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Invited paper

An assessment of contamination fingerprinting techniques for determining the impact of domestic wastewater treatment systems on private well supplies☆,☆☆

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ABSTRACT

Private wells in Ireland and elsewhere have been shown to be prone to microbial contamination with the main suspected sources being practices associated with agriculture and domestic wastewater treatment systems (DWWTS). While the microbial quality of private well water is commonly assessed using faecal indicator bacteria, such as *Escherichia coli*, such organisms are not usually source-specific, and hence cannot definitively conclude the exact origin of the contamination. This research assessed a range of different chemical contamination fingerprinting techniques (ionic ratios, artificial sweeteners, caffeine, fluorescent whitening compounds, faecal sterol profiles and pharmaceuticals) as to their use to apportion contamination of private wells between human wastewater and animal husbandry wastes in rural areas of Ireland. A one-off sampling and analysis campaign of 212 private wells found that 15% were contaminated with *E. coli*. More extensive monitoring of 24 selected wells found 58% to be contaminated with *E. coli* on at least one occasion over a 14-month period. The application of fingerprinting techniques to these monitored wells found that the use of chloride/bromide and potassium/sodium ratios is a useful low-cost fingerprinting technique capable of identifying impacts from human wastewater and organic agricultural contamination, respectively. The artificial sweetener acesulfame was detected on several occasions in a number of monitored wells, indicating its conservative nature and potential use as a fingerprinting technique for human wastewater. However, neither fluorescent whitening compounds nor caffeine were detected in any wells, and faecal sterol profiles proved inconclusive, suggesting limited suitability for the conditions investigated.

1. Introduction

In many rural areas the absence of public water supplies and sewerage networks necessitates a reliance on private water wells and domestic wastewater treatment systems (DWWTS). The effective treatment and disposal of domestic wastewater and the attainment of safe drinking water within a spatially confined rural household site requires an in-depth understanding of the contaminant transport and attenuation processes in the soil into which DWWTS effluent is usually discharged, in parallel with suitable well design and construction, to ensure that groundwater resources (and hence human health) are adequately protected. However, private wells, in Ireland as well as more internationally, are largely unregulated, untested and untreated (Hynds et al., 2013). Insufficient DWWTS performance can lead to contaminant and pathogen risks to nearby wells and therefore public health. In the U.S., for example, an estimated 750,000 to 5.9 million illnesses

☆ This paper has been recommended for acceptance by Charles Wong.

☆☆ This research marks the first time that such a range of different chemical contamination fingerprinting compounds has been tested concurrently on such a range of private wells located in different hydrogeological conditions. The suite of fingerprinting techniques evaluated included ionic ratios, fluorescent whitening compounds, faecal sterol profiles, artificial sweeteners, caffeine and pharmaceuticals, from which a strategic tiered approach for identifying a contamination source has been developed.

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Abbreviations

DWWTS	domestic wastewater treatment system
FIB	faecal indicator bacteria
FST	faecal source tracking
VTEC	verocytotoxin *E. coli*
FWC	fluorescent whitening compound
MPN/CFU	most probable number of colony forming units
PPCP	pharmaceutical and personal care products

per year have been linked to contaminated groundwater alone, resulting in an estimated 1400–9400 deaths per year (Macler and Merkle, 2000; Murphy et al., 2017; Reynolds et al., 2008).

The microbial quality of private well water is routinely analysed using faecal indicator bacteria (FIB), such as *E. coli* (Ashbolt et al., 2001; Lapworth et al., 2020), which are key parameters used internationally in drinking water legislation such as the EU Drinking Water Directive (98/83/EC) and WHO Guidelines (WHO, 2017). However, these FIB are not source-specific and provide limited information as to the origin of the contamination. It is especially important to be able to identify contamination from a human source as pathogens in human wastewater pose much more of a potential public health risk than animal waste derived risks. In addition, knowing the source of contamination can to help identify any remedial actions required e.g. need for improved DWWTS, better well protection, change to farming practice etc. A number of microbial source tracking techniques (MST) for attributing water contamination to a particular source(s) have been examined previously (Blanch et al., 2006; Hagedorn and Weisberg, 2009; Harwood et al., 2014; Lapworth et al., 2018; Pal et al., 2014; Scott et al., 2002; Simpson et al., 2002; Tran et al., 2015). These can be broadly divided into microbial and chemical based approaches. Microbial approaches use the molecular differences between groups of microorganisms to identify the host from which the organisms were derived (Harwood et al., 2014; Scott et al., 2002). Chemical methods include ionic ratios (e.g. K/Na and Cl/Br ratios), contaminants of emerging concern (CECs) (e.g. personal care products and pharmaceuticals, fluorescent whitening compounds (FWC) and artificial sweeteners) and faecal sterol profile analysis. Ionic ratio techniques rely on the distinct ratio signatures associated with the potential contaminant sources (e.g. DWWTS effluent) which can be used as a diagnostic tool for testing contaminated waters (Brown et al., 2009; Davies et al., 1998; Kelly and Wright, 2002; Vengosh and Pankratov, 1998). Equally, the anthropogenic origin of several CECs has led to their application as tracers of wastewater contamination (Buerge et al., 2009; Lapworth et al., 2012; Spoelstra et al., 2017). Much of the research into the performance of these MST techniques, however, has focused on identifying impacts from large scale wastewater treatment systems and mixed land use in catchments, with considerably less research on the applicability of the techniques to the impacts of DWWTS on private domestic wells.

In Ireland, extensive research has been carried out examining the treatment efficiencies of different types of DWWTS in various hydrogeological conditions (Gill et al., 2009a, 2009b; Gill and Mockler, 2016; O'Luanaigh et al., 2012). Results have shown variations in performance between the different DWWTS and unsaturated zone conditions, with episodic breakthroughs of faecal indicator organisms into the underlying groundwater. During a national inspection programme, approximately 48% of the DWWTS inspected did not meet the required standards due to poor maintenance, design or siting (EPA, 2015). Equally, studies of private wells in Ireland have found that approximately 30% contained microbial contamination (Hynds et al., 2012), with sources believed to be DWWTS, the land-spreading of manure, grazing animals and farmyard run-off (EPA, 2010). Ireland has displayed the highest incident rate of verocytotoxin producing *E. coli* (VTEC) of any European Union Member State (Garvey et al., 2011; O'haiseadha et al., 2017), with research (Morris et al., 2015) showing that hospitalised victims of the pathogen are up to four times more likely have been consumers of untreated water from private wells.

The aim of this study was to assess several fingerprinting techniques with respect to their ability to attribute private well contamination to a particular source, either human wastewater or animal husbandry related wastes. The research involved the monitoring and assessment of private wells in four hydrogeologically distinct study areas in Ireland. The fingerprinting techniques assessed include simple ionic ratios, artificial sweeteners, fluorescent whitening compounds, faecal sterols, caffeine and pharmaceuticals.

2. Experimental

2.1. Site selection

Four geologically distinct areas were selected for the study (Fig. S.1): two areas (SA1 and SA3) characterised to be of *Extreme* groundwater vulnerability to pollution, as delineated by DELG et al. (1999), the other two areas (SA2 and SA4) were of *Low* vulnerability, also defined as likely to provide inadequate soil percolation characteristics for DWWTS effluent. While such areas of inadequate percolation may offer more protection to groundwater, this results in surface ponding of effluent that can pose a contamination risk to surface water bodies as well poorly sealed wells. More detail on the geology and land use of the study areas is presented in Supplemental Information.

