Calculation of wastewater effluent leakage to pristine water sources by the weighted average of multiple tracer approach

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Abstract A methodology used to estimate the percentage of wastewater effluent in an otherwise pristine water site is proposed on the basis of the weighted mean of the level of a consortium of indicator pollutants. This method considers the levels of uncertainty in the evaluation of each of the indicators in the site, potential effluent sources, and uncontaminated surroundings. A detailed demonstrative study was conducted on a site that is potentially subject to wastewater leakage. The research concentrated on several perched springs that are influenced to an unknown extent by agricultural communities. A comparison was made to a heavily contaminated site receiving wastewater effluent and surface water runoff. We investigated six springs in two nearby ridges where fecal contamination was detected in the past; the major sources of pollution in the area have since been diverted to a wastewater treatment system. We used chloride, acesulfame, and carbamazepine as domestic pollution tracers. Good correlation ($R^2 > 0.86$) was observed between the mixing ratio predictions based on the two organic tracers (the slope of the linear regression was 1.05), whereas the chloride predictions differed considerably. This methodology is potentially useful, particularly for cases in which detailed hydrological modeling is unavailable but in which quantification of wastewater penetration is required. We demonstrate that the use of more than one tracer for estimation of the mixing ratio reduces the combined uncertainty level associated with the estimate and can also help to disqualify biased tracers.

1. Introduction

Quantification of wastewater or wastewater effluent leakage into otherwise pristine water sources is a long-standing challenge. For more than a century, health authorities and drinking water suppliers have increasingly relied on indicators to warn against the leakage of effluent and wastewater into pristine water sources. Although total coliforms, *Escherichia coli*, fecal coliforms, and to some extent also fecal Streptococci, *Clostridium perfringens*, and Enterococcus [*Gronewold et al.*, 2008] have become indispensable indicators of septic pollution, other indicators and tracers are gradually emerging for more sensitive and accurate quantification of leakage. In this paper, the term "indicator" is reserved for reference to a chemical or biological entity that indicates the mere presence of domestic pollution, whereas the term "tracer" is used for a quantitative marker of pollution. These indicators are also important because pathogens are not the only concern. Organic and inorganic contaminants in well-treated wastewater effluent also constitute health risks. In numerous locations, both in developed and underdeveloped countries, the dilution of wastewater with pristine water is taken as an inevitable fact of life. This situation occurs in many regions where either planned or unplanned indirect potable reuse is practiced such that treated wastewater effluents are discharged into streams that ultimately supply drinking water to downstream residencies [*Atkinson et al.*, 2009; *Goda and Nakanishi*, 1991; *National Research Council*, 1998]. This situation also occurs when a large percentage of reverse osmosis desalinated wastewater is mixed with desalinated sea and surface water, which is a common practice in Singapore [*Pisani*, 2006]. In these cases, the effluent sources are well-known and well-characterized. However, in numerous other cases, it is necessary to quantify the wastewater-pristine water ratio. This requirement may stem from a sociological motive, which is sometimes referred to as the eek factor. In other cases, the emergence of a new source of pollution that may have originated from improperly treated waste is of particular importance to health authorities. It may point to the existence of an unknown pathogenic risk or to exposure to an unknown adverse health effect source due to chemical contamination. In Israel, particularly within its mountain aquifers in which surface water can easily leak through fractures

with overlaying Karst structures, there is a strong objection to any sort of leakage of wastewater or wastewater effluent into drinking water sources, and microbial indicators are clearly insufficient for ensuring the absence of such leaks in many vulnerable sites.

Conservative anions, particularly chloride and nitrate, have emerged as chemical tracers for wastewater pollution because anions are less retarded by the soil compared with neutral and positively charged moieties, and they are often present in high concentrations in wastewater and wastewater effluents. However, nitrate can also originate from agricultural fertilization, and its level in wastewater is largely dependent on the type of waste treatment and whether a nitrification-denitrification process is employed.

Chloride is a highly popular tracer for domestic wastewater and is frequently used to model the mixing of domestic wastewater and pristine water because the concentration of chloride in domestic wastewater is approximately 50–150 mg/L higher than that in tap water [*Schmidt et al.*, 2013; *Gasser et al.*, 2010; *Edmunds and Gaye*, 1994; *Eriksson and Khunaksem*, 1969; *Katz et al.*, 2011; *Kelly et al.*, 2010; *Marei et al.*, 2010]. However, chloride is not specific to wastewater effluent, particularly in Israel, which has high chloride levels in its aquifers, and salination occurs in many of its water sources. Other anions (e.g., boron) [*Vengosh et al.*, 1994] and ratio between anions (e.g., bromide to chloride) were used for quantification [*Vengosh and Pankratov*, 1998], although these anions are less abundant in wastewater. Thus, the uncertainty associated with quantification based on these tracers is large. The same, in our opinion, applies to quantification of wastewater based on isotope enrichments [*Vengosh and Pankratov*, 1998], although this is yet to be proven since we are not aware of uncertainty quantification of mixing ratio estimates based on isotope analysis.

Recent advances in analytical chemistry, particularly the advent of liquid chromatography coupled with electrospray mass spectrometry, have revealed an abundance of refractory organic micropollutants that are sometimes specific to domestic wastes and can potentially serve as septic pollution tracers. In a recent study conducted in a carefully monitored soil aquifer treatment site in Israel and which included approximately 200 organic micropollutants, two pollutants were detected to be the most resistive to biodegradation. These include the antiepileptic and antidepressant drug carbamazepine (CBZ), and the artificial beverage sweetener acesulfame-K, which contains the acesulfame anion (ACS) [*Lev et al.*, 2011]. Among the proposed domestic waste tracers, it appears that gadolinium (Gd) is another well-studied waste tracer. The tracer's anthropogenic contribution is quantified as gadolinium anomaly—its relative concentration to the weighted average of the concentrations of two other lanthanides, Samarium and Terbium [*Knappe et al.*, 2005]. However, because the gadolinium anomaly is typically associated with its use in hospitals and large clinics as a magnetic resonance imaging (MRI) contrast agent, it is less useful for the characterization of village wastes or septic tank leakage. Although Gd is administered as a *negatively* charged chelate with high soil mobility (which is also the reason why we mention it as an organic micropollutant), it is a less useful tracer when long-term soil transport is involved because the mobility of the dissociated rare earth cation is retarded in the subsoil.

In a recent study, we quantified the leakage from a soil aquifer treatment (SAT) system by using two tracers, chloride, and CBZ [*Gasser et al.*, 2010, 2011]. We demonstrated that chloride is a more precise quantitative tracer for wastewater leakage in locations with high concentrations of wastewater effluent (higher than approximately 30% for the researched SAT site), whereas CBZ gave a more precise quantification of minute wastewater leakages.

Numerous attempts to quantify the leakage of domestic wastes to otherwise pristine water sources based on multiple tracers or to correlate between the signals of various organic tracers have been reported [*Robertson et al.*, 2013; *Daneshvar et al.*, 2012; *Hillebrand et al.*, 2012; *Kuroda et al.*, 2012; *Oppenheimer et al.*, 2011; *Williams et al.*, 2013], although, a truly quantitative combined approach has not been documented. *Scheurer et al.* [2011] demonstrated a very good correlation between CBZ and ACS levels in a wide range of water sources, which showed that both are suitable wastewater effluent tracers. *Stempvoort et al.* [2013] used correlations among a consortium of tracers to distinguish between single-source and multiple-source contaminations. They concluded that a constant ratio between the concentrations of various tracers signifies a single source, whereas a variable ratio may signify multiple sources.

