of 7 sites).

EOCs were found in both unconfined (27 sites) and confined (8 sites) aquifers with a wider range (44 compounds, 5 categories) and higher concentrations under unconfined conditions. This is consistent with European studies (Stuart et al., 2012; Lopez et al., 2015). Chloridazon degradates were found in high concentrations regardless of confinement. Industrial compounds were only detected in shallow (<20 m) wells.

4.4. Relationship with groundwater age

EOCs were detected in all groundwater MRT groups (Fig. 8, Table S3). The 21 compounds found in the 'old' MRT category were also found in the 'young' and 'intermediate' MRT groundwaters, generally at lower concentrations. This included herbicide degradates (atrazine, chloridazon). Thirty-five compounds were detected in intermediate MRT groundwater at intermediate concentrations. Fifty-eight compounds were detected in younger groundwaters. Generally, a wider range of pesticides and industrial compounds was found in younger groundwaters (12 pesticides in older groundwater, 25 in intermediate groundwaters and 40 pesticides in young groundwaters). Preservatives and food additives occurred at concentrations several orders of magnitude higher in the young MRT group than in the intermediate and old MRT groups.

The wide range of sources and pathways (Fig. 1) is consistent with the ubiquity of EOCs, including in older groundwaters. Sand, pumice, ignimbrite and basalt lithologies included all MRT groups and may not unequivocally relate to aquifers. Understanding pathways will require a handle on groundwater age distribution at individual sites. The conjunctive use of groundwater age distribution and EOC occurrence has been demonstrated to ascertain deep groundwater vulnerability due to

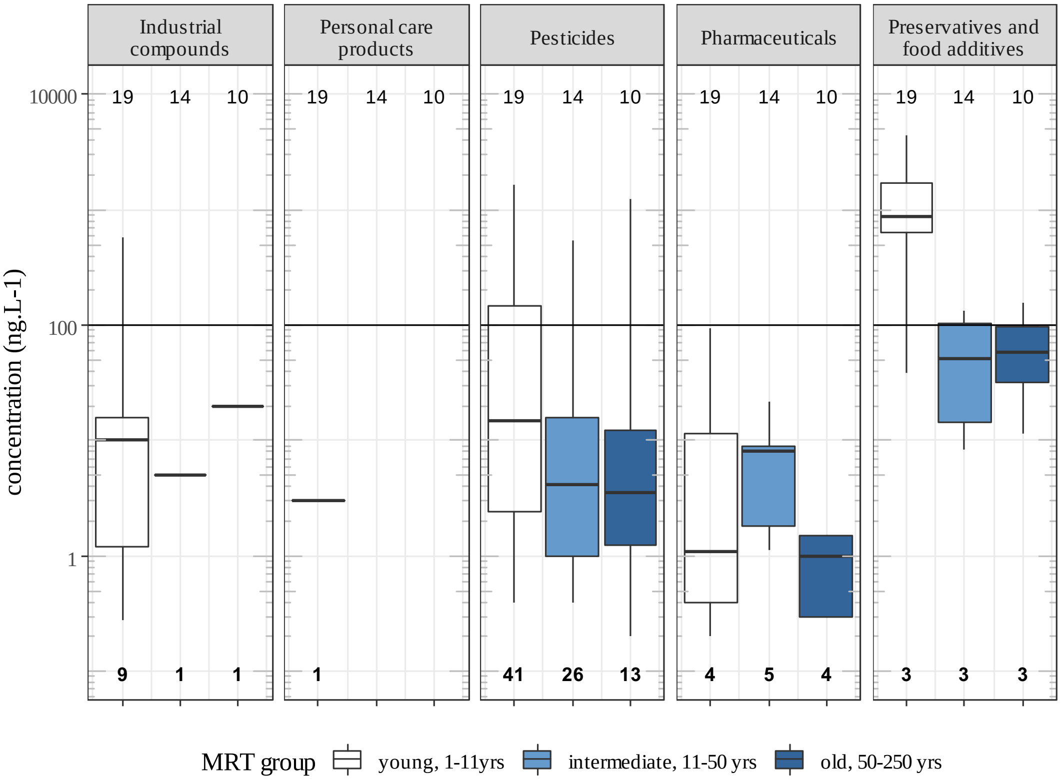

Fig. 8. Boxplot of EOC concentrations measured at SOE sites in the Waikato region, per age group. The number of site is shown at the top, whereas the number of compound is displayed at the bottom. The horizontal lines in the middle of each box are median values and the upper and lower limit of the box are the 75th and 25th percentiles, respectively. The vertical lines extend from the 95th to the 5th percentiles.