2.2. Site assessment and well sampling

61, 53, 48 and 50 private water wells within each respective study area (212 in total) were located and permission to sample them agreed with the householders. A site assessment survey (adapted from Hynds et al. [2012]) was carried out which involved recording general site details (e.g. gradient, ground conditions), well details (e.g. age, depth, construction materials, treatment used etc.), well head details (e.g. presence/absence of cap, cover concrete surface apron etc.), local land use and DWWTS details (e.g. type, age, location, maintenance etc.). In general, the ~70% of the DWWTS found in these areas were septic tanks discharging effluent by gravity into either a soak pit or a percolation area, with inevitable poor distribution of effluent leading to high effluent loading onto small areas of soil (Dubber and Gill, 2017; Patel et al., 2008). The other 30% of DWWTS were packaged secondary treatment plants, again discharging into percolation areas. The typical well construction in the areas was unlined boreholes into bedrock, with only surface casings, often not grouted, and with poor headworks (Hynds et al., 2013).

Prior to sampling, the well water level was measured using an electric contact gauge (dip meter), which was rinsed in deionized water between every site. All samples were tested for temperature, electrical conductivity (EC) and pH onsite using a Hanna Instruments HI-98129 pH and Water Analysis Meter. pH was calibrated each morning using two buffer solutions. The sampling protocols used were centred upon those outlined by the USGS (2015). Samples were collected at cold-water taps linked directly to each borehole. Taps were run for 5 min to remove any stagnant water from the pipework and borehole prior to sampling. The

primary sample was collected using 500 mL polypropylene containers with care taken to ensure as little air as possible was present in the bottle headspace. All containers were detergent washed and autoclaved at 121 °C for 15 min prior to sample collection. A second 30 mL sample was collected for trace element analysis in disposable sterile polystyrene (PS) containers. All sample vessels and lids were rinsed three times immediately before sample collection using the well water. All samples were then stored in an ice box below 4 °C for transport back to the laboratory and analysis within 6 h. Two types of "blank" samples for quality control purposes in accordance with USGS (2015) and Misstear et al. (2017). Firstly, trip or transport blanks were used to determine whether the handling, storage or transport of the well samples had any effect on their integrity, and if they had attributed to any contamination or cross-contamination of samples. Additionally, duplicate samples were taken as an extra quality control measure. This involved taking two samples sequentially from the same well source during the same sampling event.

2.3. Routine sample analysis

Laboratory testing was carried out on the same day as sample collection, with the exception of 30 mL samples for trace element analysis which, upon return to the laboratory, were filtered with 0.45 μm glass microfiber filters and acidified with nitric acid to a pH < 2.

Alkalinity was determined by titration of the water samples in accordance with APHA/AWWA/WEF (2005). Total coliforms and *E. coli* were analysed using an IDEXX Colilert-18 test kit. Nitrate, chloride, sulphate and ammonium were analysed using a Spectroquant Nova 60 spectrophotometer (Merck, New Jersey) and associated reagent test kits. Elemental analysis was carried out by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian-Liberty AX Sequential AES. The elements analysed for were calcium (Ca), iron (Fe), manganese (Mn), magnesium (Mg), potassium (K) and sodium (Na). Post analysis, ion balance errors were calculated to assess analytical integrity (Misstear et al., 2017).

2.4. Monitoring well selection and tracer analysis

Six wells from each study area (24 in total – see Table 1) were selected for monthly monitoring over a 13-month period (M1-M13 referring to months 1–14 from July 2015 to August 2016). These were chosen to be representative across the 212 wells that had undergone one-off sampling with respect to the different contamination susceptibility scenarios (as defined by the site selection criteria) versus the actual water quality results from the once-off sampling campaign.

K/Na ionic ratios were evaluated as a contamination fingerprinting technique over the 14-month period. The suitability of all the other fingerprinting techniques was investigated during two monthly monitoring events (M11 –May 2016) and M13 (July 2016).

2.4.1. Ionic ratios (K/Na and Cl/Br)

Potassium and sodium concentrations in groundwater samples were measured by ICP-AES (Varian-Liberty AX, California). Samples from the M11 and M13 monitoring events were analysed for chloride using a Merck Spectroquant Nova 60 spectrophotometer and for bromide using a Dionex ICS 3000 (ThermoFisher Scientific, Massachusetts) direct injection ion chromatography system using an electrolytically generated potassium hydroxide eluent and selective column with suppressed conductivity detection. Note, any wells fitted with a water softener (n = 4; where no sampling source was available without this pre-treatment) have been interpreted accordingly – i.e. elevated levels of sodium, potassium and chloride are most likely due to the softening process, not necessarily evidence of contamination.

2.4.2. Contaminants of emerging concern

Samples from the M11 and M13 monitoring events were analysed for carbamazepine, sulfamethoxazole, acesulfame, aspartame, cyclamate, sucralose, saccharin and caffeine. High performance liquid chromatography (HPLC) coupled with electrospray ionization tandem mass spectrometer (ESI-MS) (Shimadzu, Japan) was utilised for detection based on a method developed by Tran et al. (2013) – see Supplemental Information for more details.

2.4.3. Sterol analysis

Due to the time-intensive nature of the extraction procedure and analytical methods, sterol analysis was carried out on water samples from only four wells from each study area (i.e. 16 in total) from the M11 and M13 monitoring events. These wells were selected based on the previous monitoring records and likelihood of them being contaminated. Each sample was analysed for 11 sterols and stanols (cholestane, cholesterol, coprostanol, epicoprostanol, cholestanol, campesterol, stigmasterol, β-Sitosterol, 24-ethyl-coprostanol, 24-ethyl-epicoprostanol and sitostanol) as detailed in Table S.1.

20 L of water were taken from each well and sample preparation and extraction methods were based on those described by Shah et al. (2006) – see Supplemental Information for more details.

2.4.4. Fluorescent whitening compounds (FWC) analysis

Samples for FWC analysis were collected in amber glass bottles. Fluorescence was measured by a LS55 Fluorescence Spectrometer (PerkinElmer, Massachusetts) using PMMA cuvettes with 10 mm optical path length. The emission wavelength was set at $\lambda_{em} = 436$ nm with a slit width of either 5 or 10 nm. The presence or absence of FWCs was determined using the photodecay method recommended by Dubber and Gill (2017). The photodecay of the samples was measured in triplicate by recording the fluorescence signal after 0, 1, and 10-min of exposure to UV light. A dark box containing a sun lamp with 4 Philips Cleo 15W UV tubes was used to control UV exposure. The sample cuvettes were placed into a LDPE holder, centrally positioned in front of the UV tubes at a height and distance of 16 and 5 cm respectively. Ventilation of the box was maintained throughout each exposure to minimise any heat accumulation. The ratio of the reduction after 1 min to the reduction after 10 min of UV exposure was determined and samples with a ratio (1/10 min) > 0.25 are considered to contain FWCs (Dubber and Gill, 2017).

2.5. Statistical analysis

All data have been analysed using IBM SPSS Statistics v22.0 software. Due to the varied nature of the data (categorical/nominal and continuous), all data were first tested for normality by graphical means and Shapiro-Wilk tests, with parametric (*t*-test and one-way analysis of variance (ANOVA)) non-parametric (Mann-Whitney U, Spearman rank correlation and Chi-squared) statistical tests then used accordingly (Helsel and Hirsch, 2002). Where the significance value of the Shapiro-Wilk Test was greater than 0.05, the data was considered normal while a value below 0.05 indicated that the data significantly deviated from a normal distribution. Where data are not normally distributed, log transformations were utilised in an attempt to induce normality. As outlined by Helsel and Hirsch (2002) when dealing with non-normal data nonparametric tests can be many times more powerful than parametric tests. Where chemical data results could not be specified as they were less than

Table 1
Results of different contamination fingerprinting techniques on the 24 monitoring wells for the M11 and M13 sampling events. ▭ = negative; ▭ = positive (but not source specific); ▭ = positive (DWWTS specific); ▭ = not tested.

