PESTICIDE CONTAMINATION OF GROUNDWATER IN THE TROPICAL REGION

Data de submissão: 08/05/2023 *Data de aceite: 02/06/2023*

Eliana Freire Gaspar de Carvalho Dores
Federal University of Mato Grosso,
Graduate Program on Water Resources
Cuiabá – Mato Grosso
http://lattes.cnpq.br/4094572237082106
ORCID 0000-0001-5175-3537

Claudio Aparecido Spadotto
Embrapa Agricultura Digital
Campinas - São Paulo
http://lattes.cnpq.br/3404384601903230
ORCID: 0000-0001-5713-1261

Rafael Mingoti
Embrapa Territorial
Campinas - São Paulo
http://lattes.cnpq.br/3479283038505977
ORCID 0000-0003-4873-7565

ABSTRACT: Pesticides residues have been detected in groundwater all around the world, but most published studies were carried out in temperate climate countries despite the intensive use of these substances in tropical agricultural areas. A review regarding pesticides in groundwater in tropical regions up to 2020 is presented based on Scopus®, Web of Science®, and Google Scholar® where the earliest study found dated 1998. Very few papers related the hydrogeological conditions to pesticides occurrence although the detection of a great variety of molecules (persistent and non-persistent) have been reported, even ones not classified as leachable. Moreover, no temporal variations were discussed since many of the described studies reported results from very few sampling campaigns. The contamination of groundwaters used for human supply have been described in some countries bringing concern on risks to human health. Therefore, more studies should be stimulated aiming to produce information that could base discussions on climate influence on contamination processes.

KEYWORDS: tropics, agriculture, environment, leaching, drinking water

CONTAMINAÇÃO POR PESTICIDAS DE ÁGUAS SUBTERRÂNEAS NA REGIÃO TROPICAL

RESUMO: Resíduos de pesticidas têm sido detectados em água subterrânea em todo o mundo, mas a maior parte do estudos publicados foram desenvolvidos em países de clima temperado apesar do uso intensivo dessas substância em áreas de agricultura tropical. Foi realizada uma revisão de publicações sobre ocorrência de pesticidas em águas subterrâneas em regiões tropicais até 2020 baseada nas bases de dados Scopus®, Web of Science® e Google Scholar® onde o estudo mais recente encontrado foi publicado em 1988. Poucos artigos relacionam as condições hidrogeológicas com a ocorrência de pesticidas embora tenha sido reportada uma grande variedade de moléculas (persistentes e não persistentes) mesmo aquelas não classificadas como lixiviáveis. Além disso, não foram verificadas discussões sobre variações temporais uma vez que a maioria dos resultados reportados foram obtidos em poucas campanhas de coleta. A contaminação de águas subterrâneas usadas para consumo humano foi verificada em vários países levando a preocupação com a saúde humana. Portanto, mais estudos deveriam ser estimulados de modo a produzir informações que possam basear discussões sobre os efeitos do clima tropical sobre processos de contaminação.

PALAVRAS-CHAVE: trópicos, agricultura, ambiente, lixiviação, água potável

1 | INTRODUCTION

Groundwater is one of the most important natural resources globally (GURDAK; HANSON; GREEN, 2009) and, as recently pointed out by Poeter *et al.* (2020), groundwater must be included in the solution to the global water crisis because it represents up 99% of Earth's liquid fresh water – as early noted by Shiklomanov (1993) – and is vital for the sustenance of rivers, lakes, wetlands, and ecological systems.

As the world's largest distributed store of fresh water, ground water plays a central part in sustaining ecosystems and enabling human adaptation to climate variability and change (TAYLOR *et al.*, 2013). In many regions, groundwater is fundamental to the water-food-energy-climate nexus (GREEN, 2016).

Groundwater vulnerability is strongly dependent on factors such as depth-to-water table, recharge and land use and land cover (LULC) conditions, all of which are influenced by climate conditions and human activities (LI, 2012).

The territorial distribution of agriculture, as well as its technological development, is totally related to the occupation of lands by humanity. Over the centuries, agricultural activities, initially in fertile areas along the banks of large rivers, occupied areas with good distribution of rain and with fertile soils. With the development of irrigation systems, from the simplest, as flooding in rice growing areas, to complex systems used in fruit crops in semiarid regions, agriculture reached the current distribution, occupying a total of 1.874 billion hectares of croplands in the world, roughly 12.6% of the global terrestrial area (THENKABAIL *et al.*, 2012; TELUGUNTLA *et al.*, 2015).

Agriculture fulfilled in the tropical region of the globe has a greater occurrence of pests that requires more intense control practices, usually by using more pesticides than in temperate regions. As a matter of fact, several studies have reported the presence of pesticides in water bodies in the tropics. The potential for groundwater contamination is assessed in view of pesticides properties, soil and geologic attributes and processes, as well as the meteorological conditions. The behavior of pesticides in tropical soils and climates is differentiated, which has been evidenced in sorption, degradation, and transport studies.

Compared to surface water, groundwater contamination by pesticides is much less studied probably because it is considered inherently safe (GWENZI; CHAUKURA, 2018). Countries in the tropics, most of them developing countries, are great food producers and use pesticides extensively (SHARMA *et al.*, 2018). However, studies on pesticides occurrence in groundwater are much less frequent than in temperate regions.

The Food and Agriculture Organization of the United Nations statistics (FAO, 2020) reports a world consumption of 4,122,334 t of pesticides active ingredients in 2018, with Asia as the greatest consumer (2,161,869 t) and South America in second (719,183 t). Brazil is the country with the largest land area in the tropics (JUO; FRANZLUEBBERS, 2003) and used 377,176 t of pesticides in 2018. Despite being the continent with the largest tropical area, Africa consumed much less (82,851 t) in 2018.

Once applied in the field the pesticides undergo several processes of retention (sorption-desorption), biotic and abiotic transformation and transport, while leaching downward the soil profile is the most important means responsible for the contamination of groundwater.

2 | GROUNDWATER IN THE TROPICAL REGION

Contamination of groundwater by pesticides used in agricultural areas occurs mainly when a mass of the chemical, carried by downward water flow, leaches in the soil unsaturated zone (vadose zone) and reaches the top of an unconfined aquifer (water table). An unconfined aquifer is bounded only at its base by a confining unit and that can be an aquitard, which is a partially permeable to water. As pointed out by Cohen and Cherry (2020), the aquitard and aquifers, above and below it, are all water-saturated and hydraulically connected.

Large aquifers of the world are partly or totally in the tropical regions and many of them are transboundary aquifers (PURI; AUPELI, 2009). Aquifers underlie large areas of the humid tropics at shallow depth (FOSTER; SMEDLEY; CANDELA, 2002). As surface water and ground water are connected, groundwater systems are an integral element of the humid tropical ecosystem (FOSTER, 1995) and clearing natural vegetation for agricultural cultivation will also affect the groundwater recharge and flow regime (FOSTER; SMEDLEY; CANDELA, 2002).

In the humid tropical and equatorial regions, groundwater resources are often abundant and irregularly distributed (MARGAT; GUN, 2013). According to Foster *et al.* (2002), the land area of the humid tropics includes a wide range of geological formation, and the groundwater systems can be classified in distinctive types: (a) weathered crystalline basement; (b) major alluvial formations; (c) recent volcanic deposits; (d) intermontane valley-fill; (e) karstic limestone; and (f) sedimentary basin aquifer. These groundwater systems also occur in subhumid tropics.

Geographical distribution and vulnerability to contamination of the main groundwater systems of the humid tropics are presented in **Table 1**. Aquifer vulnerability is used to indicate the extent to which an aquifer can be adversely affected by an imposed contaminant load (FOSTER; HIRATA, 1988). Vulnerability to contamination is a function of the intrinsic characteristics of the vadose zone or the confining unit and areas of the same aquifer system may have different vulnerability due to spatial variations in vadose zone thickness or the character of confining unit (Foster *et al*., 2002).

Groundwater System	Geographical Distribution	Vulnerability to Contamination
Weathered Crystalline Basement	Extremely extensive inland areas	Moderate, since preferential flow paths are possible
Major Alluvial Formations	Numerous large river basins and important coastal regions	Moderate in case of shallower parts (higher levels only to persistent contaminants)
Recent Volcanic Deposits	Elongated areas often bordering fertile valleys	Extremely variable and high where lavas outcrop
Intermontane Valley Fill	Elongated tectonic valleys of limited distribution	Very variable, generally higher along valley margins despite deeper water table
Karstic Limestone	Mainly coastal regions of limited distribution	Extremely high, but reduces where primary porosity is preserved, and water table is deep
Sedimentary Basin Aquifer	Fairly extensive in some regions	Moderate to high, but in unconfined aquifers only

Table 1 – Geographical distribution and vulnerability to contamination of the main groundwater systems of the humid tropics.

Extensive areas of deep aquifers in sedimentary basins occur in the arid zone of the tropical and subtropical regions, particularly in northern Africa and central-western Australia (MARGAT; GUN, 2013).

Aquifers are recharged mainly by precipitation or through interaction with surface water bodies and groundwater systems are linked with changes in climate over space and time, which affects key aspects of subsurface hydrology (GREEN, 2016). One of the major impacts of climate change, due to the combined effect of change in temperature and precipitation regimes, is on aquifer recharge (OLIVEIRA; NOVO; FERREIRA, 2005).

The groundwater recharge is the outcoming flux of water added to the saturated zone resulting from losses of precipitation and any variation in precipitation, together with variations in temperature and evapotranspiration, affects groundwater recharge (DRAGONI; SUKHIJA, 2008). Thus, climate is the primary factor driving spatiotemporal variability in groundwater recharge, and precipitation, considering amount and intensity, is the climate element that most directly affects groundwater recharge, irrespective of the recharge pathway (AMANAMBU *et al.*, 2020).

In the tropics, as mentioned by Amanambu *et al.* (2020), future groundwater recharge will be influenced primarily by rainfall intensity and a breakdown of recharge studies by climate revealed that recharge and storage are expected to decrease even more acutely in the tropical region. Although estimates of recharge alteration had considerable uncertainty, recharge was found to be decreasing in most of the studies in tropical climate regions; even in the rainy humid tropics, the majority of studies indicate decreasing recharge by the end of this century, relative to baseline estimates (AMANAMBU *et al.*, 2020).

There is evidence of possibly changing distribution of precipitation in the tropics by the shifting position of the Intertropical Convergence Zone (ZHANG *et al.*, 2007), but the regional details of these changes remain very uncertain (HARDING *et al.*, 2014). A synthesis of 40 modeling studies suggests that the future groundwater changes by climate will result in a decrease in groundwater recharge, storage, and levels, particularly in the arid and semiarid tropics and secondarily in the humid tropics (AMANAMBU *et al.*, 2020).