intensive pumping at depth (Lapworth et al., 2018b) and should be explored in New Zealand.

4.5. Physico-chemical characteristics

The mobility of EOCs is generally characterised by their physico-chemical properties, such as water solubility or octanol-water partition coefficient (K_{ow}), with low values ($\log K_{ow} < 4$) indicating hydrophobic compounds prone to bioaccumulation and sorption (Jurado et al., 2012). Log K_{ow} values for 27 detected compounds ranged from −0.07 to 5.12 (Jurado et al., 2012; Lapworth et al., 2012; International Union of Pure and Applied Chemistry, 2018), suggesting that caution should be used when inferring EOC mobility in New Zealand groundwaters based on this metric. Other factors influencing EOCs migration through the soil and the unsaturated zone are: sorption predominantly to organic matter and clay minerals, ion exchange (soil and aquifer), and microbial degradation or transformation (Lapworth et al., 2012).

The degradability of EOCs is influenced by the physico-chemical characteristics of aquifers, whereby typically strong reducing environments have been reported to inhibit or delay EOC degradation (Lapworth et al., 2012). In the Waikato survey a wide range of physico-chemical conditions were encountered with dissolved oxygen 0.19–10.2 $\mathrm{mg.L^{-1}}$, pH 4.94–7.97, temperature 12.3–21.3 °C, and electrical conductivity 80.7–780 $\mu\mathrm{S\cdot cm^{-1}}$. However, there was no evidence of physico-chemical control on EOC occurrence or concentrations. To extend this to redox conditions will require comparison with hydrochemistry.

The Groundwater Ubiquity Score (GUS) index has been used to estimate the potential for pesticides to contaminate groundwater (Hadfield and Smith, 1999; Stuart et al., 2012; Jurado et al., 2012; Lopez et al., 2015; Close and Humphries, 2016). The GUS index can be experimentally calculated from pesticide half-life and sorption potential (Gustafson, 1989). A GUS index above 2.8 suggests that the pesticide is prone to leaching. The limited data available (ten of the detected compounds) indicated GUS indexes from 1.83 to 4.39 with corresponding maximum concentrations of 440 and 7800 $\mathrm{ng\cdot L^{-1}}$, respectively. The highest concentrations are associated with a higher GUS score.

4.6. Potential use of EOCs as tracers

Typically desirable qualities of a source tracer are stability in water, persistence, low detection and low or absent natural background concentrations. Acesulfame, saccharin and sucralose were found at several sites at concentrations above 30 $\mathrm{ng\cdot L^{-1}}$ (Table 3) in Waikato groundwaters. Artificial sweeteners have been widely used as tracers for waste-water contamination in the environment (Lim et al., 2017 and references therein; Yang et al., 2018). It was recently shown that acesulfame can be biodegraded under anaerobic conditions and therefore it should be monitored in conjunction with the degradation products (Castronovo et al., 2017).

The distribution and relative concentrations of co-tracers can also be used to differentiate waste-water sources. For instance, artificial sweeteners (acesulfame, cyclamate, saccharin), pharmaceuticals (carbamazepine, ibuprofen, primidone), and degradation products from nicotine (cotinine) were used to delineate a municipal waste-water plume from domestic sources (Van Stempvoort et al., 2013). Use of EOCs as tracers will require adequate quality assurance measures and a suitable sampling protocol. Carbamazepine, cotinine and ibuprofen were not detected at Waikato SOE sites but were found in high concentrations at targeted sites (Table 3). EOC tracers identified in the recent review from Lim et al. (2017) and measured at Waikato targeted sites are listed in Table 3.