SA1	**CX23**		**CX43**		**CX45**		**CX52**		**CX53**		**CX54**	
sampling event	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*
E. coli												
K/Na												
Cl/Br												
Acesulfame												
Cyclamate												
Caffeine												
Carbamazepine												
Sulfamethoxazole												
Faecal sterols												
FWCs												

SA2	**BL16**		**BL25**		**BL32**		**BL37**		**BL43**		**BL44**	
sampling event	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*
E. coli												
K/Na												
Cl/Br												
Acesulfame												
Cyclamate												
Caffeine												
Carbamazepine												
Sulfamethoxazole												
Faecal sterols												
FWCs												

SA3	**KX4**		**KX10**		**KX13**		**KX29**		**KX31**		**KX38**	
sampling event	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*
E. coli												
K/Na												
Cl/Br												
Acesulfame												
Cyclamate												
Caffeine												
Carbamazepine												
Sulfamethoxazole												
Faecal sterols												
FWCs												

SA4	**CL2**		**CL9**		**CL11**		**CL22**		**CL30**		**CL44**	
sampling event	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*	*M11*	*M13*
E. coli												
K/Na												
Cl/Br												
Acesulfame												
Cyclamate												
Caffeine												
Carbamazepine												
Sulfamethoxazole												
Faecal sterols												
FWCs												

the limit of detection (LOD) of the analytical procedure, their value was assigned using a maximum likelihood estimation approach (Helsel, 2006) for any subsequent statistical analysis, by substituting values according the underlying distribution (for some transformed) of the dataset. A significance level of 0.05 is used throughout unless stated otherwise.

3. Results and discussion

3.1. One-off analysis

Of the 212 wells sampled, 16%, 17%, 10% and 16% tested positive for *E. coli* in SA1 (Co. Wexford), SA2 (Co. Wicklow), SA3 (Co. Kilkenny) and SA4 (Co. Cavan), respectively (see Table S.2) - the fraction of wells testing positive/negative not being significantly different between the four study areas ($X^2 = 1.08$, $p = 0.78$). There was no significant difference in the mean quantitative concentrations of *E. coli* for the wells that tested positive between study areas.

Nitrate concentrations varied between the four sites, with higher median concentrations found in SA1 and SA3, and with a larger proportion of samples from SA2 and SA4 found to have concentrations below the methods detection limit (as discussed in Supplemental Information and shown in Fig. S.2) but no statistical relationships were found between *E. coli* and nitrate (i.e. Mann Whitney U $P < 0.05$). Nitrate concentrations were also examined with respect to potential sources (e.g. DWWTS and agricultural) and pathway variables (e.g. geological setting and wells design) (Tedd et al., 2014). Although beyond the scope of this paper, pathway components including topsoil, aquifer and subsoil type, groundwater vulnerability class were generally found to be more important than source components with respect to nitrate. While DWWTS and agriculture are known sources of nitrogen contamination, elevated sampling results alone cannot pinpoint the source.

The distinct hydrochemical signatures from the sampling of the four areas have been identified using a Piper plot (Fig. S.3) which shows the influence of limestone geology in SA3 and SA4 with a clear Ca–Mg–HCO_3 type geochemistry. In contrast, SA1 is less dominated by Ca and HCO_3 and with higher contributions from Mg, Na, K, Cl and SO_4. SA2 shares characteristics of both SA1 and SA3/SA4. SA1 and SA2 are mainly underlain by Lower Palaeozoic metasedimentary rocks, in contrast to the more carbonate-rich rocks underlying SA3 and SA4.

3.2. Monthly monitoring

The *E. coli* monitoring results for the 24 wells are illustrated in Fig. 1. Fewer wells in SA2 tested positive for *E. coli* (at lower levels and more infrequently) compared to the other sites, with relatively low concentrations also found in SA4; note that both SA2 and SA4 are areas defined as having Low groundwater vulnerability. There are noticeable fluctuations in water quality over time. For example, in October 2015 17% of the 24 wells were contaminated with *E. coli* compared to the preceding September which revealed that 37% were contaminated. Furthermore, it should be noted that 58% of the wells tested positive for *E. coli* at least once during the 14-month period. This highlights how the timing and frequency of sampling can influence the interpretation of such monitoring. As illustrated, the same four wells (CX52, KX10, KX29 and CL2) tested positive for *E. coli* in M11 (May 2016) and M13 (July 2016).

The results from the sampling and analysis of specific contamination fingerprinting techniques are now presented. A summary of the comparison of the times when all the contamination fingerprinting techniques were tested at the same time on the 24 private wells (i.e. in monthly monitoring events M11 and M13) is presented in Table 1.

3.3. K/Na ratio

During the breakdown of vegetable matter, both Na and K are released in a soluble form, with higher volumes of K released with respect to Na (Daly and Daly, 1982). The concentrations released are elevated with respect to those usually found in Irish groundwater, where K is generally less than 3.0 mg/L, and K/Na ratios are generally less than 0.4 (Tedd et al., 2017). Daly and Daly (1982) suggested that groundwater K concentrations greater than 5 mg/L, and K/Na ratios >0.3 can be indicative of contamination from local sources of decaying organic matter, such as farmyard runoff. Findings from several studies indicate that DWWTS effluent has a distinctly lower K/Na ratio, much closer to 0.2 (Arienzo et al., 2009; Brandes, 1978; Patterson, 1997; Richards et al., 2016). These distinct K/Na signatures have been used to distinguish between contamination sources in previous Irish studies (Cunningham et al., 2003; Kelly and Wright, 2002).

K/Na mass ratios for SA1, SA2, SA3 and SA4 over the 14 monitoring months are shown in Fig. 2. Wells treated with a water softener are illustrated using solid grey lines. In SA1, little variation is seen in the K concentrations and the K/Na ratios in five wells. A noticeable increase in both K and K/Na in CX52, from October to March coincides with a rise in the recorded levels of *E. coli*. Both K and K/Na are significantly correlated with *E. coli* ($r = 0.77$, and $r = 0.73$; $p < 0.01$, respectively) but not with nitrate ($r = 0.23$, and $r = 028$; $p < 0.01$, respectively). This period also coincides with the housing of animals during the winter, which could be a potential causal factor, linked with an impact from the adjoining farmyard. In SA2, where no wells seemed to be close to any agricultural point sources, no elevated levels are apparent and little temporal variation is seen in the K concentrations or K/Na ratios of the four wells that are not treated by a water softener. In SA3, elevated K concentrations and K/Na ratios were measured consistently in KX29 and KX13 indicating a possible impact from agricultural point sources (although the levels fluctuate across the boundary indicative of DWWTS contamination). The KX29 wellhead is situated directly beside a poultry coop while KX13 is close to an animal drinking trough with ingress clearly visible (Fig. S.4). Both KX29 and KX13 tested positive for *E. coli* on several occasions over the monitoring period. In SA4, consistently elevated K and K/Na values are evident in CL2 which is immediately down gradient of a mixed sheep and cattle farmyard, with a high potential for direct ingress.

3.4. Cl/Br

The ratio of chloride to bromide (Cl/Br) concentration generally remains relatively stable in groundwater over time. However, due to geochemical differences different aquifers can have distinct Cl/Br ratios: for example, water influenced by halite can have much higher Cl/Br ratios of between 1000 and 10,000 and more importantly, domestic wastewater has a Cl/Br ratio of 300–600 (Davies et al., 1998). These ratios and/or changes in ratios have been used to reconstruct the history of groundwater systems, as well as identify sources of pollution (Brown et al., 2009; Davies et al., 1998; Dumouchelle, 2006; Jagucki and Darner, 2001; Katz et al., 2011; McArthur et al., 2012; Panno et al., 2006).

Fig. 3(a) shows the Cl/Br ratios for the 24 wells sampled during the M11 and M13 monitoring events, as well as the corresponding results for presence/absence of *E. coli*. For the M11 event, all wells had quantifiable concentrations of Br, except for KX13, which was lower than the detection limit (1.67 μg/L). The Cl/Br ratios in the wells ranged from 125 to 1208. During the M13 event, all wells (except for CX23) had quantifiable concentrations of Br, with Cl/Br ratios ranging from 21 to 953.