3 I GROUNDWATER CONTAMINATION BY PESTICIDES IN THE TROPICAL REGION

This part of the chapter presents a review on the occurrence of pesticides in groundwater in countries of the tropical region with the purpose of showing the scenario of pesticides contamination in the tropics. Literature from the databases Scopus®, Web of Science®, and Google Scholar® were obtained using the following terms: 'pesticides and groundwater and (name of the country or continent)'. Very few results were obtained when the words "tropical country" or "tropical region" were used. Although it was not intended as a comprehensive review, we tried to join a great quantity of evidence in order to understand the potential for pesticides contamination of groundwater in the tropical region.

3.1 Pesticides in groundwater in South America

In South America, the most relevant tropical countries regarding pesticides (expressed in active ingredient) usage are Brazil (377,176 t), Ecuador (60,733 t), Colombia (37,773 t) and Paraguay (19,662 t) (FAO, 2020). Despite having used 60,733 t of pesticides in 2018, no study on pesticides in groundwater in Ecuador was found. Brazil is by far the country that has published more data on pesticides in groundwater in South America, however, few studies showed an in-depth assessment of the contamination by these substances (**Table 2**).

Country Reference	Groundwater Description	Detected Pesticides: µg L^{-1} (detection frequency %)
Brazil Gomes et al. (2001)	Well (depth 53 m)	Tebuthiuron: 0.01-0.09
Brazil Filizola et al. (2002)	Tubular wells (8 to 100 m deep) Monitoring wells (water table depth 1-4 m)	No detection
Brazil Souza et al. (2004)	Tubular wells (depth 12-70 m)	Atrazine: 0.07 (11%) Metolachlor: 0.09-0.41 (18) Carbofuran: 1.02-1.08 (7%) Imidacloprid: 3.41 (3%) Parathion methyl: 0.14-0.17 (11%) Diuron: 2.0 (3%)
Brazil Bortoluzzi et al. (2007)	Drinking water wells (no information on depth)	Chlorpyrifos: 0.08-0.22 Imidacloprid: 0.27-6.22 Atrazine: 0.19-0.69 Simazine: 0.81 Clomazone: 2.68-10.84
Brazil Dores et al. (2008)	Tubular wells (depth up to 15 m)	Deethylatrazine: 0.048 - 0.69 (20%) Simazine: 0.047 - 0.14 (12%) Metribuzin: 0.085 - 0.88 (48%) Trifluralin: <0.102 - 0.182 (2%) Metolachlor: <0.206 - 0.836 (7%)
Brazil Carbo et al. (2008)	Monitoring wells (water table depth less than 4.5 m)	Acetamiprid: nd – 6.31 (3%) Aldicarb: nd - <1.01(1%) Carbendazim: nd - <0.41(1%) Carbofuran: nd – 68.79(8%) Diuron: nd – 0.78 (0.5%) Imidacloprid: nd - <1.98 (0.5%) Methomyl: nd – 22.81 (0.5%) Teflubenzuron: (1%)
Brazil Arraes et al. (2008)	Wells (no information on depth)	Atrazine: up to 9.95 (75%)
Brazil Morais (2009)	Monitoring wells (water table depth 1-3 m)	Imazaquin: 0.002-0.009 (62%) Imazethapyr: 0.003-0.008 (50%) Carbofuran: 0.002-0.005 (88%) Atrazine: 0.001-0.005 (100%) Chlorimuron ethyl: 0.002-0.004 (62%) Linuron: 0.002-0.007 (62%) Diflubenzuron: 0.004-0.016 (100%)
Brazil Menezes et al. (2009)	Shallow wells and tubular wells (no information on water level)	Methyl parathion: 0.667 (1%) Lindano: 0.012-0.024 (α+β) endosulfan: 0.102
Brazil Pinheiro et al. (2010)	Shallow wells used for human consumption (no information on depth)	2,4-D: 0.88-1.15 Pyrazosulfuron ethyl: 0.84-1.46 Metconazole: 85.8-167.4 Tebuconazole: 217.7-295.1 Lambda-cyhalothrin: 1.09-7.96
Brazil Menezes Filho et al. (2010)	Wells used for human consumption (no information on water depth)	Methyl parathion: 0.13-0.23 (20%) Bifenthrin: 1.89-2.57 (1%) Pyraclostrobin: 2.48-3.65 (1%) Azoxystrobin: 0.13-0.19 (1%)
Brazil Caldas et al. (2010)	Drinking water wells (depth 2.5-37 m)	Carbofuran: up to 10.4 Clomazone: up to 0.82 (70%) Tebuconazole: up to 3.65

Brazil Silva et al. (2011)	Drinking water wells (depth 3.5–64 m)	Clomazone: up to 0.032 Imazapic: up to 0.014 Imazethapyr: up to 0.057 Quinclorac: up to 0.060 Fipronil: up to 3.44
Brazil Casara et al. (2012)	5 monitoring wells (water table depth 0-5 m)	Deisopropylatrazine: 0.64 - 0.91 (9%) Atrazine: 0.20 - 0.28 (3%) Metolachlor: 0.02 - 1.16 (40%) Flutriafol: 0.15 - 0.75 (6%) β-endosulfan: 0.02 - 0.33 (13%) Endosulfan sulfate: 0.22 - 0.62 (13%)
Brazil Nogueira et al. (2012)	Tubular wells (depth from 30 to 120 m)	α-Endosulfan: 0.28-0.91 (18%) β-Endosulfan: 0.12-0.39 (22%) Flutriafol: 0.06-0.29 (31%) Metolachlor: 0.02-0.59 (13%)
Brazil Moreira et al. (2012)	Tubular wells (no information on water depth)	Atrazine: 0.02 – 4.92 (9%) Chlorpyrifos: 0.02-0.12 (10%) α-endosulfan: 0.72-0.82 (21%) β-endosulfan: 0.01-0.21 (20%) Endosulfan sulfate: 0.01-0.10 (12%) Flutriafol: 0.01-0.40 (30%) Malathion: 0.02-8.83 (9%) Metolachlor: 0.01-0.24 (10%) Permethrin: 1.4 (0.4%)
Brazil Torres et al. (2015)	Tubular wells (no information on water depth)	No detection
Brazil Olivo et al. (2015)	Deep wells (no information on water depth)	Glyphosate: 0.25 – 6.8
Brazil Rocha et al. (2015)	Monitoring wells (depth 3-4 m)	Atrazine – 0.02 - 4.84 (4%)
Brazil Beserra (2017)	Tubular wells (depth not informed)	Metolachlor – 0.34 - 0.46 Atrazine – 0.12 - 0.28
Brazil Portal et al. (2019)	Shallow wells	Atrazine: 0.112-0.470 Carbaryl: 0.390-0.473 Hexazinone: 0.140-0.302 Methyl parathion: 0.527-2.00
Brazil Almeida et al. (2019)	Well (no information on water depth)	Carbendazim: 0.08-0.22 Imidacloprid: 0.07-0.16 Hexazinone: 0.04-0.11 Ametryn: 0.01 Atrazine: 1.02-1.4 Imazaquin: 0.01-0.02 Tebuthiuron: 0.01-0.02 Diuron: 1.04-1.56 Propiconazole: 0.01 Tebuconazole: 0.10-0.18
Brazil Correia et al. (2020)	6 cisterns and 10 wells (no information on water depth)	Atrazine, clomazone, haloxyfop-methyl, and metribuzin (individual concentrations of pesticides detected in groundwater not given)
Brazil Pires et al. (2020)	Shallow wells	Glyphosate: 1.5 – 9.7 (70%)
Colombia Martinéz-Garcia et al. (2019)	Deep wells used for human consumption	“Critical concentrations of pesticides were not detected” (information as given by the authors)

Paraguay Houben et al. (2015)	Wells that take water from the sandstone, some from the basalt (depth 60 to 200 m)	No detection

Table 2 – Studies reporting pesticides concentrations in groundwater in South America.

In the 26 publications listed in **Table 2**, 94 different active ingredients were analyzed with atrazine (and its metabolites) as the most studied one (14 studies), metolachlor as the second one (9 studies), followed by parathion-methyl and chlorpyrifos (8 studies), endosulfan isomers and metabolites (7 studies), azoxystrobin, carbofuran, diuron and malathion (6 studies), imidacloprid (5 studies), glyphosate, tebuconazole, clomazone and trifluralin (4 studies).

The Brazilian legislation establishes limits for pesticides in groundwater depending on the intended water use (BRASIL, 2008) for about 30 active ingredients and drinking water (BRASIL, 2021) for about 40 ingredients, many of them persistent whose use in agriculture has been banned since the 1980s (e.g., DDT, lindane, aldrin). Therefore, most pesticides analyzed are not listed in the Brazilian legislation and are intensively used in agriculture.

The most frequently detected pesticides (**Table 2**) were atrazine (10 out of 14 reported studies); metolachlor (7 out of 9); parathion-methyl (4 out of 8); endosulfan isomers and metabolites (4 out of 7); carbofuran (4 out of 6); imidacloprid (4 out of 5) and clomazone (4 out of 4).

Considering the leaching potential, many of the studied molecules are considered potentially low leachers such as glyphosate, endosulfan, chlorpyrifos and many others. However, these molecules have been detected in groundwater (**Table 2**). Some authors attributed this detection to preferential flow due to the presence of macropores (DORES *et al.*, 2008) which is a common characteristic found in Brazilian soils such as Oxisols, as classified by the Soil Taxonomy (SOIL SURVEY STAFF, 2014). Furthermore, many studies analyzed shallow groundwater which is more vulnerable to contamination.

It is also important to notice that many of the studies analyzed water from drinking water wells detecting considerable concentrations of some pesticides like for example the results reported by Pinheiro, Silva e Kraisch (2010) who collected samples in small farms from shallow wells that are used for human consumption and detected concentrations as high as 295 μg L^{-1} of tebuconazole. If compared to the general EU limit for pesticides in drinking water of 0.1 μg L^{-1}, this concentration is extremely high, however this limit does not take into consideration specific toxicity of individual pesticides. Nevertheless, this concentration also exceeds the limit of 180 μg L^{-1} established in the recently approved Brazilian normative for drinking water (BRAZIL, 2021). Fipronil detected at concentrations up to 3.44 μg L^{-1} also surpass the established limit of 1.2 μg L^{-1}.

Metconazole was also detected at high concentrations reaching values as high as 167 μg L^{-1} but no limits are established in the Brazilian legislation. Considering that the general EU limit for drinking water does not consider toxicity data, another parameter that can be used to evaluate potential health risk is the Human Health Benchmark established in the USA. For metconazole, a benchmark of 300 μg L^{-1} for chronic exposure was determined indicating that the above-mentioned concentration may not present a risk to consumers.