Engelhardt et al. [*2013*] presented an approach relying on the incorporation of a micropollutant and temperature data in hydrological models. Their analysis showed that ACS is less useful than the temperature record, although ACS behaved as a conservative tracer in their system. We believe that the reason for the
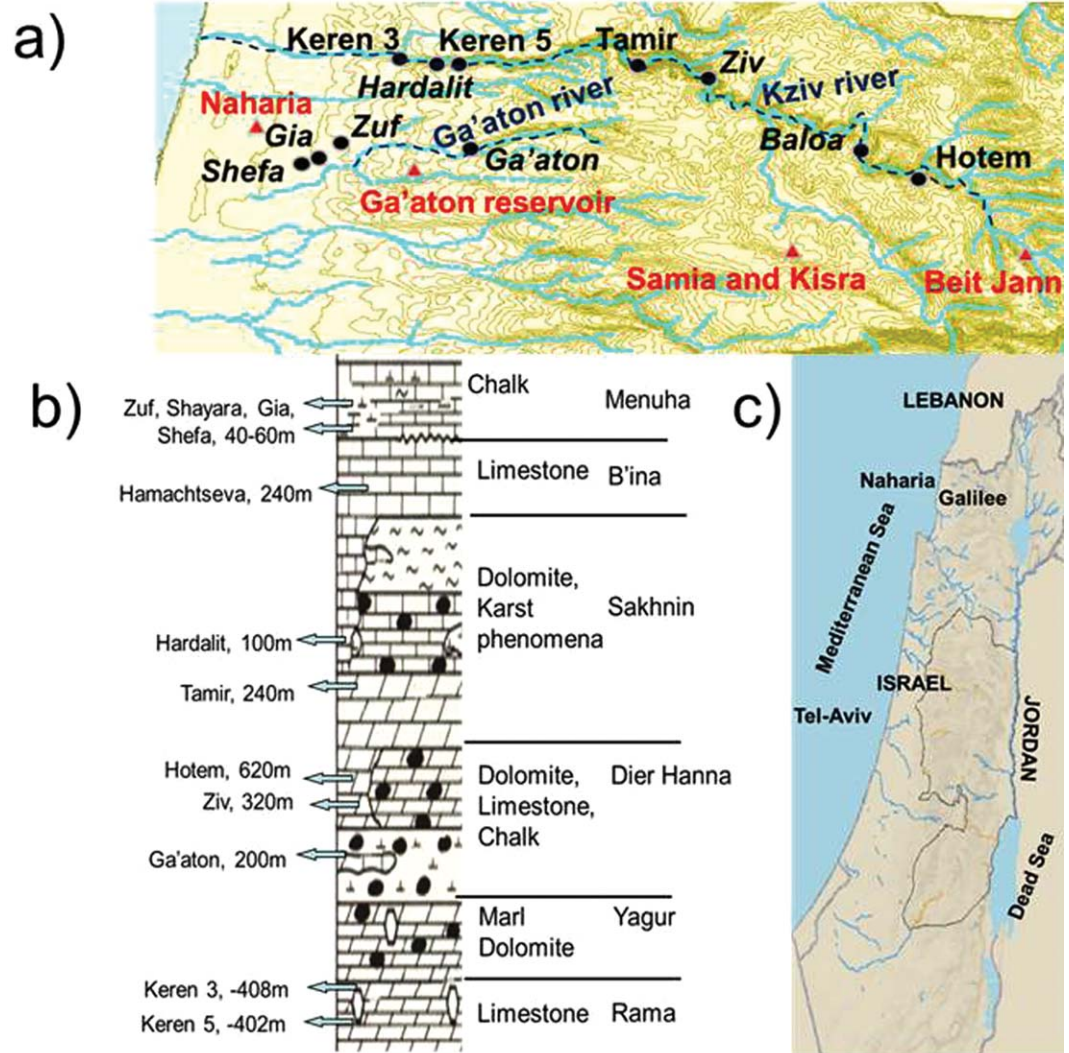
Figure 1. (a) The studied springs (in italics), the Baloa sinkhole, and the water sources (in red), (b) the lithostratigraphy and elevation of the various springs above sea level, and (c) the location of the study area in Israel.

inferiority of ACS in this particular case was the low ratio between the concentration of the tracer at the pollution source and that at the measured site, which was on average less than 2. However, hydrological models that may at times have superior prediction capabilities compared with our approach require extensive data that is unavailable in most cases where a decision regarding possible site contamination must to be taken by a water-quality supervising authority.

Our approach is largely an extension of that described in our previous study [*Gasser et al.*, 2010] and uses mixing ratio (M.R.) as the fundamental target parameter. The calculated M.R. is a normalized, dimensionless parameter, and is thus more informative than individual tracer concentrations. Therefore, M.R. can be associated with an uncertainty level that provides a means to quantitatively assess the MR's significance. We believe that a ratio between M.R. values, which are normalized parameters, is more meaningful than a ratio between tracer concentrations, particularly when assessing nonselective tracers. In this paper, we analyze a specific set of nearby water springs to demonstrate the manner in which a combination of multiple tracers and their uncertainty-based weighted average can decrease uncertainty levels associated with M.R. calculations. Moreover, measurement of multiple tracers and their predicted MR calculation can allow a rational selection of the tracers with a lower systematic error. We demonstrate the protocol for several perched springs in a Cretaceous chalk aquifer in Upper Galilee in northern Israel (Figure 1).
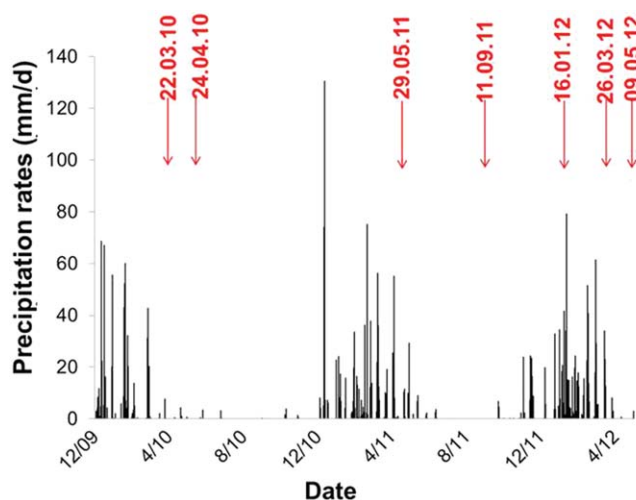
Figure 2. Sampling dates and daily precipitation rates.

2. Experimental Section

2.1. The Study Site

We studied six springs located on two ridges near the Kziv (Ziv and Hardalit springs) and Ga'aton wadies (Gia, Shefa, Zuf, and Ga'aton springs) in northern Israel, which are delineated in Figures 1a and 1c. Additionally, we studied the Baloa sinkhole at the Kziv River. The sinkhole captures surface drainage from various sources along the upper Kziv River and effluent from the Beit Jann wastewater treatment system, and the water drains into the subsurface.