Mixing curves have been developed from previous studies (see

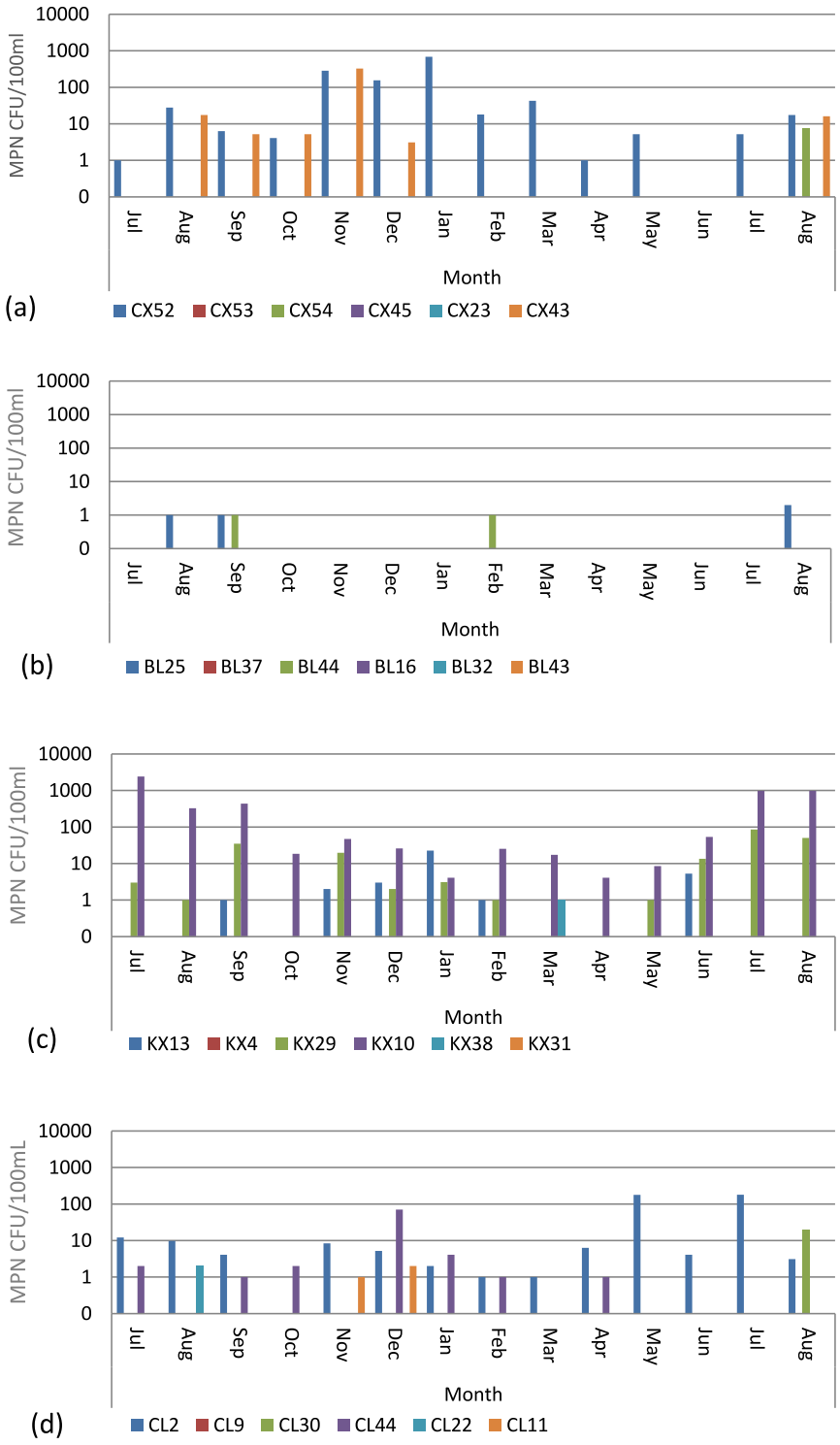

Fig. 1. Monthly groundwater *E. coli* results for areas (a) SA1, (b) SA2 (c) SA3 and (d) SA4.

above) to illustrate how the Cl concentration and Cl/Br ratio of natural groundwater changes with additional Cl/Br ratio waters mixed in. These plots can be used to infer if a groundwater sample has been influenced by an anthropogenic source. Fig. 3(b) shows the Cl/Br ratios plotted against the corresponding chloride concentrations for all wells analysed against the different Cl and Cl/Br diagnostic ranges, as developed by Davies et al. (1998), Katz et al. (2011), Panno et al. (2006) and Vengosh and Pankratov (1998).

No firm conclusions can be made with respect to any human impacts on waters with Cl/Br ratios between 200 and 400 due to background variations in hydrochemistry linked to local geology (Jagucki and Darner, 2001). However, a higher Cl/Br range of 400–1100 and chloride concentrations of 20–100 mg/L has been used to identify wells that are influenced by septic tank effluent (Katz et al., 2011). Of the four wells from M11 with ratios greater than 400 (KX29, KX4, KX10 and BL37), three fall within this range.

