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Emerging contaminants and nutrients in a saline aquifer of a complex environment ☆

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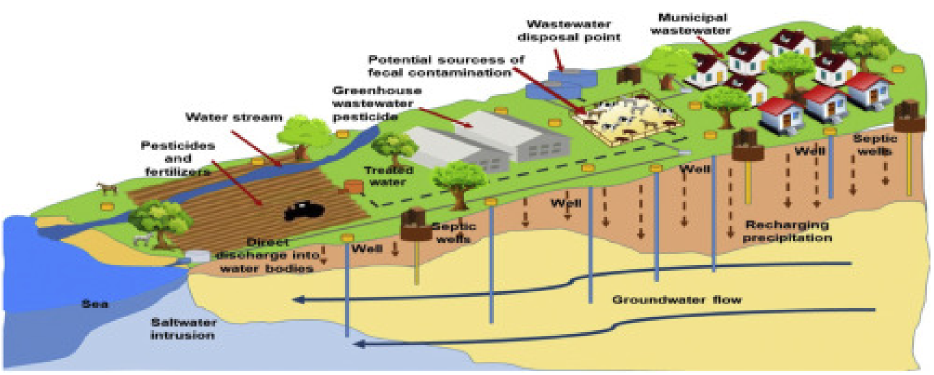
Highlights

- Fecal sterols and alkylphenols were considered as emerging contaminants.
- Modern and old pesticides were present in water wells from Valley of Maneadero.
- Emerging contaminants prevail in this complex environment.
- Seasonal variability showed fast response of the aquifer despite scarce rain.
- Marine algae sterols strengthen the theory of seawater infiltrating the aquifer.

Abstract

The quality and availability of water has become a pressing issue worldwide, being particularly important in semi-arid regions, where climate change has aggravated the problem. The use of anthropogenic chemicals, classified as emerging pollutants, adds to the problem representing a treat, since they are not regulated and have a potential impact on human and environmental health. This pressing problem has not been studied widely in complex environments like the one we present here. Distribution and seasonal variability of fecal sterols, alkylphenols, pesticides (emerging pollutants) and nutrients were determined in 35 wells used for agriculture and human consumption in the Valley of Maneadero, located in the semi-arid region of Baja California, Mexico. The presence of the tested pollutants in the saline aquifer was heterogeneous, showing important differences in concentration and distribution. Wells destined for household use showed the highest variability. In these wells, anthropogenic fecal sterols were detected and, alkylphenols, such as octyphenol and nonylphenol had maximum concentrations (2.7 ng/mL). In agriculture and urban wells, we identified DDT and organochlorine pesticides, as well as myclobutanil, which is considered a modern pesticide. Nitrates were identified in concentrations above international standards, mainly during the dry season, in both the agricultural and urban areas. As emerging pollutants represent a negative effect on environmental and human health, this is the first paper showing the importance of measuring this type of pollutant in agricultural/semi-urban areas, especially in aquifers that have been overexploited and communities that have relied on the use of septic tanks for decades.

Graphical abstract



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Introduction

As the world's population increases, the challenges of supplying clean water for human consumption rise in every country highlighting the importance of monitoring the quality and quantity of the resource in order to guarantee sustainable consumption. Water pollution due to residual water from daily human activity leads to the contamination of groundwater and negative impacts on environmental and human health (Hench et al., 2003; Nelson et al., 2004; Foley et al., 2005; Wu et al., 2016).

Besides legacy contaminants, other emerging contaminants can also be found in wastewater. These emerging contaminants are typically unregulated chemical substances, and are suspected to affect the environment (Daughton, 2004). However, these emerging contaminants are recognized as potential pollutants for their adverse effects on the environment and human health. Among these emerging contaminants that have not been considered are: fecal sterols recognized as indicators of fecal contamination (Leeming et al., 1996; Mudge and Duce, 2005), and alkylphenols (nonylphenol, octyphenol, etc.) known as endocrine disruptors, neither of which is regulated (Barrios-Estrada et al., 2018). Although, both are persistent in the environment (Kelly, 1995; Lee et al., 2018).