The geology of the area is dominated by Cretaceous carbonate formations of the Judea Group and chalk and marl exposures of the Mount Scopus Group directly above it (Figure 1b). The Judea Group in the area is composed of a 900 m thick sequence of permeable limestone and dolomite interrupted by a 400 m thick Dier Hanna formation aquitard, which is composed mostly of finely crystalline dolomite. The upper aquifer, which is composed of dolomites and limestone, is approximately 200 m thick and displays Karst features with high effective permeability. The studied springs drain in this upper aquifer, although some of them are located at the upper part of the Dier Hanna Formation. The study area is exposed to a Mediterranean climate with 800–900 mm of winter precipitation and warm and dry summer (April–September). The precipitation events and the sampling dates in the study period are depicted in Figure 2.

To assess the uncontaminated background concentration levels of the various tracers in the area, we sampled four water sources at the upper and lower aquifers. The Hotem and Tamir springs and Keren 3 and Keren 5 water wells were sampled. The main stratigraphic units of the Judea and Mount Scopus groups in the area are depicted in Figure 1b with indications of the corresponding draining aquifers and the elevation above sea level. The one-dimensional representation of the spring locations in the figure does not correspond to the elevation of the springs above sea level due to the geological folds and faults.

2.2. History of Pollution in the Cabri and Kziv Springs

The north Galilee springs supplied approximately 12 Mm^3/y of drinking water for many years until a high-turbidity episode with septic pollution occurred in 1989, which shut down the drinking water supply. In 2000, the drinking water supply was reinitiated after a filtration unit was constructed. In November 2006, another major pollution event caused deterioration of water quality attributes, including increased levels of total organic carbon (TOC), ultraviolet (UV) radiation absorption, and dissolved iron and manganese. This event shut down the drinking water supply once again. In 2007, wastewater from the nearby villages of Samia and Kisra were collected and sent to a wastewater treatment plant. The septic tanks in other villages have not been treated yet. The drinking water supply was not reinitiated after the 2006 event because the pollution source could not be identified and the pollution could not be quantified. The complex hydrology involved and the numerous pollution sources in the area made it impossible to preclude the possibility that some wastewater or wastewater effluent in the area continue to contaminate the perched aquifers from which the various springs emanate. The current research was partly aimed at quantifying the wastewater leakage to the various springs by taking an overall approach that circumvents the necessity to map underground hydrological streamlines, a task which we regard as unattainable based on the existing monitoring wells in the area.

2.3. Materials and Methods

CBZ and caffeine were analyzed by an Agilent G6410A Triple Quadrupole mass spectrometer for liquid chromatography-tandem mass spectrometry (LC–MS/MS) with an electrospray ionization source, according

to Environmental Protection Agency (EPA) method 1694. CBZ quantification was performed with respect to CBZ-d_{10}. The limit of quantitation (LOQ) of CBZ was 0.1 ng/L. Caffeine was quantified with respect to caffeine $^{13}C_3$. The LOQ of caffeine was 10 ng/L. The same instrumentation and columns were used for ACS analysis after solid phase extraction with styrol-divinylbenzene cartridges, according to a reported method [*Scheurer et al.*, 2011]. ACS quantification was performed with respect to ACS-d_4. The LOQ of ACS was 10 ng/L. Chloride was determined by a Dionex ion chromatograph, according to EPA method 300.1. Additional analytical details are given in supporting information section.

2.4. Chemicals
The sources of chemicals, solvents, and reference materials are specified in supporting information.

2.5. Sampling Sites and Sampling Protocol
Duplicate grab samples from each water source were collected in 1 L brown glass bottles. Samples were stored without any addition of preservation agents at 4.

To confirm that grab sampling gives valid results in this particular study area, we conducted six consecutive samplings of one representative spring and the effluent of one wastewater treatment plant within the research area. Table S1 in supporting information shows the raw results of the consecutive sampling during a 2 day period of the Zuf spring. The diurnal variation of the two tracers, which reflects sampling, analysis, and diurnal source variation, demonstrates that the relative standard deviation (RSD) of the two tracers in the spring source were $< 3\%$ and $< 9.5\%$ for CBZ and ACS, respectively. For the Ga'aton wastewater treatment plant, the respective RSD values were 10 and 8%. These results prove that it is not necessary to sample the various springs and water sources by composite sampling.

3. Effluent Leakage Prediction Schemes

3.1. Mixing Ratio Calculations and Error Estimates
In two recent articles [*Gasser et al.*, 2010, 2011], we considered a model involving the mixing of a wastewater effluent stream containing a concentration $[X]_{ef}$ of a tracer and a stream originating from the surrounding aquifer with a background concentration $[X]_b$ of the tracer. Mixing of the two streams gave the observed concentration of the tracer, $[X]_i$, at the sampled site. The sampled site can be a stream, spring, or water well. The M.R. was defined as the fraction of effluent-originated water at the site, given by

$$M.R. = \frac{\text{Effluents}}{\text{Effluents} + \text{Pristine Water}} = \frac{[X]_i - [X]_b}{[X]_{ef} - [X]_b} \tag{1}$$

The mixing ratio expressed in percentage is simply M.R. multiplied by 100. Equation (1) is valid only when the concentration at the examined site, $[X]_i$, is larger than that at the background. After rearrangement, first-order Taylor series expansion of equation (1) and division by M.R. gives a three-term equation for the uncertainty in M.R. estimation:

$$\Delta E = \left[\left(\frac{1}{[X]_i - [X]_b} \Delta[X]_i \right)^2 + \left(\frac{-([X]_{ef} - [X]_i)}{([X]_{ef} - [X]_b)([X]_i - [X]_b)} \Delta[X]_b \right)^2 + \left(\frac{1}{[X]_{ef} - [X]_b} \Delta[X]_{ef} \right)^2 \right]^{1/2} \tag{2}$$

ΔE, the ratio between the uncertainty level and the predicted M.R. value, depends on $\Delta[X]_{ef}$, $\Delta[X]_i$, and $\Delta[X]_b$. These three values correspond to the uncertainty levels in the determination of the average concentration of the effluent source, the concentration of the tracer at the studied site, and the concentration of the tracer in the vicinity of the studied site, respectively. In this study, we used a conservative estimate of $\Delta[X]_i$ based on actual seasonal measurements at the site. However, $\Delta[X]_i$ can be estimated by diurnal monitoring, which does not consider seasonal variations and gives lower estimate of the uncertainty level, an example of which is given in supporting information.