As a large country, Brazil presents quite different characteristics throughout its area regarding soil, geology, relief, and climate. The regions with higher agricultural production are the central west, southeast and south. The central west region of Brazil, predominantly Cerrado biome, is known by its production of grains in extensive areas, with a high-technology agriculture and intensive use of pesticides. This is the region where the higher number of studies were found (SOUZA *et al.*, 2004; CARBO *et al.*, 2008; DORES *et al.*, 2008; MORAIS, 2009; CASARA *et al.*, 2012; NOGUEIRA *et al.*, 2012; MOREIRA *et al.*, 2012; lewisROCHA *et al.*, 2015; BESERRA, 2017; CORREIA; CARBONARI, VELINI, 2020). In those studies, several pesticides were detected (Table 2.1) in either deep or shallow groundwater, ranging from 1 to 120 m deep sampling water depth. Higher concentrations and frequency of detection were found in shallow waters (ROCHA *et al.*, 2015; CASARA *et al.*, 2012; CARBO *et al.*, 2008, MORAIS, 2009) but there were also pesticides detected in deep wells (DORES *et al.*, 2008; NOGUEIRA *et al.*, 2012; SOUZA *et al.*, 2004). The effect of rainfall precipitation was detected mainly in shallow waters. In the Central west region of Brazil, rainfall events are concentrated from October to March which coincide with pesticides application period in temporary crops so that intense rains just after pesticide application is likely to occur in this region, thus intensifying leaching vulnerability. Moreover, the main agricultural soils in this region are Oxisols, which are well drained and have medium permeability. Sandy soils are also found in some agricultural areas, leading to detection of pesticides in groundwater (MORAIS, 2009) at high frequency. Several studies on groundwater contamination were carried out in that region as can be observed in **Table 2**, particularly in Mato Grosso state that is first grain producer in Brazil and Goiás state, the second national grain producer.

In the north region of Brazil, the agricultural activities are of extensive character. Soybean is a crop in expansion but still vegetal extractivism and extensive livestock production are the main activities there. In that region, glyphosate, AMPA (aminomethylphosphonic acid) and glufosinate were determined in groundwater of the Santarém plateau, located in western region of Pará state, whose landscape is composed by a mosaic of tropical forest (Amazon Biome) cut by a dense water drainage network and occupied by soybean fields and livestock as reported by Pires *et al.* (2020). These authors analyzed 10 groundwater (shallow wells) samples collected in May 2017. Glyphosate, despite its low leaching potential, was found in seven samples with concentrations ranging from 1.5 to 9.7 μg L^{-1}. Compared to the limit of 500 μg L^{-1} established in the Brazilian legislation (BRAZIL, 2008) for groundwater used for human consumption, these concentrations can be considered very low.

Many rural properties in the Northeast of Brazil are small in size, where fruits (mainly watermelon, grape, mango, and pineapple) are important agricultural activities, while sugar cane and soybean are cultivated in large farms (IBGE, 2017). Arraes, Barreto e de Araújo (2008) analyzed atrazine in groundwater samples collected in Tinguá, a municipality that is formed by three distinct hydrogeological districts: crystalline bedrock (fissural aquifers), sedimentary bedrock and alluvial deposits and the groundwater wells were located in the sedimentary bedrock. Atrazine was detected in 75% of the samples and in 42 out of 87 samples at concentrations above the Brazilian legal limit of 2.0 μg L^{-1} with a maximum of 9.95 µg L^{-1}. In only two of the nine monitored wells average atrazine concentration did not exceed this limit.

Coffee, sugar cane and fruits (particularly orange) are the main crops grown in the Southeast region of Brazil. Other less important plantation also found are cotton, peanut, maize, manioc, rice, bean, and soybean. Climate in that region is tropical and subtropical.

The Guarany Aquifer is one of the largest and most important groundwater reservoir in the Southern Cone of Latin America. Many cities of São Paulo state depend on that aquifer for drinking water supply. In the most representative recharge area of the Guarany Aquifer, predominates sandy soils such as *Neossolos Quartzarênicos* and *Latossolos Vermelho Distrófico psamítico*, according to the Brazilian Soil Classification System – SiBCS (SANTOS *et al.*, 2018) indicating high natural vulnerability. Three studies analyzed different pesticides in water from this aquifer at different depths. Tebuthiuron, one of the most used pesticides in the recharge area of this aquifer and a highly leachable molecule, was analyzed in samples collected in a tubular 53-m well (GOMES; SPADOTTO; LANCHOTTE, 2001). This herbicide was detected in all samples at a maximum concentration of 0.09 μg L^{-1} with the higher values occurring in the rainy period. Filizola *et al.* (2002) analyzed water from two tubular wells (8 and 14-m deep) and three monitoring wells for water table sampling and Torres, Ferreira e Américo (2015) analyzed pesticides 23 pesticides and three metabolites listed in the Brazilian legislation in groundwater samples collected in a rural area in São Paulo state from wells used for human consumption and no pesticides were detected as well in either of them. Those authors attributed this fact to the presence of a basalt layer which has low permeability leading to a low water infiltration velocity leading to a low vulnerability to contamination.

In the Rio de Janeiro state, Southeastern Brazil, Portal *et al.* (2019) determined six pesticides (**Table 2**), in shallow wells built by family farmers at the Zumbi dos Palmares farm settlement where pineapple, cassava and sugarcane are grown. Atrazine, hexazinone, parathion-methyl and carbaryl were detected at least in one sample with parathion-methyl detected at the highest concentration of 2.0 μg L^{-1}, all within the standards of Brazilian legislation (BRASIL, 2008) but only parathion-methyl and atrazine have limits stablished there.

In another region of Rio de Janeiro state, Menezes *et al.* (2009) analyzed groundwater quality from São Domingos watershed where the water resources have been impacted by tomato plantations, which requires high water volumes for irrigation and uses pesticides and fertilizers intensively. Organochlorine and organophosphate pesticides (**Table 2**) were determined in water from seven wells (three shallow wells and four tubular wells) and three molecules were detected (parathion-methyl in one sample of shallow well and lindane and endosulfan in tubular wells). It is noteworthy that lindane, that has been banned in the 1980s, and endosulfan are hydrophobic pesticides but were detected in deeper wells.

In the south region of Brazil, climate is mostly subtropical. The agricultural production is characterized by the expansion of soybean. Other important crops in this region are maize, sugar cane, cotton, rice, and wheat. The south region is also responsible for more than 90% of the Brazilian production of tobacco.

Almeida *et al.* (2019) collected groundwater samples in the Tibagi River Basin area which is recognized for its intense agricultural activity (mainly soy, wheat, and corn). Samples were collected in 2015, March, June, September, and December and twelve pesticides were determined in one well located in a small village. The two pesticides detected at higher concentrations were atrazine ranging from 1.02 to 1.40 µg L^{-1} and diuron ranging from 1.03 to 1.56 µg L^{-1}. Carbendazim, ametryn, imidacloprid, imazaquin, hexazinone, tebuthiuron, propiconazole, and tebuconazole were also detected in all samples with concentrations up to 0.22 µg L^{-1}. Except for atrazine, none of these pesticides have threshold limits stablished in the Brazilian legislation for groundwater, but if compared to the general EU limit for pesticides in drinking water of 0.1 μg L^{-1}, these concentrations exceed this limit.

Olivo *et al.* (2015) analyzed glyphosate in samples taken from thirteen deep wells within the boundaries of Chapecó, Santa Catarina state, South of Brazil, in a rural area with strong agricultural influence. No information was given regarding sampling date and wells depth. Glyphosate was detected in five samples at concentrations ranging from 0.45 to 6.8 μg L^{-1}, despite its high sorption to soil particles.

In a sub-tropical area in Santa Catarina state, South Brazil, in the Itajaí River basin, Pinheiro, Silva e Kraisch (2010) analyzed seven herbicides, three fungicides and one insecticide (**Table 2**) used in rice plantation. Groundwater samples were collected from seven low depth water wells used for human consumption. The fungicide tebuconazole was detected in only two samples but at a concentration as high as 295 μg L^{-1}, value that is much higher than the limit established for drinking water of 180 μg L^{-1}. Relatively high limits of detection of 1 μg L^{-1} were reported by the authors indicating that the low detection frequency may be due to the inability of the method to detect the low concentrations that are more commonly detected in environmental samples.

Caldas *et al.* (2010) analyzed carbofuran, 2,4-D, clomazone and tebuconazole residues in 120 groundwater samples (ten drinking water wells with depths ranging from 2.5 up to 37 m). Carbofuran and clomazone were the most frequently detected pesticides (both in shallow and deep wells). The authors attributed this detection to the high leaching potential of these molecules. The authors observed no time trends regarding the occurrence of these pesticides in groundwaters, seeming not to be a seasonal phenomenon although persistent.

The occurrence of pesticides in groundwater in areas surrounding irrigated rice plantations was studies in seven producing regions in the South of Brazil during the 2007/2008 crop season (SILVA *et al.*, 2011) (**Table 2**). Water was sampled from 21 wells (3.5 to 60 m deep) in three periods, i.e., before seeding, during the crop growing and after harvest with the higher concentrations occurring after harvesting.

For the other South American tropical countries only two other studies were found, one in Paraguay and one in Colombia (**Table 2**). In Paraguay, we found one very thorough study reporting pesticides analysis in groundwater in wells in the region of the Guarany Aquifer (**Table 2**). Houben *et al.* (2015) analyzed a total of 598 pesticides and metabolites in seven wells 60 to 200 m deep, located in agricultural areas, six of them in soils derived from basalt. The authors described the wells as open boreholes, with casing usually installed only in the upper 20–30 m, so groundwater samples were considered as a mix from the entire uncased borehole length. No traces of pesticides and metabolites were detected in groundwater fact that was attributed to a combination of the effects of no-till agriculture and the subtropical climate. Even the most common pesticide, glyphosate and its main metabolite AMPA were not detected, probably due to their high sorption to organic matter and iron and aluminium oxides, all of which are highly abundant in the Terra Rossa soils. Other reason reported by those authors is the continuous microbial activity of the subtropical no-till soil since glyphosate is readily degraded microbially.

Martinéz-Garcia, Jaramillo-Colorado and Fernández-Maestre (2019) reported having analyzed organochlorine and organophosphorus compounds (individual pesticides not informed) in deep wells used for human consumption in rural areas of Colombian Caribbean towns with no detection of pesticides.