For decades, the use of biological indicators that are able to distinguish between various sources of fecal pollution has been proposed (Leeming and Nichols, 1996; Sinton et al., 1998; Bull et al., 2002; Lyons et al., 2015), and is considered complementary or supplementary to traditional bacterial counts. One of the steroidal chemical indicators proposed as a fecal contamination indicator is coprostanol. It is the main element among neutral sterols found in animal feces and remains unaltered in water after treatments such as chlorination (Murtaugh and Bunch, 1967; Kirchmer, 1971; Leeming et al., 1996; Leeming and Nichols, 1996; Sinton et al., 1998; Bull et al., 2002; Cabral et al., 2018). Previous studies have shown that coprostanol concentrations correlate with coliform bacteria counts, particularly in environments contaminated with wastewater (Leeming and Nichols, 1996; Isobe et al., 2002). This makes coprostanol an ideal indicator for tracing human pollution in various environmental systems (O'Rourke, 1980; Writer et al., 1995; Mudge and Seguel, 1999; Carreira et al., 2004; Peng et al., 2005; Reeves and Patton, 2005; Ayebo et al., 2006; Field and Samadpour, 2007).

Among the most widely used indicators of fecal contamination is the ratio of coprostanol to cholesterol, which enables an evaluation of the degree of pollution of residual water (Leeming and Nichols, 1996; Isobe et al., 2002; Cabral and Martins, 2018). Cholesterol is a useful indicator of fecal pollution due to its ubiquitous nature and its origin from ingested plant material (Murtaugh and Bunch, 1967; Furtula et al., 2012). Sterol ratios commonly used include: a) [coprostanol/(coprostanol+β-cholestanol)], which identifies whether the sterol source is biogenic or residual water (Grimalt et al., 1990); b) coprostanol/epicoprostanol, which discerns between human and non-human pollution (Reeves and Patton, 2005); c) coprostanol/cholestanol, which differentiates between human and algal sterols (Nash et al., 2005; Devane et al., 2015); and d) coprostanol/cholesterol, which distinguishes between biogenic sources (Reeves and Patton, 2001; Peng et al., 2005).

Another pollutant in domestic residual water is alkylphenol, a type of surfactant widely used as part of industrial and household detergents and in pesticides for agriculture and various industrial products. Alkylphenols are used as alkylphenol ethoxylate, an alkylphenol with an ethoxy sidechain (Céspedes et al., 2008). Human exposure to alkylphenols occurs mainly through drinking water, eating contaminated food (Chrostowski, 2002), or during manufacturing (Luo et al., 2015; Liu et al., 2016). These chemical compounds have attracted the attention of scientists and environmentalists

(Robles-Molina et al., 2014; Deyerling et al., 2016; Spindola-Vilela et al., 2018) since this type of compound interferes with the endocrine systems and bioaccumulates in aquatic organisms (Geyer et al., 2000; Spindola-Vilela et al., 2018). The main sources of water contamination include direct discharge of leachates, direct use of pesticides (Ying et al., 2002), and industrial and domestic water treatment plants (Pryor et al., 2002; Harrison et al., 2006; Stuart et al., 2012; Liao and Kannan, 2014; Gavrilescu et al., 2015).

Some pesticides are recognized as emerging contaminants (Murray et al., 2010; Barrios-Estrada et al., 2018) and are chemical mixtures designed to avoid, repel and kill pests, including herbicides, insecticides, fungicides, nematicides and acaricides. They can be classified according to their physicochemical characteristics, composition, or environmental half-life as organochlorines, organophosphates, carbamates, and triazines among others. Baja California is considered to be one of the 13 states in Mexico with the highest pesticide use. It is estimated that 80% of the total pesticide used in the country is used in Baja California (Camarena-Ojinaga et al., 2012). Despite the presence of these products in Mexicali Valley, little research has been conducted on their effects on public health and the environment (Moreno and López, 2005).