Additional details on the meanings of each of these terms and the multiplication factors preceding each uncertainty level are provided in our previous publication [*Gasser et al.*, 2010]. Analysis of the third term on

the right-hand side (RHS) of equation (2) illuminates one of the strengths of tracer specificity. The systematic error of a tracer arising from degradation of the tracer on the way from the effluent source is given by

$$\frac{\Delta M.R.}{M.R.} = \frac{\Delta[X]_{ef}}{[X]_{ef} - [X]_b}$$

(3)

where $\Delta[X]_{ef}$ in this case is the degraded concentration. The RHS of equation (3) is minimal for a specific tracer, i.e. when $[X]_b = 0$. The importance of the conservative nature of the tracer is often overestimated compared with the specificity requirement. Nonspecificity may introduce large amplification factors in all three terms of the RHS of equation (2). For example, consider a case in which the background concentration is 50% of the effluent concentration. Here, the RHS of equation (3) is twice the value of that obtained for a specific domestic waste tracer with the same $\Delta[X]_{ef}$. Therefore, the range between $[X]_b$ or the minimum detection level, whichever is larger, and $[X]_{ef}$ is highly significant, as noted in previous studies [*Benotti and Brownawell*, 2007]. This range was denoted as the dynamic range of the tracer in an analogy with metrology. The dynamic range of the organic micropollutant tracer is very large and spans 0.1–1650 ng/L and 10–28,500 ng/L for CBZ and ACS, respectively. The dynamic range for chloride (23–152 mg/L) is considerably small compared with the organic tracers.

3.2. Prediction of the Mixing Ratio Based on Two or More Tracers
It is reasonable to base the decision on the mean mixing obtained by averaging the M.R. values of the various tracers. Averaging the various tracers would give erroneously large weights for the more abundant tracers. However, greater weight should be given to low-uncertainty-level observations, which can be done using the inverse of the observed variance as a weight. The weighted mean in this case is given by

$$\overline{M.R.} = \frac{\sum_{i=1}^{n} w_i (M.R.)_i}{\sum_{i=1}^{n} w_i}$$

(4)

where i is the tracer index, and w_i is given by the inverse of the respective variances (the squared inverse of the standard deviation) of the calculated mixing ratios:

$$w_i = \frac{1}{\left[(\Delta E)_i (M.R.)_i \right]^2}$$

(5)

Note that $\Sigma w_i = 1$. The variance of the weighted mean mix ratio is then given by

$$\overline{\Delta E (M.R.)}^2 = \frac{1}{\sum_{i=1}^{n} \frac{1}{\left[(\Delta E)_i (M.R.)_i \right]^2}}$$

(6)

where the relative uncertainty level in the estimation of the mean is given by $(\overline{\Delta E})$.

4. Results

4.1. Selection of the Tracers
Table A2 in supporting information gives the time dependence of the potential tracers and other pertinent water quality parameters that were sampled in this research. The observed levels of the three tracers at the six different target springs and the Baloa sinkhole are depicted in Figures 3a–3c. The correspondence among the levels of the organic tracers within the various Ga'aton springs (Ga'aton, Zuf, Shefa, and Gia) is apparent, whereas Ziv and Hardalit, located on the nearby ridge of the Kziv wadi, behaved differently. The correspondence of the four Ga'aton springs is somewhat less apparent based on the chloride monitoring.

Inspection of the various potential tracers within the different springs (Table S2 in supporting information) reaffirms the postulate regarding the usefulness of inorganic tracers, as noted in Introduction. Nitrate is not
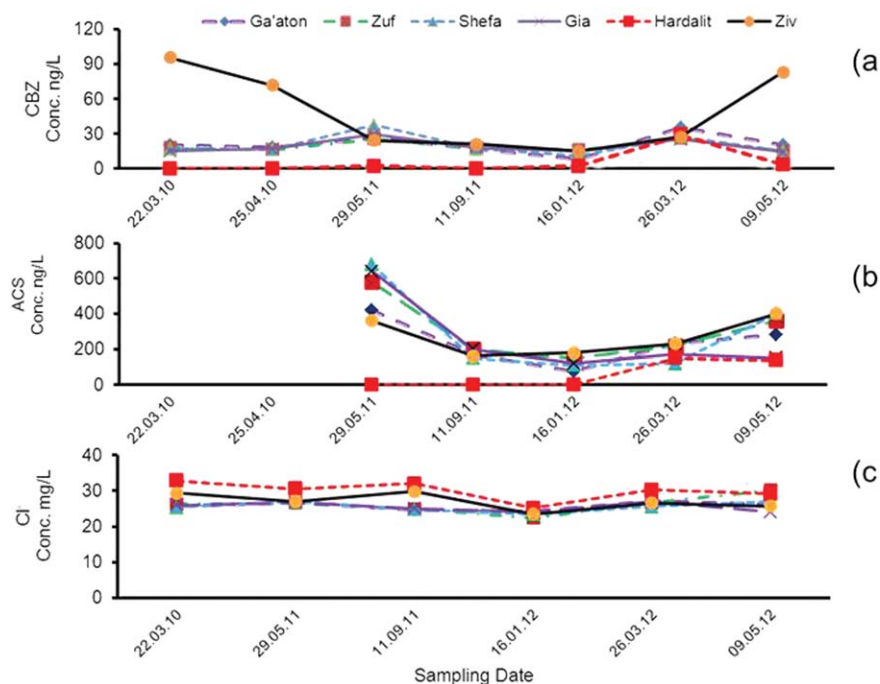
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Figure 3. Tracer concentration in the target wells: (a) carbamazepine (CBZ), (b) acesulfame anion (ACS), and (c) chloride. The *x* axis depicts discrete monitoring events and does not describe the linear time coordinate.

a good tracer because its concentration in all four wells was higher than that in two of the three effluent sources in the vicinity (Beit Jann and Naharia wastewater plants) and was only slightly lower than the nitrate level in the Ga'aton reservoir. The correlation coefficients between chloride, which is a truly conservative tracer, and nitrate, which can be formed by nitrification or destroyed by denitrification downstream of a treatment plant, are given in Table 1. The observed correlation coefficients between nitrate and chloride were always negative for the springs, indicating different nitrate and chloride sources. Moreover, nitrate was negatively correlated to most other wastewater tracers. These conflicting trends of nitrate and chloride, in addition to the other wastewater tracers, can be explained by a conceptual model involving mixing of two streams. The first stream has a high nitrate level likely highly influenced by agricultural runoffs, and the second stream has a high chloride level. Increased flow rate of the first stream increases the nitrate level at the site but dilutes the chloride level and vice versa. This conceptual discussion demonstrates the importance of an overall mixing prediction approach in circumventing the necessity of hydrological mapping because even when the postulated streams cannot be mapped, the quantification of the various mixing ratios of wastewater and pristine water within the springs is necessary.

The use of caffeine as an untreated wastewater tracer was proposed by *Daneshvar et al.* [2012]. However, in our study, we could not use caffeine as a specific tracer for improperly treated wastewater or to discriminate between treated and untreated effluent leakage because all of the treated wastewater effluent in the area contained high levels of caffeine. In addition, caffeine was detected in concentrations exceeding the

Table 1. Correlation Coefficients Among Tracer Dynamics[a]

Location	Correlation Coefficient $NO_3^- $-$Cl^-$	Correlation Coefficient NO_3^--CBZ	Correlation Coefficient Cl^--CBZ	Correlation Coefficient CBZ-ACE	Correlation Coefficient Caffeine-CBZ
Ziv	−0.86 (6)	−0.58 (6)	0.27 (7)	0.74 (5)	−0.56(4)
Hardalit	−0.53 (6)	0.65 (6)	−0.02 (7)	0.70 (5)	----
Gia	−0.24 (6)	−0.26 (6)	0.84 (7)	0.79 (5)	----
Shefa	−0.81 (6)	−0.62 (6)	0.62 (7)	0.82 (5)	----
Zuf	−0.37 (6)	−0.13 (6)	−0.31 (7)	0.53 (5)	----
Ga'aton	−0.35 (6)	−0.30 (6)	0.93 (7)	0.61 (5)	----

[a]"----" signifies that most of the data values of one of the parameters are zero. Number of measurements is given in parentheses.