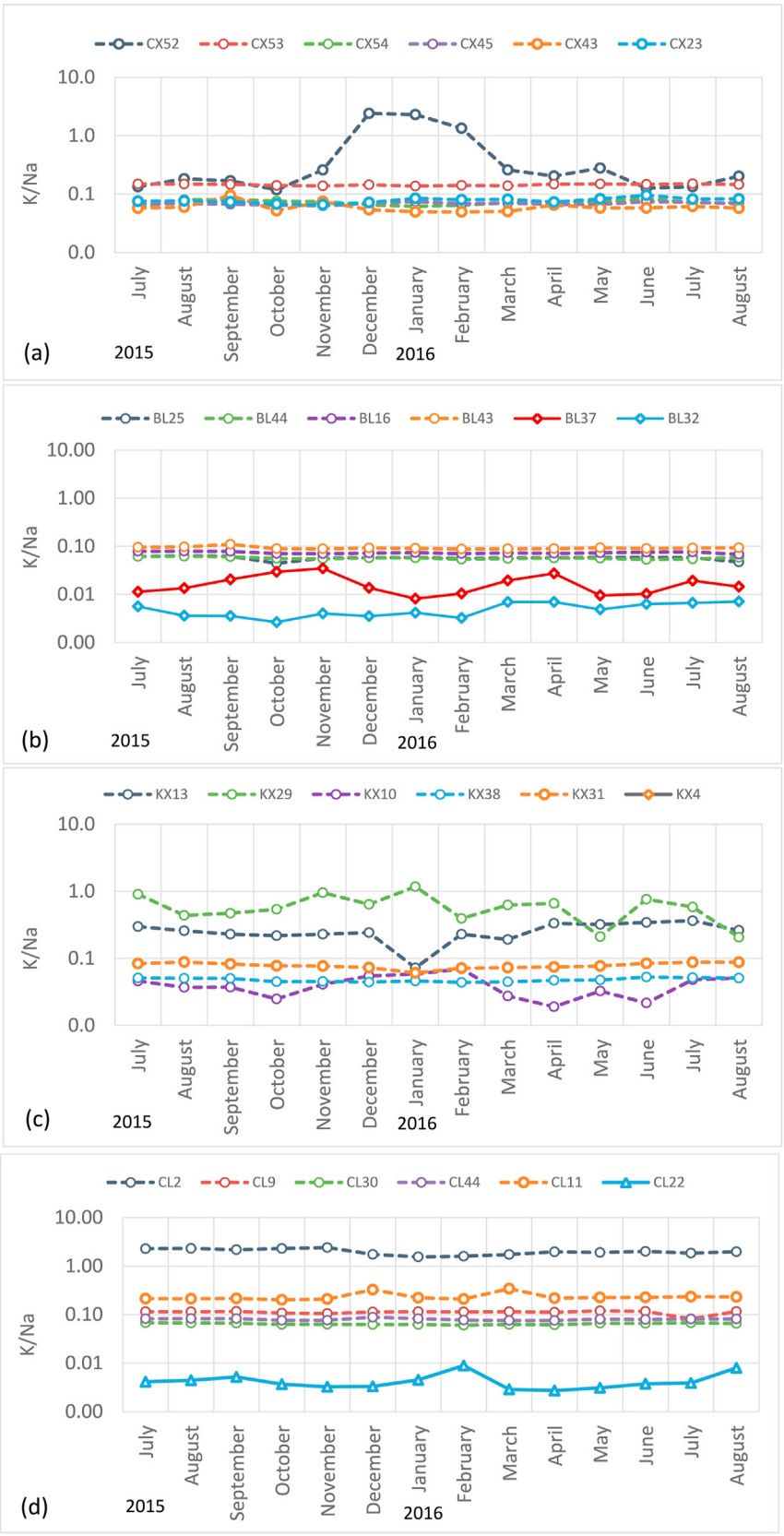

Fig. 2. Temporal variation of K/Na ratios (log scale) in monitored wells in (a) SA1, (b) SA2 (c) SA3 and (d) SA4. Wells treated with a water softener are illustrated using solid lines.

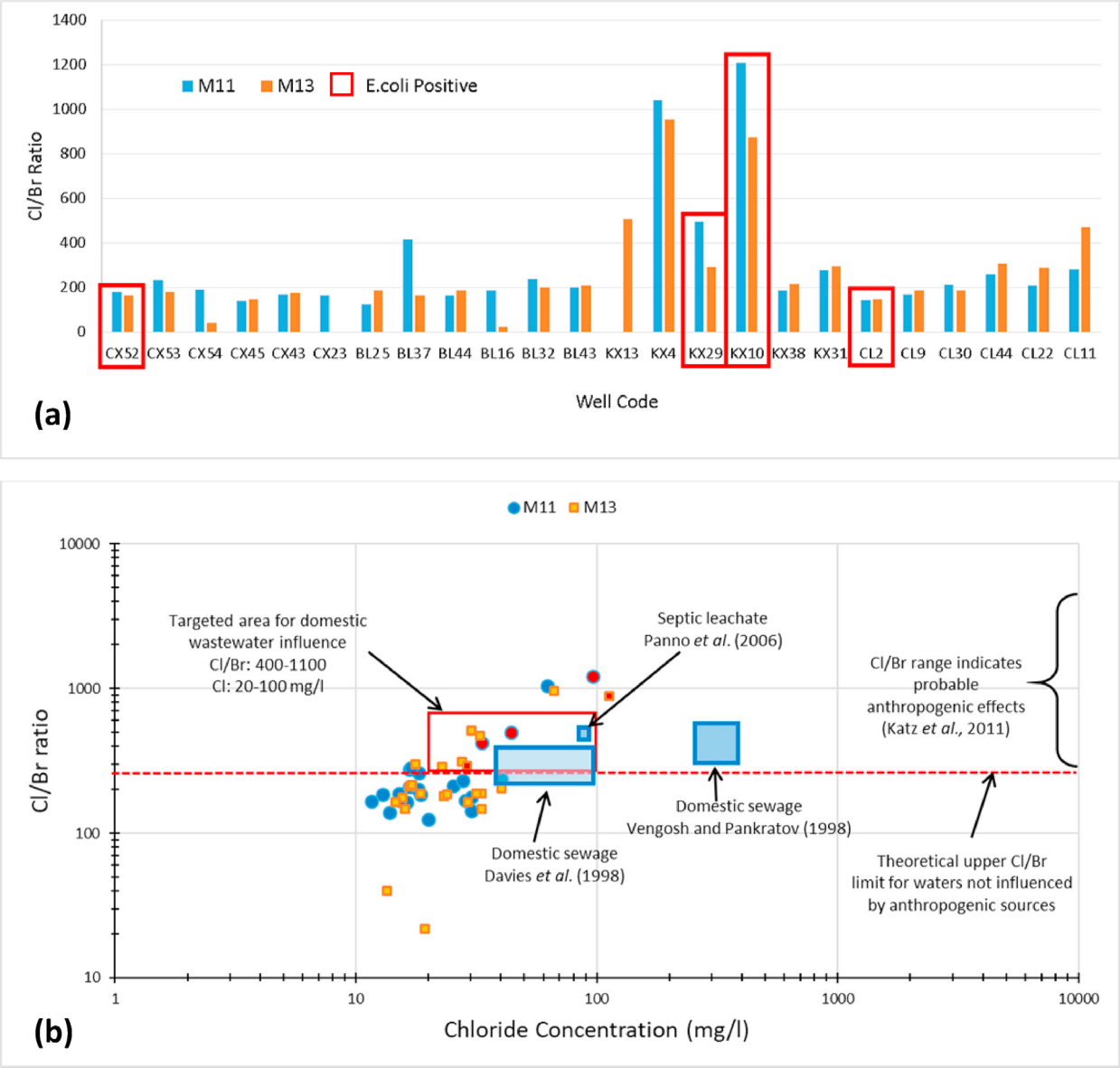

Fig. 3. (a) Cl/Br ratios for all wells in M11 and M13 monitoring periods. Also shown are the wells that tested positive for *E. coli*. (b) Cl/Br ratio versus chloride concentration for M11 and M13 monitoring event (n = 24 wells). Points marked red indicate those wells that tested positive for *E. coli*. Included are previous measured ranges for domestic wastewater and thresholds for indicating potential influences from anthropogenic activities. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The remaining well (KX10) only slightly exceeds the 1100 Cl/Br threshold. Similarly, four wells have Cl/Br ratios greater than 400 (CL11, KX13 and KX10 and KX4) in M13. Of the wells with Cl/Br ratios over 400, two (KX4 and BL37) are fitted with a water softener (a potential source of halite), with no access available to sample the source prior to treatment. Hence, no conclusions can be drawn on these wells with regards to a potential impact from a DWWTS. This is an obvious limitation of the method.

For the M11 event, the two remaining wells that had high Cl/Br ratios of 493 (KX29) and 1207 (KX10) also tested positive for *E. coli* (as well as throughout the monitoring period), which is consistent with a DWWTS impact. Although both of these houses use a water softener, the sample analysed was taken from a non-treated source and so Cl/Br ratio of the raw water source is valid. However, the DWWTS effluents from these houses (derived from water that has already passed through the softener) would be expected to have elevated chloride concentrations and Cl/Br ratios (Thomas, 2000) which potentially explains why the elevated Cl/Br ratio was identified in these two wells.

For the M13 sampling event, once KX4 is excluded (due to water softening) three wells have elevated Cl/Br ratios (CL11, KX13 and KX10). KX10 exhibits consistent elevated Cl/Br ratios supporting the conclusion of a DWWTS impact. Furthermore, the consistently low K/Na ratio (see Section 3.3) suggests that organic agricultural waste is not the *E. coli* source, indicating how the two ratios can be used in combination. Conversely, for KX29, while the Cl/Br ratio in M11 indicated an impact from the DWWTS, the lower Cl/Br ratio during M13 does not. This might indicate that the impact from DWWTS effluent is transient. However, as *E. coli* was present in both M11 and M13 samples as well as consistently elevated K/Na

ratios, this may indicate an impact from another source of contamination, such as agriculture.