Table 2
Number of sites (n), number of compounds (shown in brackets in the n rows) and EOC concentrations ($\mathrm{ng\cdot L^{-1}}$) at SOE sites across categories of land use, aquifer lithology and MRT.

		Industrial compounds	Personal care products	Pesticides	Pharmaceuticals	Preservatives and food additives
Landuse						
# overlapping compound		7	0	18	3	3
Agriculture	n			4 (14)	4 (4)	2 (3)
	Conc			0.2–3000	0.2–8.9	7–630
	n	2 (1)		15 (12)	7 (6)	4 (3)
Dairy	Conc	5–20		0.2–290	0.3–56	30–180
	n			1(14)		1(1)
Forestry	Conc			0.6–3800		11
	n	2 (8)		10 (41)	5 (5)	3 (3)
Horticultural	Conc	0.2–590		0.1–7800	1–27	7.8–5700
	n	1 (8)	1 (1)	4 (7)	2(3)	2(2)
Urban	Conc	6–570	3	0.2–640	0.2–120	85–880
Lithology						
# overlapping compound		1	0	14	4	3
	n	1 (1)		7 (39)	5 (4)	4 (3)
Basalt	Conc	0.2–0.2		0.1–7800	1–27	7–5700
	n	2 (1)		5 (4)	4 (4)	1 (2)
Ignimbrite	Conc	5–20		0.2–230	0.2–10	110–140
	n	2 (9)	1 (1)	12 (20)	3 (3)	4 (3)
Sand	Conc	0.3–590	3–3	0.2–640	0.2–120	33–880
Gravel	n			1 (4)	1 (1)	
	Conc			0.4–1.7	1.5–1.5	
	n			8 (9)	5 (6)	2 (1)
Pumice	Conc			0.2–120	0.3–56	32–180
	n					1 (1)
Greywacke	Conc					30–30
MRT						
# overlapping compound		1	0	20	4	3
	n	3 (9)	1 (1)	18 (40)	7 (5)	3 (3)
young	Conc	0.2–590	3–3	0.1–7800	0.2–120	19–5700
	n	1 (1)		12 (25)	6 (6)	5 (3)
intermediate	Conc	5–5		0.2–3800	1–27	7.8–140
	n	1 (1)		4 (12)	5 (5)	4 (3)
old	coNc	20–20		0.2–3000	0.3–22	7–180

Table 3
Concentrations (ng·L^{-1}) of selected regulated (NZ or international) or monitored (grey shading) EOC compounds. The number of sites is indicated in brackets. Compounds currently on an EU watchlist are marked with an asterisk. Recommended compounds for future monitoring in the Waikato region at SOE sites are shown in bold. Reported tracers are indicated by (T) (Van Stempvoort et al., 2013; Lim et al., 2017).