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Table 2. Average Levels and Standard Deviations of the Tracers in the Target Springs and the Sinkhole[a]

Location	Cl^- (mg/L)	NO_3^- (mg/L)	CBZ (ng/L)	ACS (ng/L)	Caffeine (ng/L)
Ziv	30.3 ± 8.8, (7)	25 ± 1, (6)	48.0 ± 34.0, (7)	266 ± 108, (5)	40 ± 32, (4)
Hardalit	30.0 ± 2.7, (7)	15 ± 3, (6)	5.1 ± 10.6, (7)	57 ± 79, (5)	ND (4)
Gia	25.5 ± 1.3, (7)	27 ± 3, (6)	19.0 ± 5.7, (7)	256 ± 217, (5)	ND (4)
Shefa	26.4 ± 2.6, (7)	26 ± 4, (6)	20.1 ± 9.0, (7)	292 ± 248, (5)	ND (4)
Zuf	28.0 ± 6.5, (7)	26 ± 3, (6)	18.1 ± 5.3, (7)	278 ± 166, (5)	ND (4)
Ga'aton	25.8 ± 1.2, (7)	27 ± 5, (6)	20.6 ± 8.3, (7)	235 ± 129, (5)	ND (4)
Baloa	51.4 ± 37, (6)	10 ± 7, (6)	503 ± 289, (4)	9530 ± 4180, (4)	805 ± 1140, (4)

[a]ND corresponds to less than 0.1, 10, and 10 ng/L for CBZ, ACS and caffeine, respectively. Values in parentheses indicate number of measurements.

minimum detection level (10 ng/L) only in a single spring; therefore, caffeine is clearly not sensitive enough for detection of minute wastewater leakage in these sites. Based on these considerations, we were left with ACS, CBZ, and chloride as potential tracers. Table 1 shows that ACS and CBZ levels were well correlated in all the springs despite differences in charges and hydrophobicity. The individual correlation coefficient between these pairs in each of the various target springs was also either moderate (0.53 and 0.61 for Zuf and Ga'aton, respectively) or good (> 0.7 for all other springs). The correlation coefficient, r, of all the observation pairs of CBZ and ACS in the various springs and the Baloa, excluding the pollution sources, was 0.86 (n = 34), and we determined r = 0.92 between all pairs of measurements including the wastewater effluent sources (n = 40). Both CBZ and ACS are considerably mobile in subsoil. The octanol-water partition coefficient, Log P, of CBZ is 1.51 [*Scheytt et al.*, 2005], and Log P of ACS at pH 5.5 and 7.4 equals −2.88 [www.chemspider.com]. The correlation coefficients between chloride and the organic tracers in the target springs span a rather wide range (−0.31 to 0.93), although this factor alone should not exclude either from serving as a tracer.

The raw data on the concentration of the tracers in the wastewater effluent sources in the vicinity of the target springs are given in Table S3 (in supporting information), and the concentrations of the tracers in nearby pristine, uncontaminated underground wells in the area are given in Table A4. The organic tracer concentrations in all of the pristine springs were below detection limits (0.1 and 10 ng/L for CBZ and ACS, respectively). Thus, the background concentration of the organic tracers, $[X]_b$, should be taken as 0 because there are no industrial sources for the organic tracers in the nearby area. Therefore, all of the ACS and CBZ originated from domestic wastewater sources (CBZ is not a veterinary drug, and Acesulfame K is for human consumption only.). The background concentration of chloride spanned a wider range of 22.7 ± 5.2 mg/L (Table S4 in supporting information).

The average concentrations of the tracers in the treated wastewater sources $[X]_{ef}$ in the area were considerably larger at 1650 ± 788 ng/L, 28,500 ± 5410 ng/L, and 152 ± 31.9 mg/L for CBZ, ACS, and chloride, respectively. The level of CBZ differed considerably in the various wastewater sources at 1650 ± 788 ng/L. The average concentration level detected in this study was slightly higher than that of CBZ in the effluents of wastewater treatment plants in Israel (1321 ± 204 ng/L) [*Gasser et al.*, 2010], and the corresponding RSD was nearly three times higher than the uncertainty level based on the average concentration of CBZ in Israel. The RSD in the estimation of the CBZ level (0.48) was significantly higher than that of chloride and ACS (0.21 and 0.19, respectively) in the nearby effluent sources.

4.2. Quantification of the Mixing Ratio in the Target Wells by the Individual Tracers

To evaluate the mixing ratios in each of the water wells based on the individual tracers, we estimated the concentration of the tracers in the target springs, in the unperturbed background, and in the relevant wastewater sources. We also determined the uncertainty level, ΔE, of each of these terms. The average concentrations of the tracers at the various springs and the associated standard deviations were determined by averaging the concentrations of CBZ, ACS, and chloride present in the various springs during the last 2 years (Table 2). The standard deviation sums the uncertainties associated with the sampling and chemical analysis, and the natural fluctuations of the tracers at the source due to complex hydraulics and the fluctuating flow rate of the input streams. The average concentrations and the associated standard deviations are given in Table 2.

To calculate the mixing ratios and the associated uncertainty levels, we used the data from Tables S2–S4 in supporting information. The minimum detection levels of ACS and CBZ were taken as the uncertainty levels in the determination of the respective background levels.

There are three possible approaches for the estimation of the average concentration of a tracer in an effluent source: (i) when the source is known, sampling the source and assessing the average concentration of the effluent and the associated uncertainty level by repeated sampling should be straightforward, (ii) surveying potential wastewater sources in an area and averaging the various concentrations of the tracers in the relevant effluents, and (iii) using the average concentration of these tracers in wastewaters in Israel. In our two recent studies, we have used the first and third approaches [*Gasser et al.*, 2010, 2011]. In the study, however, because the sociological characteristics of the neighboring agricultural communities and towns in the area are diverse, the first approach was preferable, despite the fact that the actual wastewater source is likely unknown and can be different from those surveyed in this study. Therefore, the effluent concentrations in equations (1) and (2) were set to 28,500 ± 5410, 1650 ± 788, and 152 ± 31.9 mg/L for ACS, CBZ, and chloride, respectively.

The upper four frames of Figure 4 depict the calculated mixing ratios and the associated uncertainty levels for each of the water wells (Ziv and Hardalit on the left and the Ga'aton springs (Gia, Shefa, Zuf, and Ga'aton) on the right)) based on CBZ and ACS. The mixing ratios were calculated based on the monitoring results at the specific dates and the average background and effluent concentrations. The error bars denote the uncertainty level based on equation (2). The corresponding data based in chloride monitoring are depicted in the upper two frames of Figure S1 in supporting information. The corresponding data for the Baloa site as well as the entire set of M.R. values for each spring at each sampling date are given in Tables S5–S7 in supporting information.