Many of the above cited studies had as primary objective analytical method development with application to water samples (e.g., PIRES *et al.*, 2020; OLIVO *et al.*, 2015; ROCHA *et al.*, 2015; MENEZES FILHO; SANTOS; PEREIRA, 2010; CALDAS *et al.*, 2010; MORAIS, 2009; CARBO *et al.*, 2008). So, in most of them information regarding groundwater depth, soil or geology description and pesticides usage is lacking. Few manuscripts present a critical discussion of pesticides occurrence regarding pesticides usage, period of occurrence and physical characteristics of the monitored areas.

Nonetheless, many pesticides occurred in groundwater in agricultural areas in Brazil showing the importance of more studies to better understand the extension of the problem as well as the occurrence of highly adsorbed pesticides in groundwater that point out to the relevance of preferential flow in some kinds of soils, e.g., Oxisols (REICHENBERGER *et al.*, 2002) or a possible transport associated to soluble organic matter (LETEY *et al.*, 2000).

3.2 Pesticides in groundwater in Central America and Caribbean

Guatemala (20,489 t of active ingredients) and Costa Rica (12,811 t) are the countries in Central America which applied the highest amounts of pesticides in 2018 (FAO, 2020). Honduras (7,195 t), Dominican Republic (7,070 t), Nicaragua (4,414 t), Panama (2,403 t) and Belize (1,384) follows as pesticide users. According to FAO (2019), historically, agriculture has played a central role in the Caribbean economies, with sugar and bananas produced agricultural commodities for exports representing an important sector for the economy, however this activity makes up a smaller share of the local economy and is changing to a more diversified agriculture. Regarding groundwater contamination by pesticides, studies carried on Costa Rica, Guatemala, Nicaragua, and Barbados were found (**Table 3**).

Country / Region Reference	Groundwater Description	Detected Pesticides: $\mu g\ L^{-1}$ (detection frequency %)
Costa Rica Ruepert et al. (2005)	Wells in farms, pesticides pulverization airfields, schools, and houses in the rural area	Bromacil: 0.5-20 Clorotalonil: 0.07-0.2 Propiconazole: 0.2 Triadimefon: detected in one sample, concentration not informed
Costa Rica De Jode et al. (2016)	Banana farm and private wells	Mn: 30.7-1,093 (94%) ETU: 0.15 to 0.25 (6%)
Guadalupe Charlier et al. (2009)	Formations of nuées ardentes and lava flows shelter a deep aquifer (2.7 to 22.6 m deep) on which the lapilli deposits shelter a shallow aquifer (0.6 to 3.4 m)	Cadusafos: max 15.34 in shallow groundwater max 0.05 in deep groundwater
Barbados Edwards et al. (2019)	Five wells (pumping depth – 6 to 71 m)	Chlorotalonil: detected below LOQ (<0.5) Hydroxychlorotalonil: 0.8-0.710
Nicaragua Moncrieff et al. (2008)	9 drilled wells and 6 hand-dug wells	p,p'-DDT: not informed p,p'-DDE: 0.00037 - 0.00337 (52%) p,p'-DDD: not informed Toxaphene: not informed Heptachlor: not informed Dieldrin: 0.0051 - 0.038 (48%) Endrin: not informed

Table 3 – Studies reporting pesticides concentrations in groundwater in Central America and Caribbean.

Ruepert *et al.* (2005) presented a report of a project carried out with the general objective of obtaining scientific data of a specific area in the Atlantic region of Costa Rica, characterized by a high production of banana e an increasing production of pinaple, aiming to evaluate groundwater contamination risk by pesticides. They analyzed 34 pesticides (**Table 3**) in samples collected from 97 wells and three springs which were selected based on contamination vulnerability during 32 sampling campaigns from January 2002 and June 2004. Only four out of the 34 pesticides analyzed were detected, with bromacil as the most frequently detected (18% of analyzed samples) and at higher concentration (up to 20 μg L^{-1}), followed by chlorothalonil and propiconazole. Bromacil, which is relatively mobile and persistent in soil, was used in pineapple plantation and was found in two springs and in the wells situated near them.

Aiming to study the dynamics of cadusafos in the Fefé catchment in Guadalupe, Charlier *et al.* (2009) sampled groundwater from six shallow piezometers at depths between 1.5 and 5 m in the lapilli formation and two deep piezometers between 15 and 30 m in the nuée ardentes and lava formations, located cross two transects upstream and downstream from the catchment. Soils over the catchment were volcanic soils, classified as Umbric Andosols, according to the World Reference Base for Soil Resources – WRB (IUSS WORKING GROUP, 2015). Samples were taken before and after application of cadusafos. At the shallow piezometers, before application, concentrations of cadusafos were much lower than the values observed 6 to 7 days after application decreasing to again two weeks later. In the deep piezometers, concentrations reached after application 0.05 µg L^{-1} and cadusafos was not detected 6 weeks after application.

Manganese (Mn) is found naturally in waters depending on geological formation but there can be a contribution from anthropogenic sources, particularly, Mn-containing fungicides such as mancozeb. De Joode *et al.* (2016) analyzed Mn and ethylenethiourea - ETU (a transformation product of mancozeb) in groundwater collected in villages neighboring banana plantations where mancozeb is used. Deep wells (30 to 75 m deep) and shallow wells (3 to 10 m deep) were monitored between May and October 2011. While ETU was only detected in a few drinking water samples (6%), median concentration of manganese in farm and private wells was 391 μg L^{-1} (interquartile range: 30.7 to 1093 μg L^{-1}) with relatively high levels of Mn in deep wells, suggesting a contribution of natural Mn in groundwater. The highest concentrations of Mn were observed in water from wells operated by banana farm companies and private wells located less than 50 m distant from banana plantations, mostly shallow wells. The authors concluded that elevated Mn in drinking water in this area may come from two sources: natural and external contamination, probably due to mancozeb spraying.

Edwards *et al.* (2019) analyzed chlorothalonil (CTL) and its metabolite 4-hydroxychlorothalonil (HCTL) in samples from five groundwater pumping stations located in St. Michael and West Coast catchment, at the west coast of Barbados in June 2013. From the five wells, one was located within an agricultural area, one was near several golf courses, three in residential areas and the shallowest one was not potable because of high salinity. Pumping depth ranged from 6 to 71 m. Chlorothalonil was not detected in any sample while 4-hydroxychlorothalonil was detected in all, at higher concentrations in the well installed within the agricultural area (0.710 μg L^{-1}) and the one near golf courses (0.126 μg L^{-1}), while the concentrations were below 0.029 μg L^{-1} in the ones in urban areas. This is consistent with the higher mobility and persistence of HCTL.

In Nicaragua, Moncrieff, Bentley and Palma (2008) analyzed groundwater at the León-Chinandega region, which is underlain by a shallow, unconfined aquifer, where most soils are coarse-grained and loamy, loamy-clayey, or loamy-sandy. Nineteen wells were sampled, twelve drilled wells and seven hand-dug, where several organochlorines were detected with DDE and dieldrin as the ones that occurred in higher concentrations (**Table 3**). The authors observed lower concentration in drilled wells than in hand-dug wells. These authors attributed the transport of hydrophobic pesticides to the shallow groundwater to preferential flow, but also considered the possibility of direct contamination of hand-dug wells from windblown materials or contaminated surface waters delivered by shortcutting of infiltrating water around the wellbore since these wells are often poorly constructed. Another hypothesis presented is the colloidal transport in the unsaturated zone and in groundwater, and in this case, the authors alerted that “current understanding of contaminant transport in the area may be greatly flawed, as such transport has the potential to move much greater quantities of hydrophobic contaminants than does dissolved-phase transport”.

3.3 Pesticides in groundwater in North America

Mexico is the only country in North America that has a large area with tropical climate. In 2018, according to FAO (2020), Mexico used 53,144 t of active ingredients. Hawaii is a state of the United States of America that also has a tropical climate, so it was included in this review.

Banana is an important agricultural product in state of Tabasco, SE Mexico, where mancozeb is largely used. Geissen *et al.* (2010) analyzed the metabolite ethylenethiourea (ETU) and the heavy metals manganese (Mn) and zinc (Zn) from decomposing mancozeb in subsurface (SS) water samples collected from five shallow wells (3–5 m) and ground water (GW) samples from five deep wells (80 m) in the watershed of the lake Sitio Grande, where Gleysols and Fluvisols predominate – **Table 4**. ETU was detected only in shallow wells, manganese concentrations in shallow and deep wells were remarkably similar (2.3±0.1 and 2.4±0.1 μg L^{-1}, respectively) different to the observations of De Joode *et al.* (2016) in Costa Rica, who observed higher Mn concentrations in shallow wells.

The occurrence of the organochlorine pesticides DDT (dichlorodiphenyltrichloroethane) and HCH (hexaclorociclohexano), whose use was banned in 1999 in Mexico, was studied by Giácoman-Vallejos *et al.* (2018) in groundwater from a karstic aquifer. The studied region was described as a plain formed because of the appearance of a marine platform, that is composed of calcareous rock and bodies of water called “cenotes” (flooded dolina of karstic origin). The groundwater samples were taken from 29 wells 40 to 60 m deep located along the Mérida-Progreso transect in the years 2012 and 2014, during three different seasons of the year (rain, June to October; dry, March to May and the “north winds season,” November to February) and at two different depths in the groundwater column (between 10 and 20 m). The temporal analysis showed an increase in concentrations of both pesticides (total DDT and total HCH) in the north winds season. The concentrations of p,p’-DDE a metabolite of p,p’-DDT were higher than p,p’-DDT and p,p’-DDD, throughout the three tested seasons, indicating that p,p’-DDT had not been recently used the studied area. On contrary, the α/γ-HCH ratio was over the unit during the three tested seasons, suggesting a more recent use of HCH.

Country, State Reference	**Groundwater Description**	**Detected Pesticides: $\mu g\ L^{-1}$ (detection frequency %)**
Mexico Geissen et al. (2010)	Sub superficial water (SS) depth of 3–5 m Ground water table (GW) is 80 m deep and is separated from the subsurface water body through an impermeable clay layer	ETU: 4.3 (average) (subsurface water) Mn: 2.3-2.4 (average in subsurface and deep groundwater)
Mexico Giácoman-Vallejos et al. (2018)	29 wells 20-40 m deep Karstic aquifer	p,p’-DDT: 0.01-2.80 p,p’-DDE: 0.01-4.50 p,p’-DDE: 0.05-14.0 α-HCH: 0.02-37.4 β-HCH: 0.01-13.2 γ-HCH: 0.02-10.3 δ-HCH: 0.01-14.2
Mexico Polanco-Rodríguez et al. (2020)	Karstic Yucatan peninsula depth of water table 34 to 85 m	β-endosulfan Dieldrin Heptachlor (exact values not informed)
Mexico Rendón-von Osten and Dzul-Caamal (2017)	Karstic aquifer	Glyphosate: up to 1.41 (90%)
Mexico Ruiz-Toledo et al. (2014)	Not informed	Glyphosate: up to 18.43 (100%)
USA, Hawaii Li et al. (2001)	Not informed	Atrazine: concentrations not informed (30%) Ametryn: 0.708 Bromacil: 0.82-2.45 Hexazinone: 0.13-0.99
USA, Hawaii Knee et al. (2010)	Shallow wells	Metribuzin: 0.004-0.011 (8%)

Table 4 – Studies reporting pesticides concentrations in groundwater in North America.