	EU		NZ			
	Environmental Quality Standards					
EOC compound	**Annual Average**	**Maximum Allowable Concentration**	**Drinking–water Standard**	**SOE**	**Targeted**	**WWTP**
Drugs of abuse						
Morphine						2000 (1)
Normorphine						2200 (1)
Industrial compounds						
Perfluorooctane sulfonate (PFOS)	**650**	**36000**		**0.2–110 (3)**	**1.8–21 (6)**	**34 (1)**
Life–style compounds						
Cotinine (T)						14000 (1)
Personal care products						
Picaridin (Bayrepel)					68 (1)	1500 (1)
Pesticides						
2,4–D / 2,4–Dichlorophenoxyacetic acid			40000	29 (1)		150 (1)
Bentazone				**1.9–6000 (7)**	**2.4–14 (5)**	**2700 (1)**
Bromoxynil						11 (1)
Diuron	200	1800	20000	0.1–54 (6)	0.9–150 (5)	440 (1)
MCPP / Mecoprop			10000			340 (1)
Triclopyr			**100000**	**420 (1)**	**50 (1)**	**10 (1)**
Acetochlor				54 (1)		
Atrazine	600	200	2000	37 (1)	1.3 (1)	
Atrazine–desethyl (DEA)				1.5–21 (14)	22–470 (2)	
Atrazine–desisopropyl (DIA)				0.5–420 (12)	0.6–86 (4)	
Bromacil			400000	1.5–2.1 (2)	59 (1)	
Hexazinone			**400000**	**4.5–230 (2)**		**250 (1)**
Linuron				4.3 (1)		
Metalaxyl			**100000**	**1.1–330 (4)**		
Metolachlor				62 (1)		
Metribuzin			**70000**	**12–140 (2)**		
Propazine			70000	71 (1)		
Simazine	1000	4000	2000	15 (1)	9.4–110 (2)	
Terbuthylazine (TERBA)			8000	1.9–39 (7)	19–40 (2)	
Pirimiphos–methyl (Pirimifos–methyl)			100000	1 (1)		
Chloridazon–desphenyl				**150–7800 (7)**		
Chloridazon–desphenyl–methyl				**0.2–1700 (22)**	**0.2 (1)**	
Clothianidin*				**0.2–150 (12)**		
Dimethenamid (SAN 582H)				**0.5–1400 (6)**		
Imidacloprid*	**67**			**6.2–320 (6)**	**10–69 (3)**	
Thiamethoxam				**5.7–1800 (4)**		
Pharmaceuticals						
10,11–Dihydroxycarbazepine (T)					910–1200 (2)	11000 (1)
Atenolol (T)					2 (1)	4400 (1)
Carbamazepine (T)					16–620 (5)	1100 (1)
Celiprolol					61–140 (2)	2600 (1)
Codeine						2600 (1)
Diclofenac* (T)	**100**				**7–14 (2)**	**1000 (1)**
Gabapentin						26000 (1)
Ibuprofen (T)						1000 (1)
Levamisole						8200 (1)
Metformin						200000 (1)
Metoprolol (T)					1–1 (2)	
Sotalol					16–650 (3)	6300 (1)
Sulfamethoxazole				1.5–8 (2)	6.8–260 (5)	1700 (1)
Thiabendazole			400000	0.2–0.8 (5)		24 (1)
Tramadol					8.7–620 (4)	1300 (1)
Triclocarban (T)						290 (1)
Venlafaxine					0.7–2 (2)	1200 (1)
Preservatives and food additives						
Acesulfame–K (T)				**32–5700 (8)**	**70–5300 (6)**	**1500 (1)**
Saccharin				7–33 (6)	0.9–170 (3)	2000 (1)
Sucralose				**58–1700 (5)**	**480–24000 (5)**	**6000 (1)**

4.7. Implications for monitoring

The LCMS analytical suite included some pesticides currently monitored in New Zealand as part of the 4-yearly national pesticides survey (Close and Humphries, 2016): acid herbicides (72% overlap with pesticide survey, $n = 17$), organonitrogen herbicides (78%, $n = 18$), organophosphorus pesticides (100%, $n = 4$), and none of the organochlorine pesticides (n-22). However, the LCMS screen included 326 pesticides currently unmonitored, of which 37 were detected. For pesticides that are currently monitored, most concentrations were low ($<$ 100 ng·L^{-1}) except for bentazone (6000 ng·L^{-1}) and atrazine-desethyl (470 ng·L^{-1}) at SOE and targeted sites, respectively (Table S4). These low concentrations are consistent with previous regional surveys (Hadfield and Smith, 1999; Hadfield, 2017). In contrast, the highest concentration for unmonitored pesticides was 7800 ng·L^{-1} (chloridazon-desphenyl). Some currently unmonitored pesticides that are regulated or on the EU Surface Water Watchlist (European Commission, 2013) were detected in Waikato groundwater at concentrations as high as 320 ng·L^{-1} (imidacloprid). It is therefore recommended that the list of pesticides provided in this study is used to review the pesticide suite for the national survey to ensure that compounds with high concentrations detected in Waikato are captured in the national survey.