Water demand in Northwest Mexico, specifically in the city of Ensenada, has risen significantly over the past few decades. The population of Ensenada was estimated to be 519,813 in 2015, and is expected to reach over 623,000 by 2030 (CONAPO-SEGOB, 2014). Because of this growth trend tendency and the accompanying economical and industrial activities, as well as the development of the city in general, there is an increase in water demand. This demand is exacerbated by the decline in precipitation due to climate change and the scarcity of surface water. This work evaluated the presence and seasonal variations of emerging contaminants (fecal sterols, alkylphenols, pesticides) and nutrients in water wells used for agriculture and human consumption. The evaluated wells are part of an agricultural semi-urban environment from a saline and overexploited aquifer with human settlements that have used septic tanks for more than five decades. In this complex environment, little is known about these emerging contaminants.

The Valley of Maneadero (VM) is located northwest of Baja California, Mexico, between 116° 30′ and 116° 40′ W, and between 31° 41′ and 31° 51’ N, within the Ensenada municipality. The most important population settlement within the valley is the town Rodolfo Sánchez Taboada (commonly known as Maneadero), located in the east at the foothills of the Juarez mountain range. VM exhibits a homogenous topography with elevations between 0 and 20 m over sea level, while Maneadero town sits at a higher elevation between 40 and 80 m above sea level, surrounding the valley. The city of Ensenada lies approximately 10 km north of the town.

The Maneadero basin is adjacent to Ensenada, Real del Castillo and Ojos Negros basins to the North; the San Vicente and Laguna Salada basins to the East; the Santo Tomas basin to the South; and the Punta Banda Lagoon and Todos Santos Bay to the West (López-Fernández, 2009) (see Fig. 1).

In the site, in the last 70 years, the mean annual precipitation was 250 mm with a great inter-annual variability. Some years, rain could be over 200% from the annual mean and in the dry season it could only reach 30% of the annual mean (Huaico-Malhue, 2014). During the study, rain was 194 mm, which was 77.6% of the annual mean. In Mexico, the annual mean precipitation is 777 mm. Therefore; this zone is classified as semi-arid with rains in winter (November-April) and a dry season from May to October. The main temperatures in the zone are 12.5–15 °C in winter and 15–25 °C in summer, the zone's climate is Mediterranean (Méndez-González et al., 2008).

According to Licona-García (2011), groundwater in Maneadero is mainly used for agriculture, with 67% used for said purpose, 29% allocated for public-urban use, and the remaining 4% used for industrial activities (Luján-Flores, 2006; Huaico-Malhue, 2014). Maneadero has a 6700 ha unconfined aquifer, recharged with water coming from the San Carlos (862.5 km^2; 12.5 Mm^3) and Las Ánimas (1020.5 km^2; 20.8 Mm^3) streams. The streams are intermittent and only provide water to the aquifer during the wet season, while remaining dry the rest of the year (Mares-Olmos, 1996; Sarmiento-López, 1996; Huaico-Malhue, 2014). Within the area of the aquifer there are 321 active wells with depths lower than 40 m, as determined by the Ensenada Municipal Research and Planning Institute (IMIP, 2009; Lara-Valenzuela, 2011). This aquifer is considered the most important in the region since it provides 38% of potable water for the city of Ensenada and the town of Rodolfo Sánchez Taboada. The Maneadero aquifer has been overexploited since 1968 (Daesslé et al., 2005). Electromagnetic and geochemical analyses have indirectly shown that dissolved salts in groundwater have increased. In 2001–2002, concentrations of TDS oscillated between 540 and 9460 mg/L (Daesslé et al., 2005). In 2005–2006, according to resistivity models assuming porosities and constant coefficients of cementing and textures, applying Archie's law, the calculated values for water salinity were between 1000 and 30,000 mg/L (Luján-Flores, 2006).

The States Office of Sustainable Rural Development Information of Baja California estimated Maneadero Valley's population at 22,957 in 2010 (INEGI, 2010). According to marginalization index reports about basic services per locality, the local sewerage system became operational in 2009 with 5799 households connected and 1560 not connected to the system. Water discharged through the system is treated at the El Salitral water treatment plant, estimating four users per sewage connection. This means that the treatment plant handles the sewage from roughly 16,950 people. An estimated total of 6240 residents discharge water residues in septic tanks (CONAPO, 2010). Agriculture in VM started at the end of the 19th century, which is around the time when septic tanks where first used. Having no sanitary hydraulic infrastructure could lead to the contamination of the aquifer's water and infiltration of pathogenic contaminants, presenting a potential health and environmental risk.