Organochlorine pesticides were also analyzed in groundwater of the buffer zone of the Calakmul Biosphere Reserve, in the Maya Region of Hopelchen, Mexico where agriculture is allowed (POLANCO-RODRÍGUEZ *et al.*, 2020). Eleven sampling points, two wells for water supply and 9 dolines were sampled during the rainy season. Heptachlor, dieldrin and β-endosulfan were detected and in some cases, concentrations were above the Mexican limits for drinking water.

Another pesticide analyzed in two studies in Mexico was glyphosate (RUIZ-TOLEDO *et al.*, 2014; RENDÓN-VON OSTEN; DZUL-CAAMAL, 2017). Both studies were carried out in areas close to genetically modified soybean plantations and both detected glyphosate in groundwater (**Table 4**). Ruiz-Toledo *et al.* (2014) reported concentrations up to 18.43 $\mu g\ L^{-1}$ and considered that these high concentrations might be associated with the proximity of the sampling sites to plantations of herbicide resistant soybean. Moreover, the authors stated that the presence of glyphosate in all samples contradicts the supposedly strong sorption and relatively fast degradation of glyphosate in soil that would suggest a low leaching potential. Rendón von-Osten and Dzul-Caamal (2017) detected concentrations up to 1.41 $\mu g\ L^{-1}$ in 90% of the samples collected in the Yucatán Peninsula karstic aquifer which is highly vulnerable to pollution due to preferential flow.

In Hawaii, Li *et al.* (2001) analyzed 9 pesticides used in sugarcane and pineapple plantations in four islands, from 36 wells located near to agricultural areas from August 1997 to January 1998. Hexazinone and bromacil, known as highly leachable, were the pesticides most frequently detected in wells located in sugarcane fields and near storage areas. On contrary, the detection of ametryn that has a low leaching potential was attributed to bad well construction.

Other study in Hawaii (KNEE *et al*., 2010) determined carbaryl, metalaxyl, and metribuzin in 28 water samples from shallow wells and only metribuzin was detected. This herbicide is used to combat numerous species of broadleaf weeds on turfgrass, including golf courses and as applications of this herbicide would not follow a set seasonal pattern due to the Hawaii's semitropical climate, causing weeds to emerge at any time of year, no conclusion could be drawn on the origin of the metribuzin.

3.4 Pesticides in groundwater in Africa

According to FAO (2020), the countries in Africa that applied the highest amounts of pesticides (expressed as active ingredients) in 2018 were South Africa, which is not a tropical country, followed by Ethiopia (4,128 t); Sudan (2,469 t); Malawi (2,358 t); Mauritius (2,208 t); Zimbabwe (2,185 t); Rwanda (2,027 t); Zambia (1,670 t); Kenya (1,578 t); Cameroon (1,373 t) and Togo (1,293 t). However, these amounts are much lower than the amounts used in South America. From those countries, studies on groundwater contamination by pesticides were found in Togo, Malawi, and Ghana – **Table 5**, showing that in this continent the scenario for pesticides in groundwater is mostly unknown.

Country / Region Reference	Groundwater Description	Detected Pesticides: μg L^{-1} (detection frequency %)
Ghana, western region Affum et al. (2018)	Boreholes at a depth 55 to 70 m, with a static water level of 2 to 20 m	β-HCH: max 0.010 (18%) p,p′-DDT: max 0.055 (18%) Endrin: max 0.010 (9%) Metoxychlor: max 0.010 (64%) Methamidophos: max 0.013 (36%) Fenpopathrin: max 0.060 (18%) λ-cyhalothrin: max 0.01 (55%) Permethrin: max 0.065 (36%) Cyfluthrin: max 0.020 (36%) Cypermethrin: max 0.075 (55%) Deltamethrin: max 0.045 (9%) Chlorpyrifos: 0.030 to 2.000 (100%) Ethoprofos: max. 0.030 (27%)
Southern Malawi Kanyika-Mbewe et al. (2020)	Shallow wells (up to 15 m deep) and boreholes (up to 30 m deep)	Cypermethrin: 0.01-17.16 mg L^{-1} Carbaryl: 0.07- 0.492 mg L^{-1}
Togo Mawussi et al. (2014)	Wells at depth between 5 and 12 m Mostly sandy soils	p,p’-DDD: 0.001-0.008 (65%) α-endosulfan: 0.004-0.009 (65%) β-endosulfan: 0.003-0.004 (24%) Endosulfan sulphate: 0.003-0.116 (59%) Heptachlor epoxide: 0.005-0.012 (11.7%)

Table 5 – Studies reporting pesticides concentrations in groundwater in Africa.

In Western region of Ghana, pesticides were analyzed in groundwater from an agricultural catchment dominated by cocoa crops in the Ankobra Basin (AFFUM *et al.*, 2018). Samples were collected from boreholes at a depth 55 to 70 m. Banned and currently used pesticides were determined. From the ones in current use, pyrethroids were detected in up to 55% of samples with maximum concentrations of 0.075 μg L^{-1} and the organophosphorus chlorpyrifos was detected in all samples at concentrations as high as 2.00 μg L^{-1} (**Table 5**). It is worth mentioning that all these molecules are considered low leachers (LEWIS *et al.*, 2016). The authors attributed the ubiquity of p,p′-DDT, methoxychlor in the water resources to their current use, despite being banned for pest control on cocoa crops in Ghana. Considering the WHO guideline limits, the detected concentrations in groundwater were considered to represent low health risk to consumers.

Carbaryl and cypermethrin were monitored in Malawi by Kanyika-Mbewe *et al.* (2020) in boreholes up to 30-m deep and shallow wells up to 15-m deep in September to October 2015 and February to March 2016 (**Table 5**). The sampling points were the main sources of drinking water for most rural communities in the area. High concentrations of these two pesticides were detected reaching 17.16 mg L^{-1} of cypermethrin and 0.492 mg L^{-1} of carbaryl. These concentrations are highly above the groundwater pesticide concentrations found by most authors in tropical countries. The authors found that concentrations were higher during the rainy season, that coincides with application during cotton growing period. Since the monitored wells are sources of drinking waters these concentrations may represent a significant risk to human health.

Mawussi *et al.* (2014) conducted a study in coastal Togo analyzing common organochlorine, organophosphorus and pyrethroid insecticides in groundwater samples (n=25) collected from areas of vegetable production (**Table 5**). There was no detection of organophosphorus and pyrethroid insecticides. Among the organochlorine pesticides endosulfan isomers and its metabolite endosulfan sulfate and p,p'-DDT were detected at higher frequency (up to 65%) and the heptachlor metabolite heptachlor epoxide was found in 11.7% of samples. The authors stated that the high level of endosulfan sulphate detected in water (i.e., 0.116 µg L^{-1}) indicates a recent use although the use of organochlorine insecticides has been banned in this country since 2004.

3.5 Pesticides in groundwater in Asia

Among the Asian countries within the tropics, the ones which had consumed the largest amounts of pesticides (expressed as active ingredients) in 2018 (FAO, 2020) are: India (58,160 t), Malaysia (44,115 t), Thailand (35,287 t), Vietnam (19,154 t), Republic of Korea (18,716 t), Myanmar (15,326 t), Bangladesh (15,144 t), Philippines (12,595 t), Sri Lanka (2,260 t), Indonesia (1,597 t). From those, studies on pesticides contamination in groundwater were found for Sri Lanka, Thailand, Philippines, Bangladesh, and India – **Table 6**. India is by far the Asian country with the largest number of studies reporting groundwater contamination by pesticides. Since a paper with a thorough revision on this subject in India was published in 2020, we decided to use it as a reference. Most pesticides analyzed in groundwater in Asia (except for India) were the banned organochlorine pesticides (**Table 6**).

Country Reference	**Groundwater Description**	**Detected Pesticides: µg L^{-1} (detection frequency %)**
Bangladesh Matin et al. (1998)	Not informed	p,p'-DDT: 0.027-1.204 p,p'-DDE: 0.010-0.084 p,p'-DDD: 0.014-0.365 Heptachlor: 0.025-0.789
Bangladesh Hasanuzzaman et al. (2017)	Tubular well	Malathion: 42.58
Indonesia Rochaddi et al. (2019)	Shallow wells - alluvium deposits of fine to coarse-sized clastic sediments	Chlorpyrifos: 0.0021 ± 0.0043 (average ± standard deviation)
Thailand Hudak and Thapinta (2005)	Wells (depth 12 to 180 m) Unconsolidated aquifer in lowlands Consolidated aquifer in the western part of study area	Dicofol: up to 0.27 (36%) Aldrin+endrin: up to 3.44 (63%) Endosulfan: up to 0.298 (40%) Heptachlor+heptachlor epoxide: up to 1.269 (48%) BHC: up to 0.575 (72%) DDT: up to 9.681 (61%)
Sri Lanka Gunarathna et al. (2018)	Shallow well adjacent to agricultural field	Glyphosate: 1-4 (100%) AMPA: 2-11 (4%)

Philippines Bouman et al. (2002)	Shallow wells with loamy sand to clayey textures	Azin: up to 4.17 Butachlor: up to 1.14 Carbofuran: up to 1.15 DDT: up to 0.140 Diazinon: up to 0.510 Endosulfan: up to 1.90 Endrin: up to 0.101 Lindane: up to 0.220 Malathion: up to 0.132 MIPC: up to 0.260 Parathion: up to 0.250
Philippines Navarrete et al. (2018)	Tubular wells used for human consumption	Dieldrin: 0.028-0.029 Endrin aldehyde: 0.504-0.998 α-HCH: 0.037-0.039 β-HCH:0.015-0.055 γ-HCH: 0.029-0.030 δ-HCH: 0.030-0.042 γ-chlordane: 0.019-0.021 Endosulfan II: 0.019-0.021 Heptachlor: 0.028-0.029 Heptachlor epoxide: 0.022
India Sakaria and Elango (2020)	This is a review on the occurrence of pesticides in groundwater in India. Details on specific regions and pesticides analyzed and detected are given in the text.	

Table 6 – Studies reporting pesticides concentrations in groundwater in Asia.