We present the M.R. based on chloride only in supporting information (Figure S1) because the M.R. shows high variability compared with the dynamic range of chloride, although this is not readily observed in Figure 3c. The upper four frames of Figure 4 show merely a normalized ratio of the data in Figure 3; however, this normalization allows for a comparison between the observed levels of mixing based on the various tracers. It is clear that there is no clear preference for either tracer. On some sampling times, the predicted mixing ratio based on CBZ was higher, and on the other dates, the mixing ratio based on ACS was higher. This implies that there is no reason to assume that one of the tracers is systematically biased (e.g., due to degradation). The chloride data spanned a much wider range and fluctuated considerably even within the same site at different sampling dates. The M.R. values for chloride were at times negative, a nonphysical value that underscores the large uncertainty in the evaluation of the chloride M.R. This result is also reflected in the uncertainty values manifested in the relative sizes of the error bars.

A minimum of 50% RSD is the maximum that assures statistical significance (p-value $< 5\%$) to a positive answer to the question of whether a particular spring was polluted on a specified date. Thus, a positive and statistically significant answer can be given based on the CBZ tracer only for four out of the 42 CBZ spring sampling cases detailed in the study. The same applies to 10 out of 30 ACS monitoring tests. Based on the ACS tracer, the Ziv spring was always contaminated, whereas CBZ tracer gave mixed results. The chloride tracer could not provide any significantly positive answer.

The correlation coefficient between all the CBZ and ACS M.R. values was 0.86 (as for the non-normalized concentration sets). However, the correlation coefficients between the M.R. pairs based on chloride and ACS and chloride and CBZ were only 0.43 and 0.59, respectively, which are lower than the 0.46 and 0.64 obtained for the non-normalized concentrations, respectively. This again underscores the importance of a comparison based on mixing ratios relative to the raw, non-normalized concentrations. The slope of the linear correlation between the M.R. values based on the various tracers makes this even more evident. The slope of the M.R. values based on CBZ versus ACS was 1.05 (i.e., very close to 1), regardless of whether the linear trendline was forced to pass through the origin. Additionally, the slopes of the linear trendlines corresponding to the CBZ and ACS M.R. values plotted against the chloride M.R. values were 0.5 and 0.3 respectively, again confirming the inferior value of chloride as a mixing tracer.

Table 3 depicts the average mixing ratio and its associated uncertainty level for each of the studied springs by each of the three tracers. The predicted mixing ratios based on CBZ and ACS were quite similar in each of the six wells with two exceptions: the average mixing ratios in Ziv and Ga'aton were substantially higher based on CBZ compared with that based on ACS, reflecting the fact that we began monitoring the ACS level only in 2011. For the individual data points, the average M.R. values based on CBZ also showed sometimes higher (Ziv) and sometimes lower (e.g. Shefa) uncertainty levels compared with that based on ACS. The
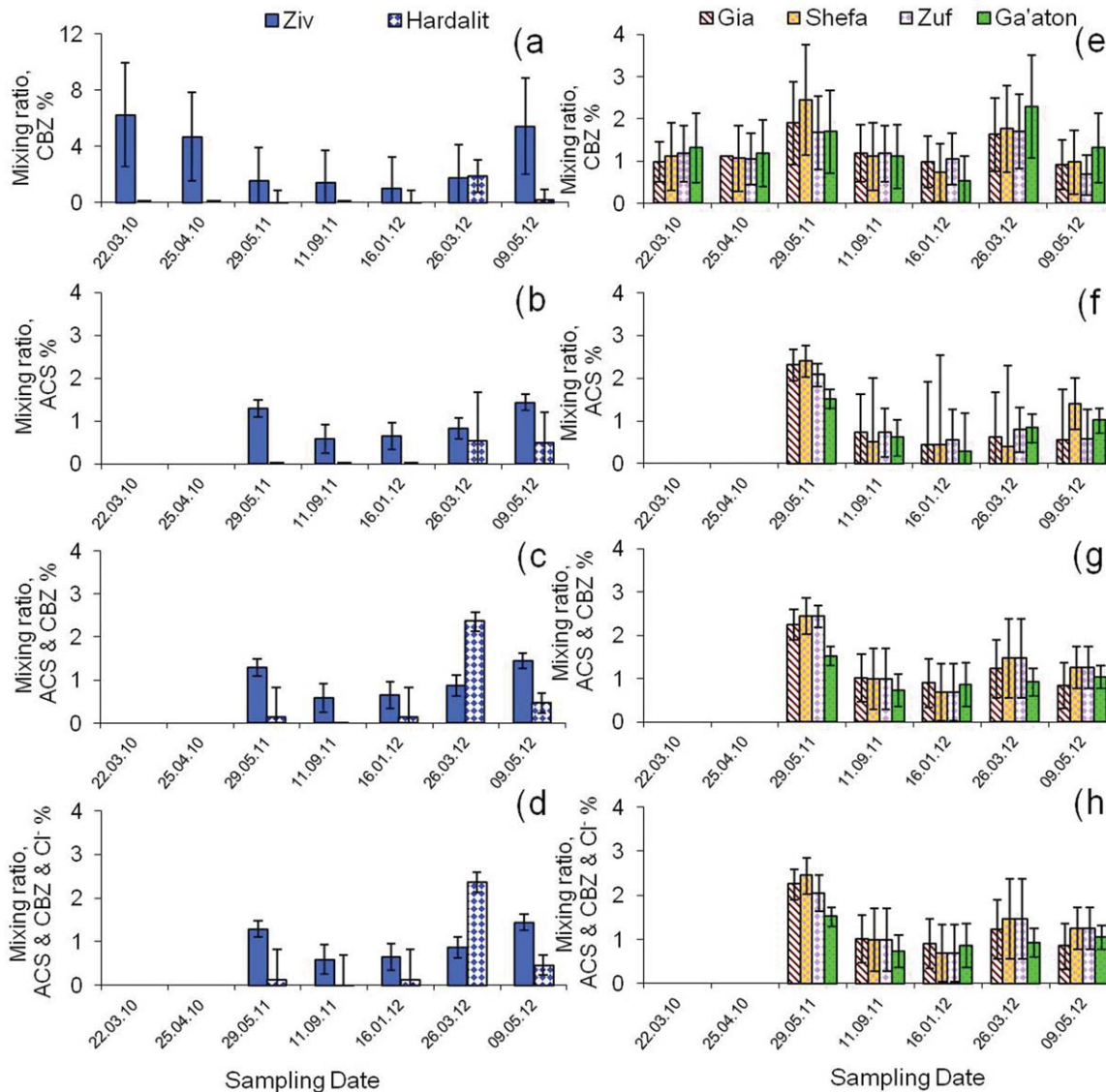
Figure 4. Mixing ratios expressing the percentages of effluent in the Ga'aton springs (Gia, Shefa, Zuf and Ga'aton, from left to right in each cluster of bars) and Ziv and Hardalit springs (left column, from left) based on (from top) CBZ, ACS, weighted average of CBZ and ACS, and weighted average of all three tracers. Error bars indicate the predicted level of uncertainty of the calculated mixing ratio. Only positive values are physical; therefore, the error bars were not extended to negative values. Calculations are based on $[ACS]_b = [CBZ]_b = 0$, $[Cl^-]_b = 22.7$ mg/L, $\Delta[CBZ]_b = 0.1$ ng/L, $\Delta[ACS]_b = 10$ ng/L, $\Delta[Cl^-]_b = 5.2$ mg/L, $[ACS]_{ef} = 28,500$, $[CBZ]_{ef} = 1650$ ng/L, $[Cl^-]_{ef} = 152$ mg/L, $\Delta[CBZ]_{ef} = 788$ ng/L, $\Delta[ACS]_{ef} = 5410$ ng/L, and $\Delta[Cl^-]_{ef} = 31.9$ mg/L.

estimate based on chloride tracer showed a consistently (but insignificant statistically) higher mixing ratio for all the studied springs, although the relative uncertainty levels were also much higher.