In this work, we analyzed faecal sterols and their relation to nutrient, pesticide and alkylphenol concentrations in wells used for drinking or field irrigation. This study was carried out in VM because it represents a complex environmental system, since it has historically been an agricultural zone where pesticides have been used indiscriminately. Furthermore, it has an unconfined aquifer that has been overexploited for 50 years with increasing salt concentrations, located in a semi-arid and semi-urban zone.

Section snippets

Sampling

Wells were selected based on the land use (i.e. agriculture, urban, etc.) and accessibility; water sampling from the wells was carried out twice a year, once during the dry season (September 2015) and once after the rainy season (March 2016). During both seasons, eight wells were sampled within the domestic-use area, four of the wells controlled by the State Public Services Commission of Ensenada (CESPE in Spanish) (C1-C4), and the remaining four from urban zones within the VM (UZ1-UZ4). In the …

Hydrogen potential (pH) and redox potential (Eh)

During both sampling seasons, 90% of samples exhibited pH values ranging from 6.88 to 7.52 (SM 1a). This is within permissible values established by current regulations for agriculture and livestock use, and for flora and fauna preservation (Aher, 2012). Our pH values show seasonal variability among samples, which may be a result of dissolved gases and solids (Patil and Nagarajan, 2015). However, pH values remain within a small range of change.

According to the oxidation/reduction potential (Eh) …

Conclusions

Emerging pollutants detected in groundwater samples include a wide range of anthropogenic substances, which have dispersed widely and are present in well water. Among the identified factors promoting the above, is the use of pesticides, including DDT, despite being prohibited for years. The use of detergents and their presence as alkylphenols are recognized as renal disruptors.

The excessive use of fertilizers is reflected in high nitrate concentrations. In addition, off course, the use of …

Acknowledgements

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References (155)

N.H. Adnan *et al.*
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J. Environ. Sci. (2012)

M.A. Alsalahi *et al.*
Sterols as biomarkers in the surface microlayer of the estuarine areas
Mar. Pollut. Bull. (2015)

C. Barrios-Estrada *et al.*
Emergent contaminants: endocrine disruptors and their laccase-assisted degradation - a review
Sci. Total Environ. (2018)

D. Berryman *et al.*
Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp and paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life
Chemosphere (2004)

P.H. Bethell *et al.*
The study of molecular markers of human activity: the use of coprostanol in the soil as an indicator of human faecal material
J. Archaeol. Sci. (1994)

C. Biache *et al.*
Thiosteranes in samples impacted by fecal materials and their potential use as marker of sewage input
Environ. Pollut. (2015)

I.D. Bull *et al.*
The origin of faeces by means of biomarker detection
Environ. Int. (2002)

A.C. Cabral *et al.*
Insights about sources, distribution, and degradation of sewage and biogenic molecular markers in surficial sediments and suspended particulate matter from a human-impacted subtropical estuary
Environ. Pollut. (2018)

A.C. Cabral *et al.*
An integrated evaluation of some faecal indicator bacteria (FIB) and chemical markers as potential tools for monitoring sewage contamination in subtropical estuaries
Environ. Pollut. (2018)

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> …General water quality parameters such as pH, dissolved oxygen, nitrogen, phosphorus, organic carbon and chlorophyll-a are monitored routinely due to their critical influence on water quality (Álvarez-Cabria et al., 2016; Ding et al., 2016). These general water quality parameters also have direct (e.g. pH (Hua et al., 2019)) or indirect (e.g. TOC (Lv et al., 2020), nutrients (Aristi et al., 2016; González-Acevedo et al., 2019) and phytoplankton (Xiong et al., 2018)) influences on the transport and fate of emerging contaminants. Shi et al. (2017) investigated the interactions between algal blooms of phytoplankton and hydrophobic organic chemicals using years of field observations and suggested that the dynamics should be included in models in the future.…

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