In Bangladesh, organochlorine pesticides were banned in 1993. Matin *et al.* (1998) analyzed these pesticides in groundwater in 1994 and 1995, and detected heptachlor, p,p'-DDT, p,p'-DDD and its metabolite p,p'-DDE in 7 out of 144 samples collected from wells all over the country. However, no information was given on the groundwater and well characteristics. In a more recent study, Hasanuzzaman, Rahman and Salam (2017) also determine DDT, DDE and DDD and the organophosphate malathion, chlorpyrifos, diazinon and carbaryl in tubular wells in the region of Dhamrai upazila. No organochlorine was detected but malathion occurred at high concentrations (42.58 μg L^{-1}).

In Thailand, Hudak and Thapinta (2005) analyzed organochlorine in groundwater from 90 wells with depth ranging from 12.2 to 180 m in the central area of the country (**Table 6**). Each pesticide was detected in at least one third of the samples. As expected, there was an inverse correlation of pesticides concentrations and well depth. In Thailand, all but dicofol and endosulfan were banned since 1980s, so the authors supposed that these residues may come from past uses due to their high persistence but could also still be in use illegally.

Other study in Asia that analyzed organochlorine pesticides was carried out in the Philippines by Navarrete *et al.* (2018) in water samples from tube wells, which are used for domestic consumption by the rural communities. Endrin aldehyde, δ-BHC, and β-BHC comprise the bulk of the total organochlorine pesticides in the samples. Endrin aldehyde, an endrin metabolite, accounted for 45 to 68% of total organochlorine but endrin was not detected in any sample, suggesting a past intense usage of endrin.

Also, in Philippines, Bouman, Castañeda e Bhuiyan (2002) determined 17 pesticides (**Table 6**) in shallow wells in areas of rice plantations. Shallow tubular wells with variable depths (6 to 21 m), were described as having concrete casing for contamination prevention and operated with manual pumps. Samples were taken from 1989 to 2000 in different times in three regions of the Philippines. In a few samples, concentrations reached values above 0.1 μg L^{-1}, with maximum values up to 1.14 – 4.17 μg L^{-1}. According to the authors, pesticides leaching potential under wetland rice may be high caused by the constantly percolating water, so the low concentrations were attributed to particular transformation processes taking place under tropical, anaerobic conditions.

In Indonesia, one study evaluated chlorpyrifos concentrations in shallow coastal groundwater (ROCHADDI; SABDONO; SAINURI, 2019), whose aquifer are alluvium deposits composed of fine to coarse-sized clastic sediments resulting from river deposition processes, implying that the flow system in the area is an inter-grain flow system. The farther the distance from pollutant sources there was a decrease in chlorpyrifos pesticide concentration and the region with the higher agricultural areas showed also higher concentrations of this insecticide.

Glyphosate and its metabolite AMPA (aminomethylphosphonic acid) were analyzed in Sri Lanka in agricultural areas in nine samples collected from shallow wells and glyphosate was detected in all samples at concentrations from 1 to 4 μg L^{-1} and AMPA in 4% of samples (GUNARATHNA *et al.*, 2018) despite the low potential risk of groundwater contamination due to leaching through soil strata.

The climate in India varies greatly within its regions, ranging from tropical in the south to temperate and alpine in the Himalayan north, where elevated regions receive sustained winter snowfall (ATTRI; TYAGI, 2010). Rainfall varies widely at different locations so this cannot be considered a typical tropical country despite its localization within the tropics. However, India is a great user of pesticides and has a significant part of its country with tropical characteristics.

The Asian country that by far published more studies on the occurrence of pesticides in groundwater is India. Sackaria and Elango (2020) published a review of articles reporting pesticides residues in groundwater from 1995 to 2019. In the tables compiled by Sackaria and Elango (2020), 31 pesticides (16 classified as organochlorine, 11 as organophosphate and 4 as pyrethroids) were referred as detected in this period, reported in 38 research papers. The organochlorine pesticides were the most studied, with at least one analyzed in each article, followed by organophosphates (9 publications) and pyrethorids (3 publications). The occurrence of endosulfan was reported in 25 research papers and was detected at a maximum concentration of 166 μg L^{-1}, an extremely high concentration when compared to concentrations reported in other countries in the tropical region. According to the authors, this pesticide is still in use in India although it has been banned in most countries after its inclusion in the Stockholm Convention (2011). The second most studied pesticide was DDT, reported in 23 papers with the maximum concentration of 6,700 μg L^{-1} also extremely high when compared to other countries. Among the organophosphate pesticides, the insecticides parathion-methyl, malathion and chlorpyrifos were the most studied ones, with malathion as the one detected at higher concentrations reaching 44,200 μg L^{-1}. The other class studied in groundwater in this country was the pyrethroids cypermethrin, deltamethrin, fenvalerate. It is noteworthy the persistence of pesticides in groundwater even after the ban bringing out the importance of wider research due to the use of these substances in India.

4 I FINAL CONSIDERATIONS

In summary, this review showed 48 studies reporting the occurrence of pesticides in groundwater, either shallow or deep water plus another 38 cited by a review paper in India. Although it was not intended as a thorough review, we tried to include as many as we found. Many papers do not bring information on groundwater depth, geological formation, soil, or type of aquifer making it difficult to discuss the processes that may lead to contamination.

The most studied chemical class of pesticides was the persistent organochlorine followed by organophosphates, triazines and pyrethroids. There is a lack of information on many current used pesticides in tropical countries.

Most studies analyzed shallow waters probably due to its higher vulnerability to contamination. Moreover, a great number of papers report analysis of groundwater used for human consumption. It could be observed that some of the drinking water from groundwater sources have concentrations that may cause impacts to human health depending on persistence of the pesticide and water consumed without treatment. A large proportion of rural population in developing countries from the tropical region rely on untreated water from shallow groundwater as source of drinking water which is susceptible to contamination by pesticides as could be seen in a high number of published papers highlighting the need for more studies.

Another aspect that calls attention is the fact the many pesticides classified as non-leachers are detected in groundwater, attributed by the researchers mainly to preferential flow, transport associated to soluble organic matter or bad well construction. In some cases, this contaminant transport may move greater quantities of hydrophobic contaminants than does dissolved-phase transport. Further study on transportation processes is necessary. In addition, the evaluation of temporal variations is also flawed since many of the described studies have very few sampling campaigns.

REFERENCES

AFFUM, A. O. *et al.* Distribution and risk assessment of banned and other current-use pesticides in surface and groundwaters consumed in an agricultural catchment dominated by cocoa crops in the Ankobra Basin, Ghana. **Science of the Total Environment**, v. 633, p. 630-640, 2018. DOI: 10.1016/j.scitotenv.2018.03.129

ALMEIDA, M. B. *et al.* Pesticide determination in water samples from a rural area by multi-target method applying liquid chromatography-tandem mass spectrometry. **Journal of the Brazilian Chemical Society**, v. 30, p. 1657-1666, 2019. DOI: 10.21577/0103-5053.20190066

AMANAMBU, A. C. *et al.* Groundwater system and climate change: Present status and future considerations. **Journal of Hydrology**, v. 589, p. 125163, 2020. DOI: 10.1016/j.jhydrol.2020.125163

ARRAES, A. A.; BARRETO, F. M. S.; DE ARAÚJO, J. C. Use of atrazine and groundwater availability in Brazil. *In*: World Water Congress, 13, 2008, Montpellier. **Proceedings** […]. Johanesburg: International Water Resources Association, 2008. v. 1, p. 1234-1238. Available at: http://www.iwra.org/congress/2008/resource/authors/abs204_article.pdf. Accessed on: 6 Apr. 2023.

ATTRI, S. D.; TYAGI, A. **Climate Profile of India**. Met Monograph No.

Environment Meteorology-01/2010. New Delhi: Environment Monitoring and Research Centre, India Meteorological Department. 2010. 130 p. Available at: http://uchai.net/pdf/knowledge_resources/Publications/Reports/Climate%20Profile%20India_IMD.pdf. Accessed on: 02 Dec. 2020.

BESERRA, L. **Agrotóxicos, vulnerabilidades socioambientais e saúde: uma avaliação participativa em municípios da bacia do rio Juruena, Mato Grosso**. 2017. 140 p. Master dissertation: Post graduation course on Public Heatlh of the Federal University of Mato Grosso, Cuiabá, 2017. Available at: https://www1.ufmt.br/ppgsc/arquivos/7482ec1ed28ff2985ffdceea860bf123.pdf?fbclid=IwAR1Azjnal37K0xy2CzPm_oT8snE5TxA4m3IxijKxvmyhb6wI1u9-o56O7Us. Accessed on: 17 Jun. 2020.

BORTOLUZZI, E. C. *et al.* Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco. **Química Nova**, v. 30, p. 1872-1876, 2007. Available at: http://static.sites.sbq.org.br/quimicanova.sbq.org.br/pdf/Vol30No8_1872_13-AR06410.pdf. Accessed on: 6 Apr. 2023.

BOUMAN, B. A. M.; CASTAÑEDA, A. R.; BHUIYAN, S. I. Nitrate and pesticide contamination of groundwater under rice-based cropping systems: past and current evidence from the Philippines. **Agriculture, Ecosystems and Environment**, v. 92, p. 185-199, 2002. DOI: 10.1016/S0167-8809(01)00297-3.

BRASIL. Ministério da Saúde. Portaria MS n. 2914, de 12 de dezembro de 2011. **Diário Oficial da União: Brasília**, DF, 14 dez. 2011. Available at: https://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html.Acessed on: 20 Dec. 2022.

BRASIL. Ministério da Saúde. Portaria de Consolidação n. 5, de 28 de setembro de 2017. **Diário Oficial da União**: Brasília, DF, 29 Mar. 2018, updated on 30 Ago. 2021. Available at: http://portalsinan.saude.gov.br/images/documentos/Legislacoes/Portaria_Consolidacao_5_28_SETEMBRO_2017.pdf. Accessed on: 6 Apr. 2023.

BRASIL. Resolução CONAMA n. 396, de 03 de abril de 2008. Conselho Nacional de Meio Ambiente (Environmental National Council). **Diário Oficial da União**: Brasília, DF, n. 66, p. 66-68, 07 abr. 2008. Available at: http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=562. Accessed on: 6 Apr. 2023.

CALDAS, S. S. *et al.* Pesticide residue determination in groundwater using solid-phase extraction and high-performance liquid chromatography with diode array detector and liquid chromatography-tandem mass spectrometry. **Journal of the Brazilian Chemical Society**, v. 21, p. 642-650, 2010. DOI: 10.1590/S0103-50532010000400009.

CARBO, L. *et al.* Determination of pesticides multiresidues in shallow groundwater in a cotton-growing region of Mato Grosso, Brazil. **Journal of the Brazilian Chemical Society**, v. 19, p. 1111-1117, 2008. DOI: 10.1590/S0103-50532008000600009.

