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Evaluation of micropollutant tracers. II. Carbamazepine tracer for wastewater contamination from a nearby water recharge system and from non-specific sources

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ABSTRACT

A quantitative approach for calculation of the percentage of water of domestic wastewater origin in contaminated water wells is presented. The article is an extension of a reported approach to quantify leakage from a wastewater recharge facility to nearby water wells pumping predominantly from a pristine aquifer. The relative contamination from a specific source, a wastewater recharge basin, and the contamination from unspecified domestic wastewater sources under near steady state conditions are calculated for several water wells in the vicinity of a wastewater recharge system. Carbamazepine (CBZ), an antiepileptic drug whose refractory behaviour was reported before is evaluated as a tracer. It is demonstrated that CBZ fulfils the requirements of source-specific as well as non-specific wastewater tracer, under Israeli conditions. In addition to being biodegradation-resistant, a survey of the effluents of domestic wastewater treatment plants in Israel revealed that the CBZ level is roughly constant, 1407 ± 204 ng/L in a wide range of water treatment facilities all over Israel. As such, at least for specific sites (e.g. Israel) CBZ can be used as a quantitative tracer for estimation of the fraction of effluent-originated water in water wells, and the uncertainty involved in such estimates can be calculated.

1. Introduction

Only in the middle of the nineteenth century did the scientific community accept the association between waterborne diseases and microorganisms, and the quest for finding indicators of wastewater contamination of drinking water sources began. Frankland and Frankland [1–3] identified coliforms as possible indicators and, later on, fecal coliform count emerged as the unrivalled indicator for wastewater contamination [4]. Over the last decades it became clear that chemical contamination should also be considered, and that wastewater effluent penetration to tap water should be avoided also because domestic effluents contain refractory trace pollutants [5,6]. Domestic wastewater tracers are therefore increasingly being used to warn against unintentional contamination of drinking water sources by treated effluents. Two different types of domestic wastewater tracers are being sought: Tracers for quantification of the penetration of domestic wastewater effluents from an unspecified source and for the contamination from a specific source.

A previous article [7] introduced a methodology to quantify leakage of treated effluents from a wastewater recharge site to nearby drinking water wells based on tracer studies, compared the wastewater–pristine water mixing predictions based on chloride and carbamazepine (CBZ) levels and quantified the uncertainty levels associated with the two different predictions. A similar analysis applies also, with appropriate modifications, to the quantification of the percentage of wastewater (originating from the water recharge basin and from all other wastewater sources) in these water wells. In this article, we outline the different requirements from source-specific (the recharged effluents in this particular case) and non-specific domestic wastewater sources. For clarity we demonstrate the calculation for the very same water wells that were discussed in our first publication.

1.1. Dilution tracers

Numerous tracers for wastewater–pristine water mixing have been proposed. Chloride is by far the most popular tracer [8–11], but other, less conservative species including, for example, nitrate, sulfate, bromide and boron, the ratio between different anions, and isotope distribution were proposed [12–15]. Although organic contaminants are prone to biodegradation, many were proposed as wastewater tracers. Aggregate attributes (e.g. UV_{254} absorption, biological and chemical oxygen demand, phenols and surfactants) and refractory organic contaminants were proposed. Numerous waste-specific contaminants were proposed as markers of sewage contamination.

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Artificial sweeteners, drugs and X-ray contrast media have attracted more attention recently since they are biorefractory by design, and they are mostly specific for human consumption [16–23]. In a recent comprehensive survey of the fate of organic compounds in the soil aquifer treatment (SAT) of the Tel-Aviv domestic wastes we have found that out of some 300 micropollutants that were included in the survey, CBZ was by far the most refractory compound. CBZ was proposed by Clara et al. [24] and numerous other researchers as a sewage marker [25–27]. The objectives of this article are to predict wastewater–pristine water mixing based on CBZ, to evaluate the uncertainty involved in such prediction, and to estimate the ratio between the contribution of the nearby SAT system and the total wastewater effluents in the specified wells. To the best of our knowledge such quantification was never described in the scientific literature.