Despite the elevated Cl/Br ratios in M13, neither KX13 nor CL11 tested positive for *E. coli* in M11 or M13. CL11 did test positive for *E. coli* in 2 out of the 14 monitoring events which again may indicate possible transient impacts from DWWTS effluent, although, as shown in the next section, no trace of artificial sweeteners were picked up in this well. Of note, while KX13 did not test positive for *E. coli* in M11 or M13, it did so in M12 which coincides with an increase in the Cl/Br ratio between M11 and M13 up to 505. The two remaining wells (CX52 and CL2) that tested positive for *E. coli* in the M11 and M13 events had low Cl/Br ratios, suggesting contamination from another source other than a DWWTS - the K/Na ratios indicated that these wells are impacted by nearby agricultural point sources of contamination (cattle farmyards). There was no significant correlation found between Cl/Br levels and nitrate across the two sampling events ($r = 0.76$, and $r = 0.71$; $p < 0.01$, respectively).

3.5. Artificial sweeteners

Artificial sweeteners are commonly added as an alternative to conventional sugar in food and drinks, as due to their high intensity sweetness they can be used in much lower quantities than sugar, thus reducing the calorie content while still maintaining the desired sweetness (Scheurer et al., 2009). Some artificial sweeteners are not completely metabolized by the human body and so pass through into wastewater effluent. Recent studies have indicated that certain artificial sweeteners are also resistant to breakdown during wastewater treatment processes and thus persist in the environment, leading to research into their use as potential tracers of contamination (Buerge et al., 2009; Buerge et al., 2011; Lange et al., 2012; Richards et al., 2016; Robertson et al., 2013; Robertson et al., 2016; Scheurer et al., 2009; Tran et al., 2014; Van Stempvoort et al., 2011a; Van Stempvoort et al., 2011b; Van Stempvoort et al., 2013; Wolf et al., 2012). For example, acesulfame, cyclamate, saccharin and sucralose were consistently detected in municipal wastewater samples in Switzerland by Buerge et al. (2009), ranging in concentrations from 2 to 65 μg/L, with cyclamate and acesulfame the most common, followed by saccharin then sucralose.

The results for the M11 and M13 monitoring events (Fig. S.5) show that all wells were negative for saccharin, sucralose and aspartame. However, during M11 25% ($n = 6/24$) tested positive for acesulfame ranging from 48 to 1973 ng/L (average concentration = 626 ng/L) whilst during M13 33%, ($n = 8/24$) tested positive for acesulfame ranging from 25 to 2625 ng/L (average concentration = 675 ng/L). In addition, a single well (CL 30) tested positive for cyclamate (40.9 ng/L). The presence of acesulfame and cyclamate in these wells is consistent with impacts from nearby DWWTS.

The absence of sucralose, saccharin and aspartame and the relatively widespread presence of acesulfame, and to lesser extent cyclamate, matches previous findings. Acesulfame has been the most widely detected sweetener in studies of surface water, groundwater and domestic wastewater (see above studies), making it a potentially suitable tracer. It is often used as a food additive in baking products, in pharmaceutical products or blended with other sweeteners in carbonated drinks. Conversely, the studies have shown that saccharin is typically not persistent during wastewater treatment processes and/or in the environment. However, given the number of studies that have shown sucralose to be persistent during wastewater treatment and in the environment (Buerge et al., 2009; Buerge et al., 2011; Robertson et al., 2013; Scheurer et al., 2009), it is somewhat surprising that it was not detected in any of the well samples, although it is consistent with studies by Buerge et al. (2009) and Van Stempvoort et al. (2013) that also failed to detect sucralose in groundwater samples. This could be related to the lower reported concentrations of sucralose in wastewater by over an order of magnitude in comparison to cyclamate, acesulfame and saccharin (Buerge et al., 2009; Scheurer et al., 2009).

The presence of cyclamate in CL30 highlights how the analysis of a suite of sweeteners, and not just acesulfame, can be useful. Cyclamate, found by Buerge et al. (2009) and Scheurer et al. (2009) to be substantially degraded during wastewater treatment processes, was the sweetener detected at the highest concentrations in raw wastewater by both those studies, and was detected in distant parts of a septic tank plume by Robertson et al. (2013) and in 43% of wells studied by Van Stempvoort et al. (2013). Hence, although acesulfame is the most persistent sweetener, the presence of cyclamate and saccharin in groundwater can indicate a more recent contamination by untreated wastewater. Therefore, the absence of cyclamate in CL30 in M11, and its presence during M13 would indicate a recent contamination event from a DWWTS.

Three of the four wells (CL2, KX10, KX29 and CX52) that tested positive for *E. coli* in the M11 and M13 monitoring events also tested positive for acesulfame (CL2, KX29 and CX52) indicating that a DWWTS may be a source of *E. coli* in these wells. However, the lack of a sweetener in KX10 suggests a different source of faecal contamination. For the remaining wells that tested positive for acesulfame, and yet were negative for *E. coli*. during M11 and M13, they all have tested positive for *E. coli* on at least one other occasion demonstrating the notable temporal variation in the presence of *E. coli*. This indicates a difference in persistence (which would be expected) between acesulfame and *E. coli*. The presence of acesulfame in a well therefore indicates an impact from a DWWTS as it has persisted during the wastewater transport and attenuation processes in a DWWTS (including the soil treatment unit), but this may not corroborate with the presence of faecal microbial contamination, which may have been attenuated before reaching the groundwater.

3.6. Caffeine

A small proportion of the caffeine consumed (approx. 3%) is not metabolized and is excreted in urine (Tang-liu et al., 1983). Wastewater systems can also receive caffeine from unconsumed caffeine products and the washing of coffee pots and cups (Chen et al., 2002; Hagedorn and Weisberg, 2009; Stavric et al., 1998). Caffeine has been detected in human wastewater, both internationally and in Ireland (Chen et al., 2002; Daneshvar et al., 2012; Gill et al., 2009b; Godfrey et al., 2007; Paxeus and Schroder, 1996; Richards et al., 2016; Seiler et al., 1999), illustrating its potential use as a fingerprinting/source tracking tool. Several studies have detected caffeine in surface waters (Buerge et al., 2003; Daneshvar et al., 2012; Knee et al., 2010; Siegener and Chen, 2002; Weigel et al., 2002), as well as in groundwater (Stuart et al., 2013). However, caffeine does not seem to act as a conservative tracer, with evidence of substantial removal during wastewater treatment (Buerge et al., 2003; Drewes et al., 2003; Froehner et al., 2012; Paxeus and Schroder, 1996). In a previous Irish study, Gill et al. (2009b) found that caffeine in septic tank effluent was considerably degraded both during secondary aerobic treatment and in the aerobic subsoil conditions beneath the percolation trenches, but remained largely untouched when passing through the anoxic/anaerobic conditions of constructed wetland treatment systems.

The results of this study in Ireland appear to confirm the previous research, as none of the 24 well samples taken during the M11 or M13 sampling events tested positive for caffeine down to a limit of detection of 25 ng/L. Hence, caffeine seems to be of limited

use as a tracer of on-site wastewater contamination if its pathway between source and receptor has been via a sufficient depth of unsaturated subsoil.

3.7. Pharmaceuticals

The main source of pharmaceuticals in the environment is understood to be domestic wastewater, with carbamazepine, ibuprofen, sulfamethoxazole and diclofenac the most commonly reported in groundwater studies (Lapworth et al., 2012; Pal et al., 2014). Carbamazepine, a drug used to control epileptic seizures and several mental disorders, has been shown to persist during wastewater treatment and in the environment, which has led to studies suggesting its suitability as a tracer (Clara et al., 2004; Godfrey et al., 2007; Matamoros et al., 2009; Müller et al., 2012; Zhang et al., 2008). Similarly, the widespread use of sulfamethoxazole for bacterial infections has resulted in its regular detection in wastewater, surface water and groundwater systems (Avisar et al., 2009; Bendz et al., 2005; Godfrey et al., 2007; Onesios et al., 2009; etc.), although its persistence in the environment is less clear given that its removal during wastewater treatment processes seems to be highly variable (Onesios et al., 2009).