CASARA, K. P. *et al.* Environmental dynamics of pesticides in the drainage area of São Lourenço River headwaters, Mato Grosso, Brazil. **Journal of the Brazilian Chemical Society**, v. 23, p. 1719-1731, 2012. DOI: 10.1590/S0103-50532012005000037.

CHARLIER, J-B. *et al.* Transport of a Nematicide in Surface and Groundwaters in a Tropical Volcanic Catchment, **Journal of Environmental Quality**, v. 38, p. 1031-1041, 2009. DOI: 10.2134/jeq2008.0355.

COHEN, A. J. B.; CHERRY, J. A. **Conceptual and visual understanding of hydraulic head and groundwater flow**. Guelph, Ontario, Canada: The Groundwater Project, 2020. E-book. 58 p. (ISBN: 978-1-7770541-6-8). Available at: https://gw-project.org/books/conceptual-and-visual-understanding-of-hydraulic-head-and-groundwater-flow/. Accessed on: 6 Apr. 2023.

CORREIA, N. M.; CARBONARI, C. A.; VELINI, E. D. Detection of herbicides in water bodies of the Samambaia River sub-basin in the Federal District and eastern Goiás. **Journal of Environmental Science and Health**, Part B, v. 55, n. 6, p. 574-582, 2020. DOI: 10.1080/03601234.2020.1742000.

De JOODE, B. van W. *et al.* Manganese concentrations in drinking water from villages near banana plantations with aerial mancozeb spraying in Costa Rica: Results from the Infants' Environmental Health Study (ISA). **Environmental Pollution**, v. 215, p. 247-257, 2016. DOI: 10.1016/j.envpol.2016.04.015.

DORES, E. F. G. C. *et al.* Pesticide Levels in Ground and Surface Waters of Primavera do Leste Region, Mato Grosso, Brazil. **Journal of Chromatographic Science**, v. 46, p. 585-590, 2008. DOI: 10.1093/chromsci/46.7.585.

DRAGONI, W.; SUKHIJA, B. S. **Climate change and groundwater**: a short review. Geological Society, London, Special Publications, 288, 1-12. 2008. DOI: 10.1144/SP288.1.

EDWARDS, Q. A. *et al.* Micropollutants related to human activity in groundwater resources in Barbados, West Indies. **Science of the Total Environment**, v. 671, p. 76-82, 2019. DOI: 10.1016/j.scitotenv.2019.03.314.

FAO - Food and Agriculture Organization of the United Nations. **Current Status of agriculture in the Caribbean and implications for Agriculture Policy and Strategy**. 2030 - Food, Agriculture and Rural Development in Latin America and the Caribbean, n. 14. Santiago de Chile: FAO, 2019. 28 p. Available at: http://www.fao.org/3/ca5527en/ca5527en.pdf. Accessed on 6 Apr. 2023

FAO - Food and Agriculture Organization of the United Nations. **Pesticides Use**. 2020. Available at http://www.fao.org/faostat/en/#data/RP/visualize. Accessed on: 21 Nov. 2020.

FILIZOLA, H. F. *et al.* Monitoramento e avaliação de risco de contaminação por pesticidas em água superficial e subterrânea na região de Guaíra. **Pesquisa Agropecuária Brasileira**, v. 37, n. 5, p. 659-667, 2002. Available at: https://seer.sct.embrapa.br/index.php/pab/article/download/6387/3444. Accessed on: 02 Nov. 2020.

FOSTER, S.; SMEDLEY, P.; CANDELA, L. Groundwater quality in the humid tropics: an overview. In: PROCEEDINGS OF THE SECOND INTERNATIONAL COLLOQUIUM, 52., 1999, Panama. Unesco, **International Hydrological Programme - IHP-V Technical Document in Hydrology**, 2002. p. 441–468. Available at: https://unesdoc.unesco.org/ark:/48223/pf0000126658. Accessed on: 21 Nov. 2020

FOSTER, S. S. D. Groundwater conditions and problems characteristic of the humid tropics. In: **Hydrology of Warm Humid Regions IAHS Publ.**, v. 216, p. 433–449, 1995. (Proc. of the Yokohama Symposium, July 1993).

FOSTER, S. S. D., HIRATA, R. C. A. **Groundwater pollution risk assessment**: a methodology using available data. Lima: CEPIS/PAHO/WHO, 1988. 86 p.

GEISSEN, V. *et al.* Soil and Water Pollution in a Banana Production Region in Tropical Mexico. **Bulletin of Environmental Contamination and Toxicology**, v.85, p. 407-413, 2010. DOI: 10.1007/s00128-010-0077-y.

GIÁCOMAN-VALLEJOS, G. *et al.* Presence of DDT and Lindane in a Karstic Groundwater Aquifer in Yucatan, Mexico. **Groundwater Monitoring & Remediation**, v. 38, n. 2, p.: 68-78, 2018. DOI: 10.1111/gwmr.12267.

GOMES, M. A. F.; SPADOTTO, C. A.; LANCHOTTE, V. L. Ocorrência do herbicida tebuthiuron na água subterrânea da microbacia do Córrego Espraiado, Ribeirão Preto – SP. **Pesticidas**: Revista de Ecotoxicologia e Meio Ambiente, v. 11, p. 65-76, 2001. DOI: 10.5380/pes.v11i0.3136.

GREEN, T.R. Linking Climate Change and Groundwater. In: JAKEMAN, A. J., BARRETEAU, O.; HUNT, R.J.; RINAUDO, J-D.; ROSS, A. (eds.), **Integrated Groundwater Management** - Concepts, Approaches and Challenges. Spring Open, Springer, Cham, 762 p. 2016. DOI: 10.1007/978-3-319-23576-9_5.

GUNARATHNA, S. *et al.* Glyphosate and AMPA of agricultural soil, surface water, groundwater and sediments in areas prevalent with chronic kidney disease of unknown etiology, Sri Lanka. **Journal of Environmental Science and Health**, Part B, 53:11, 729-737, 2018. DOI: 10.1080/03601234.2018.1480157.

GURDAK, J. J.; HANSON, R. T.; GREEN, T. R. **Effects of climate variability and change on groundwater resources of the United States**. U.S. Department of the Interior, U.S. Geological Survey, Office of Global Change. Fact Sheet 2009-3074, 2009. 4 p.

GWENZI, W.; CHAUKURA, N. Organic contaminants in African aquatic ecosystems: Current knowledge, health risks, and future research directions. **Science of the total environment**, v. 619-620, p. 1493-1514, 2018. DOI: 10.1016/jscitotenv.2017.11.121.

HARDING, R. J. *et al.* The future for global water assessment. **Journal of Hydrology**, v. 518, part B, p. 186-193. 2014. DOI: 10.1016/j.jhydrol.2014.05.014

HASANUZZAMAN, M., RAHMAN, M. A., SALAM, M. A. Identification and quantification of pesticide residues in water samples of Dhamrai Upazila, Bangladesh. **Applied Water Science**, v.7, p. 2681-2688, 2017. DOI: 10.1007/s13201-016-0485-1.

HOUBEN, G. J. *et al.* The impact of high-intensity no-till agriculture on groundwater quality in the subtropical Capiibary catchment, SE Paraguay. **Environmental Earth Sciences**, v. 74, p. 479-491, 2015. DOI: 10.1007/s12665-015-4055-x

HUDAK, P. F., THAPINTA, A. Agricultural Pesticides in Groundwater of Kanchana Buri, Ratcha Buri, and Suphan Buri Provinces, Thailand. **Bulletin of Environmental Contamination and Toxicology**, v.: 74, p.: 631-636, 2005. DOI: 10.1007/s00128-005-0630-2.

IBGE - Instituto Brasileiro de Geografia e Estatística]. Censo Agropecuário 2017. [Rio de Janeiro, 2018]. Available at: https://sidra.ibge.gov.br/pesquisa/censo-agropecuario/censo-agropecuario-2017. Accessed: 8 Jan. 2021.

IUSS - International Union of Soil Sciences, Working Group WRB, World Reference Base for Soil Resources: International soil classification system for naming soils and creating legends for soil maps. **World Soil Resources Reports No. 106**. Rome: Food and Agriculture Organization of the United Nations (FAO), 2014, update 2015.

JUO, A. S.; FRANZLUEBBERS, K. **Tropical soils:** properties and management for sustainable agriculture. Oxford: Oxford Univ. Press on Demand, 2003. 304 p.

KANYIKA-MBEWE, C. *et al.* Monitoring of carbaryl and cypermethrin concentrations in water and soil in Southern Malawi. **Environmental Monitoring and Assessment**, v. 192, article number 595, 2020. DOI: 10.1007/s10661-020-08557-y.

KNEE, K. L. *et al.* Caffeine and agricultural pesticide concentrations in surface water and groundwater on the north shore of Kauai (Hawaii, USA). **Marine Pollution Bulletin**, v.: 60, p.: 1376-1382, 2010. DOI: j.marpolbul.2010.04.019.

LETEY J. *et al.* The Role of Dissolved Organic Matter in Pesticide Transport through Soil, *In*: **ACS Symposium Series** v. 751, Chapter 22: Agrochemical Fate and Movement, p. 347-360. 2000. DOI: 10.1021/bk-2000-0751.ch022

LEWIS, K.A. *et al.* An international database for pesticide risk assessments and management. **Human and Ecological Risk Assessment**: An International Journal, v. 22, n. 4, p. 1050-1064. 2016. DOI: 10.1080/10807039.2015.1133242.

LI, Q. X.; HWANG, E.-C.; GUO, F. Occurrence of Herbicides and Their Degradates in Hawaii's Groundwater. **Bulletin of Environmental Contamination and Toxicology**, v. 66, p.: 653-659, 2001. DOI: 10.1007/ s00128-001-0058-2.

LI, R. **Groundwater pollution risk assessment under scenarios of climate and land use change in the Northern Great Plains**. Lincoln, Nebraska: ProQuest LLC. 2012. 156 p.

MARGAT, J.; GUN, J.V.D. **Groundwater around the world**: A geographic synopsis. 1. ed. London: CRC Press. 2013. DOI: 10.1201/b13977.

MARTINÉZ-GARCIA, J.; JARAMILLO-COLORADO, B. E.; FERNÁNDEZ-MAESTRE, R. Water quality of five rural Caribbean towns in Colombia. **Environmental Earth Sciences**, v. 78, article number 575, 2019. DOI: 10.1007/s12665-019-8580-x.

MATIN, M. A. *et al.* Organochlorine insecticide residues in surface and underground water from different regions of Bangladesh. **Agriculture, Ecosystems and Environment**, v.: 69, p. 11-15, 1988. DOI: 10.1016/S0167-8809(98)00094-2.