4.3. Quantification of the Mixing Ratio in the Target Wells by More Than One Tracer

The calculation of the mixing ratios based on the two organic tracers according to equations (4) and (5) and calculation of the associated uncertainty levels according to equation (6) gives the mixing ratios and the associated uncertainty levels (Table A8 and the third row of frames in Figure 4). One should not expect a large deviation between the M.R. values obtained by the weighted average of ACS and CBZ compared with those that were based on the individual values. However, the level of uncertainty was significantly reduced by the averaging, as can be visually discerned in Figure 4. In 18 out of the 30 spring sampling cases, it was possible to state confidently (p-value < 0.05) that the springs were polluted at the time of measurement, compared with 10 and 2 based on ACS or CBZ alone, respectively.

Table 3. Calculated Average Mixing Ratio and Associated Standard Deviations by Each of the Three Tracers: (a) CBZ, (b) ACS, and (c) Chloride[a]

(a) Location	Average CBZ, (ng/L)	Average Mixing Ratio based on CBZ, $\overline{(M.R.)}$, (%)	Relative Uncertainty Level, $\overline{(M.R.)(\Delta E)}$, (%)
Ziv	48.2 ± 33.8	2.9	2.5
Hardalit	5.1 ± 10.6	0.3	0.71
Gia	19 ± 5.7	1.2	0.70
Shefa	201. ± 9.0	1.3	0.81
Zuf	18.1 ± 5.3	1.3	0.81
Ga'aton	20.6 ± 8.3	1.2	0.62
Baloa	503 ± 289	30.5	23

(b) Location	Average ACS, (ng/L)	Average Mixing Ratio based on ACS, $\overline{(M.R.)}$, (%)	Relative Uncertainty Level, $\overline{(M.R.)(\Delta E)}$ (%)
Ziv	266 ± 108	0.9	0.22
Hardalit	57 ± 79	0.20	0.54
Gia	256 ± 217	0.90	0.80
Shefa	292 ± 248	1.02	0.91
Zuf	278 ± 166	1.06	0.67
Ga'aton	235 ± 129	0.82	0.51
Baloa	9530 ± 4180	42	7.2

(c) Location	Average Cl⁻, (mg/L)	Average Mixing Ratio based on Cl⁻, $\overline{(M.R.)}$, (%)	Relative Uncertainty Level, $\overline{(M.R.)(\Delta E)}$, (%)
Ziv	30.3 ± 8.8	5.9	7.9
Hardalit	30.0 ± 2.7	5.7	4.5
Gia	25.5 ± 1.3	2.2	4.1
Shefa	26.4 ± 2.6	2.8	4.5
Zuf	28.0 ± 6.5	4.1	6.4
Ga'aton	25.8 ± 1.2	2.4	4.1
Baloa	51.4 ± 37.1	37	36

[a]Calculations are based on $[ACS]_b = [CBZ]_b = 0$; $[Cl^-]_b = 22.7$ mg/L; $\Delta[CBZ]_b = 0.1$ ng/L; $\Delta[ACS]_b = 10$ ng/L; $\Delta[Cl^-]_b = 5.2$ mg/L. $[ACS]_{ef} = 28,500$, $[CBZ]_{ef} = 1,650$,ng/L, $[Cl^-]_{ef} = 152$ mg/L; $\Delta[CBZ]_{ef} = 788$ ng/L; $\Delta[ACS]_{ef} = 5,410$ ng/L; $\Delta[Cl^-]_{ef} = 31.9$ mg/L.

The calculated average mixing ratio based on the two organic tracers (Table 4) reinforces the above observations. As was expected, the weighted averages of the mixing ratio levels based on two tracers fell between the values of the predictions based on the individual tracers, and the uncertainty levels were always lower than each individual uncertainty level. The algorithm gave larger weight to the tracer with lower uncertainty level, which is particularly significant for the Ziv spring, where the ACS-derived M.R. was associated with a much lower uncertainty level than CBZ-derived M.R. The quality of the predictions based on relative or absolute uncertainty levels was substantially improved; with the exceptions of Hardalit and Zuf, the relative uncertainty levels were close to or less than 50%.

Repeating the calculations for three tracers, rather than two, did not change the results substantially. The relevant data are given in Table S9 in supporting information, and the average mixing ratios are given in Table 4b. The bottom frames in Figure 4 depict the calculated mixing ratios and the uncertainty levels. Because the uncertainty levels associated with the chloride tracer were inferior compared with the organic tracers in all six springs, chloride was given a much lower weight, and did not influence the weighted M.R. or its uncertainty level significantly. The situation was similar even for the Baloa sinkhole, where the level of contamination was substantially higher. This result is important (and welcomed) because it implies that adding a less precise tracer to the consortium of tracers does not substantially deteriorate the predictions. Thus, the practitioner does not have to choose the most precise tracers a priori; the algorithm shows auto-preference for the more precise tracers.

The uncertainty levels associated with the mixing ratios at the various springs (Tables A7–A9) were rather conservative. The uncertainty level, $\Delta[X]_i$, at the various dates was based on a series of measurements conducted by different sampling teams in various seasons. A less conservative way is to estimate $\Delta[X]_i$ based on repeated sampling and analysis conducted on the same date. Neither this method account for the uncertainty associated with different sampling teams and batch-to-batch and long-term analytical variability nor would it be affected by the seasonal variability at the site. Table S10 in supporting information compares the calculated M.R. and the associated uncertainty levels based on these two alternatives and shows that the differences may be

Table 4. Calculated Average Mixing Ratios and Associated Standard Deviations by Weighted Average of (a) CBZ and ACS Tracers and (b) CBZ, ACS, and Chloride Tracers[a]

(a) Location	Average Mixing Ratio Based on the two Tracers, $\overline{(M.R.)}$, (%)	Absolute Uncertainty Level, $\overline{(\Delta E)}(M.R.)$, (%)	Relative Uncertainty Level, $\overline{(\Delta E)}$, (%)
Ziv	0.94	0.19	19.9
Hardalit	0.25	0.43	172
Gia	1.05	0.53	48.1
Shefa	1.16	0.60	52.4
Zuf	1.11	0.46	41.0
Ga'aton	0.95	0.43	45.2
Baloa	34.6	17.2	49.6
(b) Location	Average Mixing Ratio Based on the Three Tracers, $\overline{(M.R.)}$, (%)	Absolute Uncertainty Level, $\overline{(\Delta E)}(M.R.)$, (%)	Relative Uncertainty Level, $\overline{(\Delta E)}$, (%)
Ziv	0.94	0.19	19.8
Hardalit	0.25	0.33	129.7
Gia	1.06	0.50	47.0
Shefa	1.1	0.52	47.6
Zuf	1.19	0.60	50.5
Ga'aton	1.12	0.45	40.2
Baloa	40.5	6.7	16.5