No wells tested positive for carbamazepine in either the M11 or M13 monitoring events. One well (CX43) tested positive (152 ng/L) for sulfamethoxazole during the M11 event, but negative during the M13 event, and was negative for *E. coli* in both monitoring events. However, this well tested positive for *E. coli* in M14, indicated a faecal contamination source. Given that sulfamethoxazole was detected in this well, it is likely that there is an impact from a DWWTS.

Despite the widespread detections reported internationally, the results here indicate that pharmaceuticals are of limited use as tracers of contamination of private wells by DWWTS. Much of the previous research has been conducted at large scale WWTPs which would have a greater likelihood of receiving a range of pharmaceuticals and personal care products (PPCPs). In contrast, the application of the PPCP compounds as tracers of wastewater contamination of private wells would depend on the use of those specific PPCPs by one or more of the householders, which obviously reduces their application to specific locations, in addition to raising potential privacy issues.

3.8. Faecal sterol profiles

The specific sterol (and their breakdown product – stanols) content of an animal's faeces is related, to sterols that are biosynthesised inside the animals and their diet. and to Sterols can also be biohydrogenated to stanols of various isomeric configurations by anaerobic bacteria found in the gut of some animals (Leeming et al., 1996). Humans, herbivores and birds have sufficiently different faecal sterol characteristics such that they can be used for the identification of sources of faecal contamination in waters (Derrien et al., 2012; Leeming et al., 2015; Lucas et al., 2007; Shah et al., 2007; Marvin and Brown, 2001; Moriarty and Gilpin, 2009).

Table 2 shows the results from the sterol analysis for the M11 and M13 monitoring events and has been interpreted using the decision processes developed in New Zealand by ESR (2020) as follows (Devane et al., 2018). Where the total sterol content is below a 2000 ng/L benchmark, the source should be resampled with a greater quantity of water. For the M11 sampling, seven of the sixteen wells had a total sterol content below the benchmark. The sample volume taken in this current research (20 L) is already much greater than the recommended volume and so no conclusion can be made regarding an impact (or otherwise). For the wells with a total

Table 2
Sterols and stanol results from the M11 and M13 monitoring events.

M11 Monitoring event		Site and Well I.D.															
		SA1				SA2				SA3				SA4			
		CX52	CX43	CX53	CX54	BL16	BL25	BL44	BL32	KX10	KX13	KX29	KX31	CL2	CL44	CL9	CL11
Sterols and stanols (μg/L)	Total sterol	1.72	4.27	1.75	1.68	3.19	3.25	2.58	3.79	4.94	1.84	2.05	1.70	3.61	8.45	1.56	1.57
	Coprostanol [a]	NF	NF	NF	NF	0.10	NF	NF	0.10	NF	NF	NF	NF	0.10	NF	NF	NF
	Cholesterol [b]	NF	NF	NF	NF	NF	NF	NF	NF	1.89	NF	NF	NF	NF	NF	NF	NF
	Cholestanol [a]	NF	NF	NF	NF	0.14	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	24-ethyl coprostanol [a]	NF	NF	NF	NF	NF	NF	NF	0.19	NF	NF	0.19	NF	0.20	NF	NF	NF
	24-ethylepicoprostanol [a]	NF	NF	NF	NF	NF	0.12	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	Campesterol [a]	0.00	0.11	0.10	0.00	0.11	0.11	0.11	0.00	0.12	0.00	0.00	0.11	0.11	0.11	0.00	0.00
	Stigmasterol [a]	0.22	0.36	0.23	0.23	0.32	0.34	0.32	0.34	0.31	0.25	0.23	0.22	0.33	0.26	0.21	0.21
	Sitosterol [a]	1.49	3.60	1.42	1.37	2.52	2.67	2.15	3.15	2.53	1.59	1.54	1.38	2.78	8.07	1.35	1.36
	Stigmastanol [a]	0.00	0.20	0.00	0.09	0.00	0.00	0.00	0.00	0.09	0.00	0.09	0.00	0.09	0.00	0.00	0.00
M13 Monitoring event		Site and Well I.D.															
		SA1				SA2				SA3				SA4			
		CX52	CX43	CX53	CX54	BL16	BL25	BL44	BL32	KX10	KX13	KX29	KX31	CL2	CL44	CL9	CL11
Sterols and stanols (μg/L)	Total sterol	1.24	0.89	0.81	0.56	1.01	0.95	0.61	0.51	0.66	0.77	0.52	0.50	0.62	0.46	0.47	0.33
	Coprostanol [a]	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	Cholesterol [b]	0.18	NF	0.18	NF	0.19	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	Cholestanol [a]	0.08	0.08	NF	0.08	NF	0.08	NF	NF	NF	NF	NF	NF	0.08	NF	NF	NF
	24-ethyl coprostanol [a]	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	24-ethylepicoprostanol [a]	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF
	Campesterol [a]	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	NF
	Stigmasterol [a]	0.06	0.05	0.05	0.05	0.06	0.07	0.04	0.05	0.05	0.06	0.04	0.04	0.04	0.04	0.04	0.04
	Sitosterol [a]	0.76	0.60	0.42	0.36	0.69	0.64	0.41	0.39	0.44	0.55	0.31	0.38	0.34	0.35	0.36	0.29
	Stigmastanol [a]	0.09	0.09	0.09	0.00	0.00	0.09	0.09	0.00	0.09	0.09	0.09	NF	0.09	NF	NF	NF

NF = not found.
[a] Lower limit of detection = 50 ng/l.
[b] Lower limit of detection = 100 ng/l.

sterol content greater than 2000 ng/L, the ratios of coprostanol:cholestanol and 24-ethylcopsrostanol:24-ethylcholestanol were compared. Isolated detections of coprostanol, cholesterol, cholestanol, 24-ethylcoprostanol were found in six out of these nine wells but none of them contained all four sterols, whereby the ratios could be calculated and compared. Although coprostanol, 24-ethylcoprostanol and 24-ethylepicoprostanol are associated with faeces, their presence alone cannot be used to indicate a source of contamination (Devane et al., 2018). For example, 24-ethylcoprostanol (linked more to ruminants) and coprostanol (linked more to humans) were both detected in wells CL2 and BL32. The M13 event results yielded similar conclusions since none of the wells had a total sterol content greater than the 2000 ng/L threshold. The results do highlight the almost ubiquitous presence of plant related sterols campesterol, stigmasterol and sitosterol, which account for 90% of the total sterols content for the wells tested and likely originate from the decay of plant matter.

While previous studies have successfully used sterols analysis to trace faecal contamination, the majority of research has been conducted on surface water systems (Blanch et al., 2006; Derrien et al., 2012; Grimalt et al., 1990; Leeming et al., 1998; Leeming et al., 2015; Lucas et al., 2007; Moriarty and Gilpin, 2009; Shah et al., 2007 and more). Faecal sterols and stanols, being hydrophobic, are readily adsorbed onto sediment and soils en route from their DWWTS source through the subsoil pathway to groundwater (Tran et al., 2015). Hence, sterol analysis may not be ideal for tracing faecal contamination in groundwater (which usually has very low suspended solids concentrations), which the results of this research seem to support.

3.9. Fluorescent whitening compounds (FWC)

FWCs are used as optical brighteners in laundry detergents: the two most commonly used FWCs in such detergents are distyrylbiphenylsulfonate (DSBP) and the diaminostilbene (DAS 1) (Dubber and Gill, 2017). The specificity, solubility and low potential for biodegradability of FWCs have led to studies into their use as a tracer of wastewater contamination (Tran et al., 2015), although most research has been focussed on surface waters (Boving et al., 2004; Dickerson et al.,2007; Hayakawa et al., 2007; Hayashi et al., 2002; Stoll and Giger, 1997; Shu and Ding, 2005). While limited research has been carried out on FWC occurrence of in groundwater, there have been some positive indications (Close et al., 1989; Murray et al., 2007), although other studies (Alhajjar et al., 1990) have concluded that FWC in DWWTS effluent are unlikely to reach groundwater due to the effects of decomposition and sorption to soil.