From a regional monitoring perspective, this study indicates that unmonitored, regulated EOCs are present in variable quantities in various aquifers, particularly industrial compounds and preservatives. At SOE or baseline sites, the sum of measured compounds ranged from 0.2 to 17,100 ng·L^{-1}. The combined toxicity of multiple compounds is currently poorly defined (Lapworth et al., 2012) and therefore further EOCs monitoring in the groundwaters of the Waikato region is recommended. Using compounds earmarked by watchlists as toxic and compounds detected above the EU maximum allowable concentration for total pesticides (100 ng·L^{-1}), a tentative list of EOCs to include in further monitoring is shown in Table 3. Previous pesticide studies also highlighted possible temporal variations in concentrations (Hadfield and Smith, 1999). Establishing monitoring, with a minimum timeframe over three years and a minimum quarterly frequency to capture seasonal change, would be a valuable starting point. The survey results also showed that older groundwaters exhibited a narrower EOC range and lower concentrations, supporting the use of groundwater age as a criterion to design monitoring networks.

From a national monitoring perspective, this study has shown that a wide range of EOCs exists in New Zealand groundwaters. The significant number of manufactured EOCs, and the cost and limitations of New Zealand's current analytical capability, preclude systematic analysis of all EOCs that may occur in the environment. To manage the risks associated with monitoring only a selected set of EOCs, internationally recommended monitoring strategies are usually based on risk-assessment (Stewart et al., 2016; Lapworth et al., 2018a). The four most common strategies involve targeting “representative” EOCs based on: typical mode of action (e.g., endocrine disruptors), chemical classes, high production or commonality of use, and high ecological risks (Stewart et al., 2016). An alternative and complementary way to reduce the risks associated with targeted monitoring is to make use, as done in this study, of a recently developed, cost-effective screening method covering a broad (>100) range of contaminants to support low cost, national scale investigations (Lapworth et al., 2015; Sorensen et al., 2015). It is therefore recommended to extend this kind of large screen survey to other regions or nationally to assess the breadth of EOCs that are detectable in New Zealand groundwaters. This can inform which substances laboratories should develop analytical capability for, enabling targeted environmental monitoring based on frequency and concentrations of detected compounds as well as substance hazard (Lapworth et al., 2018b). Based on the findings from this study, Table 3 outlines compounds, associated with high hazard scores based on toxicity that should be prioritised in terms of developing analytical capability in New Zealand. Extending the survey from the Waikato region, as conducted in the present study, to establish a national baseline, could also include the use of alternative analytical techniques, such as GCMS to target volatile (less polar) compounds (Mottaleb et al., 2015; Manamsa et al., 2016) which cannot be analysed by LCMS.

This study has also shown that geographical location and land use strongly affect the number and type of compounds detected in groundwater. Sedimentary and volcanic aquifers occur in other regions of New Zealand (White, 2001). It is expected that groundwaters in other regions may have different numbers and types of EOCs. It is recommended to undertake EOC monitoring nationally, which would be consistent with regional council representatives in 2016 rating investigation of EOCs in New Zealand groundwater as a research priority. This monitoring should also aim to link EOC occurrence to the contributing sources. It should be noted that designing and implementing a long-term, national EOC monitoring programme would involve site selection, sampling frequency and analytical suites to be compatible with the current national monitoring objectives and resourcing.

5. Conclusions

This regional study demonstrated that unregulated and unmonitored EOCs occur extensively in New Zealand groundwater, sometimes at concentrations exceeding 100 ng·L^{-1}. Multiple compound detections are frequent (72% of SOE sites). These findings highlight a need for New Zealand to develop EOC monitoring programmes aiming to characterise baselines and long-term trends, preferably at the national scale.

The Waikato survey used a novel sampling design for site selection and a wide EOC screen. The results highlighted a narrower EOC range and lower concentrations in older groundwaters, supporting further use of age stratification for monitoring. The wide screening approach identified unmonitored EOCs that should be prioritised in terms of laboratory capability development, based on toxicity and measured concentrations. The EOC priority list developed for the Waikato region through this study included ubiquitous pesticides measured in concentrations significantly higher than currently monitored pesticides, providing a scientific basis to review national monitoring. This list also included compounds showing high potential for groundwater tracer studies.

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Appendix. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.05.210.

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