[a]Calculations are based on $[ACS]_b = [CBZ]_b = 0$; $[Cl^-]_b = 22.7$ mg/L; $\Delta[CBZ]_b = 0.1$ ng/L; $\Delta[ACS]_b = 10$ ng/L; $\Delta[Cl^-]_b = 5.2$ mg/L. $[ACS]_{ef} = 28,500$, $[CBZ]_{ef} = 1,650$,ng/L, $[Cl^-]_{ef} = 152$ mg/L; $\Delta[CBZ]_{ef} = 788$ ng/L; $\Delta[ACS]_{ef} = 5,410$ ng/L; $\Delta[Cl^-]_{ef} = 31.9$ mg/L.

substantial despite the fact that $\Delta[X]_i$ affects only one term in equation (2). We leave this question unanswered until more experience in the evaluation of the uncertainty levels of M.R. calculations is attained and additional computer simulations comparing hydrological models and the global M.R. calculations will improve the guidance over the preferred approach. In this study, we used the more conservative approach.

5. Discussion

The concept of M.R. and the associate uncertainty level provide a framework for comparison of potential tracers based on their random uncertainty levels. Thus, our previous study and the present study show that organic micropollutant tracers are superior over the inorganic tracers for quantification of minute leakage of wastewater effluent to a pristine source. Even 1% of wastewater leakage can often be quantified by high-dynamic-range micropollutants [*Gasser et al.*, 2010].

5.1. Correlation Between Tracers or M.R. Levels

As indicated in Introduction, the use of multiple tracers is not new. We and others have correlated different tracers and even different micropollutant tracers before. However, high correlation between tracers does not necessarily mean that they are equally credible. Using Ga'aton spring as an example, the highest correlation in Table 1 is found between chloride and CBZ (0.93). However, examination of the M.R. predictions shows that the M.R. predicted by chloride is 2.7 times larger than CBZ (Table 3, columns (a) and (c)). An examination of the relative uncertainty levels shows that the relative uncertainty level associated with chloride. M.R. is very large (1.6 times larger than M.R.), which shows that the high correlation between the two tracers is more of a coincidence and that the predicted M.R. levels of chloride are imprecise.

In the case of the northern Galilee springs, the significant correlation between the organic tracers in all cases (Figures 3a and 3b), and even more importantly, the similar mixing ratios predicted by the different organic tracers (ACS and CBZ), hint that high degradation did not occur during the time between their discharges to the environment and their appearances at the springs. A high degradation rate and long retention time in the aquifer should reduce the similarity between the different M.R. values because it is less likely that the relative degradation of the two tracers will be almost equal unless they are both close to zero and/or the retention time is very short.

5.2. Instability and Retardation of the Tracers

The random attributes of the "error" in the M.R. estimation are adequately addressed in this article; however, the consistent sources of bias should be discussed separately because they are not directly addressed by

equations (1–6). The instability and different mobility (compared to water) of tracers are two important attributes of chemical tracers that may introduce systematic bias in the M.R. predictions; therefore, they are briefly addressed here.

5.3. Stability of the Tracer

The stability of the organic tracers cannot be accurately predicted because it is highly site specific, and the retention time in the aquifer is usually unknown. In principle, a tracer can have a high degradation rate, and our algorithm may still assign its M.R. with a small uncertainty level. This can be demonstrated in the case of caffeine, in which the level is highly repeatable in most water wells (i.e., below detection level, Table A2), although it is apparent from our analysis that the estimated M.R. = 0 is biased. However, the M.R. predicted by different tracers can be used as a guidance to eliminate inaccurate (biased) tracers.

A tracer with a (statistically) significantly higher M.R. should be preferred over a tracer for which the M.R. is lower. When the calculated M.R. values of two tracers deviate by more than the sum of their standard deviations, then tracers with the lower M.R. should usually be disqualified. The average M.R. values of CBZ and ACS did not deviate significantly in the northern Galilee springs, whereas they both differed significantly from the M.R. of caffeine. Moreover, the M.R. values of CBZ and ACS were not significantly lower than that of chloride (taking the sum of the standard deviations as a criterion for significant deviation), although the M.R values predicted by chloride are usually higher. Therefore, it was justified to calculate the M.R. values based on all three tracers, although in the studied springs, the calculated M.R. values were not affected much by the chloride.

The mobility of chemical tracers differs from that of water. Even the mobility of chloride may be slightly influenced by anion exclusion in high surface area soils [*Porro et al.*, 1993; *Gvirtzman and Gorelick*, 1991]. Organic tracers are often retarded by the interaction with organic matter in the soil. Further, the retardation of the organic tracers is site-specific and is determined to a large extent by the organic content in the soil. Even CBZ, which is known for its high mobility, is reported to have high retardation in some soils [*Williams et al.*, 2006; *Fenet et al.*, 2012], and its solid-water distribution coefficient, K_d, has been reported to reach up to 20 L kg^{-1}.

The mixing ratio is not affected by the mobility of the tracer when steady state conditions prevail. This, for example, was the case for the quantification of leakage from a water recharge facility that was addressed in our previous article [*Gasser et al.*, 2010]. When steady state is not attained, then there are three extreme "ideal" conditions. The first involves a case in which the input stream exhibits seasonal variations. Currently, the protocol accounts for such changes by following the changes in the effluent concentrations ($[X]_{ef}$ and $\Delta[X]_{ef}$) and by selection of micropollutants whose concentration is influenced less by seasonal variation (in order to lower $\Delta[X]_{ef}$). In the case of an unknown pollution source, this cannot be accomplished. In the second case of a monotonic change of the concentration of the tracer such as that when the sign of the time derivative does not change or when a micropollutant drug is gradually replaced by another drug, the same technique can be used. However, a covariance term should be included in equation (2), and the advantages of such a tracer should be carefully weighed to verify that there are no better alternatives. The quantitative technique is likely not suitable for the description of the third extreme case of a one-time contamination spill.

In summary, like other attempts to base a conclusion on hydrological modeling, this quantitative protocol calls for expert scrutiny and criticism to warn against its misuse. The use of multiple tracers for M.R. calculation reduces the (random) relative uncertainty level in the determination of the M.R. and provides additional quantitative criteria for selection of the best tracers for site-specific cases. Another criticism against this model is that it calls for extensive studies that are much more rigorous than what are needed for a simple correlation between tracers. However, the required effort for a reasonable 3-D hydrological modeling of a simple actual system, let alone the complex system that was studied here, is very high and in many cases unattainable. For example, a similar effort to form a 3D hydrological model of a much simpler water charge facility in Israel based on micropollutant tracers involves data from more than 200 water wells and more than 25,000 concentration data points [*Rona et al.*, 2014].

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