Fig. 4 shows the fluorescence intensity results from the M11 and M13 monitoring events. In SA1 and SA2, most values are close to the instrument's limit of detection (11.5). All values are below the photodecay threshold, defined by Dubber and Gill (2017) as 3*LOD, below which samples should not be further investigated for FWCs using that method. It can be concluded that for most wells in SA1 or SA2 this method was not applicable as it was not able to distinguish whether fluorescence signals originate from organic matter or FWCs.

Fig. 4(b) shows higher initial fluorescence values for many of the wells in SA3 and SA4 (compared to SA1 and SA2) having values above the photodecay threshold for seven wells during M11. The photodecay method was applied with their reductions in

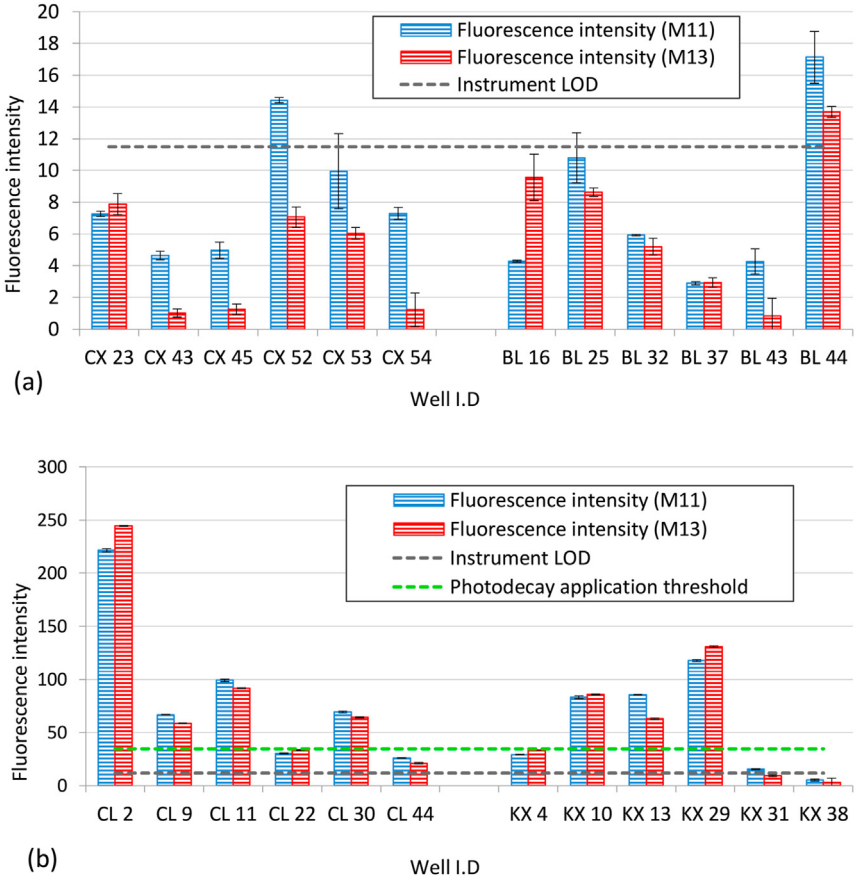

Fig. 4. Initial sample fluorescence (i.e. pre-UV light exposure) in (a) SA1 and SA2 and (b) SA3 and SA4.

fluorescence measured after the exposure to UV light for 0, 1 and 10 min. The ratios of decay however revealed (according to the predefined criteria that a ratio of >0.25 indicates presence of FWC) that no wells tested positive for FWC. The photodecay profiles were similar for the M13 event, and hence no positive results were found.

Based on the results of this research, the fluorometric and UV exposure method (described by Cao et al. (2009) and modified by Dubber and Gill (2017)) does not appear suitable for the detection of FWC in private wells. Although relatively inexpensive and easy to apply, the method provided no positive indications of FWC presence in any of the wells, despite other parameters and tracers indicating an impact from human sources of contamination. While FWC may indeed not be present in the private wells tested, it is also likely that the method does not achieve the required sensitivity. Further investigation using a more sensitive analytical technique such as liquid chromatography (Stoll and Giger, 1997), may be warranted.

3.10. Tracer comparisons and proposed tiered investigation approach

A summary of the comparison of the contamination fingerprinting techniques tested on the 24 private wells across four different areas is presented in Table 1. Although the elevated K/Na ratios appeared to coincide with the wells having potential nearby sources of decaying organic matter associated with agriculture, the same wells also tested positive for the sweetener acesulfame, which indicates contamination from DWWTS. These wells also had high Cl/Br ratios which suggest a contamination link to a DWWTS. The analyses for K/Na nor Cl/Br ratios are relatively quick and low cost, which makes them attractive, although neither seem to be definitive in terms of confirming a contaminant source. The artificial sweetener acesulfame does appear to be a promising tracer of DWWTS contamination as it was detected in several wells (in line with other studies); equally cyclamate is potentially useful, although it was only picked up in a single well in this study. The results also indicate a difference in persistence between these sweeteners and the routinely used faecal indicator bacteria, *E. coli*. The other potential fingerprinting approaches/compounds (faecal sterol profiling, FWC analysis, caffeine and carbamazepine), all returned negative results, demonstrating limited applicability, at least in such Irish hydrogeological settings. Finally, sulfamethoxazole was detected in a single well, but this cannot be deemed strong enough evidence with regards to its overall applicability as a groundwater contamination tracer.

It is therefore recommended that a tiered strategy is adopted when trying to identify human wastewater effluent as a source of contamination in private wells. This would start by employing less resource intensive techniques, such as site assessment and/or more standard water quality parameters. However, if confirmation of a human wastewater source of contamination is subsequently needed, then more resource intensive fingerprinting analyses need to be carried out. The first stage would involve a comprehensive site assessment along with sampling the well for conventional water quality chemical and microbial parameter analysis (*E. coli*, ammonia etc.), but should also include K/Na and Cl/Br ratios as more specific tracer techniques. If these procedures turn out to be ambiguous (i.e. not diagnosing an explicit source or if any infered remedial works do not rectify the contamination) then the second, more resource intensive, stage should be applied whereby the well is tested for artificial sweeteners.

4. Conclusions

This research has evaluated several potential contamination fingerprinting techniques that may be used to track private well contamination to a DWWTS. Both K/Na and Cl/Br ratios were found to be useful for identifying impacts from decaying organic matter (farmyard runoff) and DWWTS, respectively, while the artificial sweetener acesulfame was widely detected, illustrating its conservative nature and applicability as a tracer for domestic wastewater. In contrast, faecal sterol profiling, FWC, carbamazepine, sulfamethoxazole and caffeine showed limited applicability to link private wells contamination to DWWTSs in Ireland.

In view of the varying levels of resources and expertise required to apply these different techniques and the heterogeneity of private well sites (variations in well design, hydrogeology etc.) a strategic tiered approach for identifying a contamination source is proposed. As this research has indicated that a high number of private wells are at least intermittently contaminated, further research to refine fingerprinting techniques is both recommended and necessary to ensure groundwater resources and consumer health are protected.

CRediT author statement

Christopher Fennell: Data curation; Formal analysis; Investigation; Writing- original draft: Laurence Gill.: Conceptualization, Project administration; Supervision; Funding acquisition; Writing - review & editing. David O'Connell: Formal analysis. Donata Dubber: Formal analysis. Patrice Behan: Methodology. Martin Danaher: Methodology. Mary Moloney: Methodology. Bruce Misstear Conceptualization; Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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