1.2. Distinction between source-specific and non-specific wastewater tracers and their desirable attributes

In order to compare critically alternative domestic wastewater tracers, it is useful to review first the most pertinent parameters required of a successful tracer and to explain, intuitively, at this stage, why chloride and major elements cannot be used as wastewater tracers (for non-specific domestic sources). (i) *Specificity for domestic wastewater and low background level*: Chloride and practically all the other proposed inorganic tracers (which by nature are not of exclusive anthropogenic origin) are present in all water sources and thus cannot be used to indicate contamination of the site by wastewater. Despite the fact that chloride concentration in wastewater effluents is 100–200 mg/L higher than in tap water, its level in pristine Israeli aquifers varies considerably. The spatial heterogeneity of the native concentration of chloride in the Israeli aquifers relative to the domestic salination of tap water precludes its use as a non-specific tracer. CBZ is exclusively of domestic origin, as the drug has no veterinary use. However, there is at least one reservation, in agricultural areas one should also consider contamination from land application of compost which may contain some CBZ residue. The data regarding the CBZ level in compost and its contamination potential are still scarce. Martin et al. [28] reported 11 mg/ton (dry matter) of CBZ in domestic sludge [28], but the leaching propensity of the CBZ from biosolid-rich soils is considered to be very small [29]. A land survey to clarify the absence of large scale land application of compost made from domestic wastewater sludge should therefore be undertaken to assure validity of CBZ tracer tests. (ii) *High abundance*: High abundance of the tracer in the source allows quantification even after large dilution. CBZ is present at around 1500 ng/L, whereas chloride's concentration is even higher, around 300 mg/L in the Israeli effluents. (iii) *Constant concentration at the nearby wastewater source*: In order to qualify as a tracer for contamination from a specific source, it is sufficient that its concentration in the domestic waste source would be fairly constant over the time scale of the hydraulic retention time in the aquifer (i.e. the time lapse from wastewater discharge to the time it is expected to reach the examined location). Thus, from this point of view both chloride and CBZ (in contradistinction, for example, to most pesticides) qualify as wastewater tracers. (iv) *Constant concentration at different wastewater sources*: In order to qualify as a wastewater tracer the compound should be present at approximately the same level in different domestic wastewater sources over the whole relevant region. International comparison shows a large variability of the absolute level of CBZ in different countries and cultures. For example, at the low end of the scale, Miao et al. [30] reported a level of 251 ng/L in Peterborough, Ontario, Leclercq et al. [31] reported levels of 208–416 ng/L for the effluents of sewage treatment plants in France, whereas at the high end of the scale Clara et al. [24] reported a level of 2500 ng/L in some wastewater plants in Austria. This variability precludes the use of CBZ as an international tracer and calls for site specific determination of its variability in the examined area. The current research quantifies source variability of CBZ in Israel and shows that its concentration is fairly constant in different wastewater treatment systems in Israel. (v) *Conservative behaviour*: The tracer should be biorefractory, non-volatile and should not undergo redox transformations under the conditions encountered in the subsoil. In a prior research Gasser et al. [7] have shown that both chloride and CBZ possess these favourable attributes, at least under aerobic systems near the study site. Similar findings were recently reported by Arye et al., [32] for the Shafdan wastewater recharge area. (vi) *Mobility*: The tracer should be mobile, and its mobility should not be retarded significantly in the soil. This is perhaps the strongest point of chloride and inorganic anions. However, if the mixing range is not expected to be dynamic, e.g., when dealing with water recharge rather than an isolated incidence of effluents spill, then this parameter is of lower importance since near steady state conditions prevail. In addition, an inexpensive analytical method obeying the following metrological requirements should be available. (vii) *Accuracy and precision and Detection Limit*: The accuracy and precision of the method of analysis should be high. This factor favors inorganic materials and disfavors organic micropollutants, whose error margin is usually higher. In addition the analytical method should have a low detection limit, to allow quantification of small wastewater leakage.

2. Materials and methods

2.1. Analytical methods

CBZ was analyzed by gas chromatograph equipped with mass spectrometric detector, GC/MS according to the EPA method 8270.D and by liquid chromatograph equipped with tandem triple quadrupole mass spectrometer, LC/MS/MS according to the EPA method 1694. The compound was extracted by Solid Phase Extraction (SPE) with Oasis HLB cartridges (Waters, Milford, MA) from 1000 mL of sample)). Analytes were eluted by 4 mL methanol followed by 4 mL of 2% formic acid aqueous solution and 12 mL of 2% formic acid solution in methanol. The extract was concentrated to a final volume of 1 mL. Aliquots of 1 μL of the final extracts were separated at Agilent Gas Chromatograph 6890 N (DB-5MS column of 0.25×30 m, 1 μ) with MS detector 5973. The analyte was quantified in full-scan (m/z 44–450, 0.4 s/scan) or selected ion monitoring (SIM) conditions using the ions 193 and 236, and 165 and 192 ions for confirmation. The Limit of Quantification (LOQ) for GC/MS analysis was 100 ng/L. For samples with CBZ concentrations less than the GC/MS method LOQ, the analysis was performed using an Agilent G6410A Triple Quadrupole mass spectrometer (QQQ) with an electrospray ionization source. Analyte separation in this case was conducted with Agilent ZORBAX Eclipse Plus C18 (2.1×100 mm, 3.5 μ). The two multiple-reaction monitoring (MRM) transitions of mass 237 to 194 and mass 192 to 179 were used for CBZ determination. Quantification of the analyte was done with respect to CBZ-d_{10} (transitions of mass 247 to 204 and 202) purchased from the C/D/N Isotopes Ltd, Pointe-Claire, Canada. The LOQ of CBZ by LC/MS was 0.1 ng/L.

2.2. The study site

Our study concentrated on several wells near the Soreq 1 basin of the secondary wastewater recharge of the Shafdan wastewater treatment plant (Fig. 1). The study area, by and large, consists of a permeable calcareous sand perched aquifer supported on a marine clay aquiclude and partially interrupted by a horizontal marine clay aquitard. The water table reaches its maximum height under the percolation basin (36 m below the bottom of the lagoon) and has a gradual height decrease (of about 20 m/km) to a radial minimum located approximately below the outer ring of the recovery wells.