MAWUSSI, G. *et al.* Insecticide residues in soil and water in coastal areas of vegetable production in Togo. **Environmental Monitoring and Assessment**, v. 186, p. 7379-7385, 2014. DOI: 10.1007/s10661-014-3934-z.

MENEZES FILHO, A.; SANTOS, F. N.; PEREIRA, P. A. P. Development, validation and application of a method based on DI-SPME and GC–MS for determination of pesticides of different chemical groups in surface and groundwater samples. **Microchemical Journal**, v. 96, p. 139-145, 2010. DOI: 10.1016/j.microc.2010.02.018.

MENEZES, J. M. *et al.* Qualidade da água e sua relação espacial com as fontes de contaminação antrópicas e naturais: bacia hidrográfica do Rio São Domingos – RJ. **Engenharia Agrícola**, v. 29, n.4, p. 687-698, 2009. DOI: 10.1590/S0100-69162009000400019.

MONCRIEFF, J. E., BENTLEY, L. R.; PALMA, H. C. Investigating pesticide transport in the León-Chinandega aquifer, Nicaragua. **Hydrogeology Journal**, v. 16, p. 183-197, 2008. DOI: 10.1007/s10040-007-0229-2.

MORAIS, L. S. R. **Desenvolvimento e validação de métodos para a determinação de agrotóxicos em água e solo das áreas de recarga do Aquífero Guarani, na região das nascentes do Rio Araguaia, MT/GO**. 2009. 157 p. PhD thesis (Post graduation course on Analytical Chemistry). Universidade Estadual de Campinas, Campinas, 2009. Available at: http://repositorio.unicamp.br/jspui/bitstream/REPOSIP/250538/1/Morais_LaisSayuriRibeirode_D.pdf. Accessed on: 25 May 2020.

MOREIRA, J. C. *et al.* Contaminação de águas superficiais e de chuva por agrotóxicos em uma região do estado do Mato Grosso. **Ciência & Saúde Coletiva**, v. 17, n. 6, p. 1557-1568, 2012. DOI: 10.1590/S1413-81232012000600019.

NAVARRETE, I. A. *et al.* Organochlorine pesticide residues in surface water and groundwater along Pampanga River, Philippines. **Environmental Monitoring and Assessment**, v. 190, article number 289, 2018. DOI: 10.1007/s10661-018-6680-9.

NOGUEIRA, E. N. *et al.* Currently Used Pesticides in Water Matrices in Central-Western Brazil. **Journal of the Brazilian Chemical Society**, v. 23, p. 1476-1487, 2012. DOI: 10.1590/S0103-50532012005000008

OLIVEIRA, M. M.; NOVO, M. E.; FERREIRA, J. P. L. Models to predict the impact of the climate changes on aquifer recharge. In: FERREIRA, J. P. L.; FERREIRA, J. M. P.; VIEIRA (eds), Water in celtic countries: quantity, quality and climate variability. **Proceedings of the Fourth Inter-Celtic Colloquium on Hydrology and Management of Water Resources**, Guimaraes, Portugal: July 2005. Wallingford: International Association of Hydrological Sciences (IAHS Publication, 310).

OLIVO, V. E. *et al.* Rapid method for determination of glyphosate in groundwater using high performance liquid chromatography and solid-phase extraction after derivatization. **Ambiente & Água** - An Interdisciplinary Journal of Applied Science, v. 10, n. 2, p. 296-297, 2015. DOI: 10.4136/ambi-agua.1548.

PINHEIRO, A.; SILVA, M. R.; KRAISCH, R. Presença de pesticidas em águas superficiais e subterrâneas na bacia do Itajaí, SC. **Revista de Gestão de Água da América Latina**, v. 7, n. 2, p. 17-26, 2010. DOI: 10.21168/rega.v7n2.p17-26.

PIRES, N. L. *et al.* Determination of glyphosate, AMPA and glufosinate by high performance liquid chromatography with fluorescence detection in waters of the Santarém Plateau, Brazilian Amazon. **Journal of Environmental Science and Health**, Part B, v. 55, n. 9, p. 794-802, 2020. DOI: 10.1080/03601234.2020.1784668.

POETER, E. *et al.* **Groundwater in our water cycle** – getting to know Earth's most important fresh water source, Guelph, Ontario: The groundwater project. 2020. 136 p. Available at: https://gw-project.org/books/groundwater-in-our-water-cycle/. Accessed on: 6 Apr 2023.

POLANCO-RODRÍGUEZ, A. G. *et al.* Organochlorine Pesticides and Potentially Toxic Elements in Groundwater from a Protected Reserve in the Maya Region of Hopelchen, Mexico. **Bulletin of Environmental Contamination and Toxicology**, v. 104, p. 568-574, 2020. DOI: 10.1007/s00128-020-02848-3.

PORTAL, T. P. *et al.* An integrated assessment of water quality in a land reform settlement in northern Rio de Janeiro state, Brazil. **Heliyon**, v. 5, article number e01295, 2019. DOI: 10.1016/j.heliyon.2019.e01295.

PURI S.; AURELI, A. **Atlas of transboundary aquifers: global maps, regional cooperation and local inventories.** IHP (International Hydrological Programme), ISARM Programme. Paris: UNESCO. 2009. 322 p. Available at: https://unesdoc.unesco.org/ark:/48223/pf0000192145. Accessed on: 21 Nov. 2020

REICHENBERGER, S. *et al.* Pesticide displacement along preferential flow pathways in a Brazilian Oxisol, **Geoderma**, v. 110, p. 63-86, 2002. DOI: 10.1016/S0016-7061(02)00182-9.

RENDÓN-VON OSTEN, J.; DZUL-CAAMAL, R. Glyphosate Residues in Groundwater, Drinking Water and Urine of Subsistence Farmers from Intensive Agriculture Localities: A Survey in Hopelchén, Campeche, Mexico. **International Journal of Environmental Research and Public Health**, v. 14, article number 595, 2017. DOI: 10.3390/ijerph14060595.

ROCHA, A. A. *et al.* Monitoring of Pesticide Residues in Surface and Subsurface Waters, Sediments, and Fish in Center-Pivot Irrigation Areas. **Journal of the Brazilian Chemical Society**, v. 26, n. 11, p. 2269-2278, 2015. DOI: 10.5935/0103-5053.20150215.

ROCHADDI, B.; SABDONO, A.; ZAINURI, M. Preliminary study on the contamination of organophosphate pesticide (chlorpyrifos) in shallow coastal groundwater aquifer of Surabaya and Sidoarjo, East Java Indonesia. 4th International Conference on Tropical and Coastal Region Eco Development. **IOP Conf. Ser.: Earth and Environmental Science**, v. 246, article number 012079, 2019. DOI: 10.1088/1755-1315/246/1/012079.

RUEPERT, C. *et al.* **Vulnerabilidad de las águas subterráneas a la contaminación por plaguicidas en Costa Rica**. Estudio preliminar. Informe Ejecutivo, Heredia: Universidad Nacional Costa Rica. 62 p. 2005. 62 p. Available at: https://www.researchgate.net/publication/308797315. Accessed on: 16 Nov. 2021.

RUIZ-TOLEDO, J. *et al.* Occurrence of Glyphosate in Water Bodies Derived from Intensive Agriculture in a Tropical Region of Southern Mexico. **Bulletin of Environmental Contamination and Toxicology**, v. 93, p.: 289–293, 2014. DOI: 10.1007/s00128-014-1328-0.

SACKARIA, M., ELANGO, L. Organic micropollutants in groundwater of India – A review. **Journal of the Water Environment Federation**, v. 92, p. 504-523, 2020. DOI: 10.1002/wer.1243.

SANTOS, H. G. *et al.* **Sistema brasileiro de classificação de solos**. 5. ed. Brasília, DF: Embrapa. 2018. Available at: https://www.infoteca.cnptia.embrapa.br/infoteca/handle/doc/1094003. Accessed on: 6 Apr. 2023

SHIKLOMANOV, L. A. World Freshwater Resources. *In*: GLEICK, P.H., Ed., **Water in Crisis**: A Guide to World's Freshwater Resources. New York: Oxford University Press, p. 13 - 24. 1993.

SILVA, D. R. O. *et al.* Ocorrência de agrotóxicos em águas subterrâneas de áreas adjacentes a lavouras de arroz irrigado. **Química Nova**, v. 34, n. 5, p. 748-752, 2011. Available at: http://static.sites.sbq.org.br/quimicanova.sbq.org.br/pdf/Vol34No5_748_03-AR10217.pdf. Accessed on: 28 May 2020.

SOIL SURVEY STAFF. **Keys to Soil Taxonomy**, 12th ed. Washington, DC: Natural Resources Conservation Service, US Department of Agriculture, 2014.

SOUZA, V. *et al.* Determinação de pesticidas em água de poços tubulares em áreas de cultura de algodão na microrregião de Primavera do Lestes, Mato Grosso. *In*: CONGRESSO BRASILEIRO DE ÁGUAS SUBTERRÂNEAS, 13., 2004, Cuiabá. **Anais** […]. São Paulo: Associação Brasileira de Água Subterrânea. 2004. Available at: https://aguassubterraneas.abas.org/asubterraneas/article/download/23431/15516. Accessed on: 31 Oct 2020.

TAYLOR, R. G. *et al.* Groundwater and climate change. **Nature Clim Change,** v. 3, p. 322–329, 2013. DOI: 10.1038/nclimate1744.

TELUGUNTLA, P. *et al.* Global Cropland Area Database (GCAD) derived from Remote Sensing in Support of Food Security in the Twenty-first Century: Current Achievements and Future Possibilities. *In*: Thenkabail, P. S. (ed.). **Remote Sensing Handbook**: Land Resources: Monitoring, Modelling, and Mapping. V. II, chapter 7, p. 1-45. Boca Raton: Taylor & Francis, 2015.

THENKABAIL, P. S. *et al.* Assessing future risks to agricultural productivity, water resources and food security: how can remote sensing help? **Photogrammetric Engineering and Remote Sensing**, Special Issue on Global Croplands: Highlight Article, v. 78, n. 8, p. 773-782, 2012.

TORRES, N. H.; FERREIRA, L. F. R.; AMÉRICO, J. H. P. Análise de resíduos de agrotóxicos em água subterrânea proveniente do Aquífero Guarani. **Bioenergia em Revista**: diálogos, v. 5, n. 2, p. 36-49, 2015. Available at http://fatecpiracicaba.edu.br/revista/index.php/bioenergiaemrevista/article/download/176/107. Accessed on: 28 May 2005.

ZHANG, X. *et al.* Detection of human influence on twentieth-century precipitation trends. **Nature,** v. 448, p. 461-465, 2007. DOI: 10.1038/nature06025.