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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

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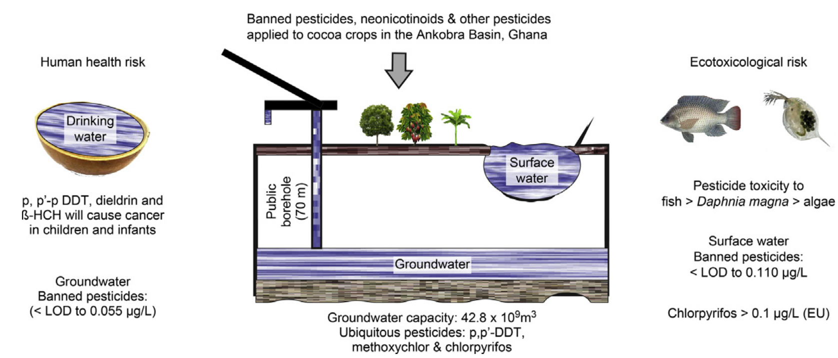
HIGHLIGHTS

- Groundwater was contaminated with some banned and non-banned pesticides.
- DDTs, βHCH, and dieldrin in some water sources may cause cancer in children/infants.
- Non-carcinogenic toxicity of pesticides have no adverse health risk on humans.
- The predicted toxicity of pesticides to fish was higher than in *Daphnia magna*/algae.
- Presence of DDT and HCH in the water were recent and of technical-grade origin.

GRAPHICAL ABSTRACT



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ABSTRACT

The existence of pesticides, such as organochlorine pesticides, parathion-ethyl, methamidophos which is banned globally and some current-use non-banned pesticides of organophosphorus and synthetic pyrethroids in freshwater sources is an ecological and public health concern in many countries, including Ghana. Prompted by this concern, the exposure levels and risk assessment of these pesticides to humans and non-target organisms via groundwater and surface water sources in an agricultural catchment dominated by cocoa crops in the Ankobra Basin, Ghana, were investigated. The individual concentrations of the banned pesticides in the surface water and groundwater samples varied from < LOD to 0.110 μg/L and < LOD to 0.055 μg/L, respectively, while the concentrations of the non-banned pesticides ranged from < LOD to 0.925 μg/L and < LOD to 2 μg/L, respectively. The mean concentrations of chlorpyrifos, cypermethrin, p,p′-DDT and pirimiphos-methyl in some water sources exceeded the EU limit of 0.1 μg/L. Some surface water sources were more contaminated with DDTs, endrin, dieldrin, methoxychlor, chlorpyrifos, and HCH isomers than were freshwater sources in river basins in some countries of the world. Chlorpyrifos, p,p′-DDT and methoxychlor were ubiquitous in both water sources. The hydrochemical and compositional profiles of the pesticides indicate that water-exchange and secondary porosities in the bedrock likely contributed to the occurrence of the pesticides in the water sources. The pesticides were of low risk to humans that consume the water, but considering the US EPA safe limit for carcinogenic effects of 10^{-6}, the high levels of DDTs, β-HCH, and dieldrin in some of the surface water and groundwater sources may cause cancer in children or infants. The toxicity of pesticide mixtures to surface water non-target organisms decreased in the order of fish > *Daphnia magna* > algae. The pesticides in the water sources were anthropogenic in origin and recently used. DDT and HCH in the water were of technical-grade origin.

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1. Introduction

Safe drinking water from groundwater and surface water is essential for sustainable human health, quality of life, and the socioeconomic development of mankind and is a prerequisite for developing countries, such as Ghana, to meet the sustainable development goal (SDG) of achieving clean water and sanitation by 2030 (CWSA, 2014; Saeedif et al., 2015). However, the existence of banned pesticides, such as organochlorine pesticides, parathion-ethyl, and methamidophos, even at low concentrations, and of current-use non-banned pesticides such as synthetic pyrethroids and organophosphorus pesticides in groundwater and surface water that are used for drinking purposes can compromise these benefits to mankind. Thus, it is essential that pesticides in such water sources comply with the health-based limits of the World Health Organization (WHO, 2011), and water quality criteria provided in the European Union (EU) Water Framework Directive 2000/60/EC and EU Council Directive 98/83/EC (EC, 1998, 2000).

Several studies have highlighted the potential risks that these pesticides pose to public health; biodiversity; and non-target organisms, such as fish, algae and aquatic invertebrates (Papadakis et al., 2015). Organochlorine pesticides can bioaccumulate and biomagnify at all levels of food chain and in human. Organochlorine pesticides, parathion-ethyl and methamidophos are known to contribute to the development of certain cancers, birth defects, dysfunctional immunity, a dysfunctional reproductive and nervous systems, and other diseases in humans (Mostafalou and Abdollahi, 2013; Shukla and George, 2011). In Ghana, the prevalence of cancer is on the rise, necessitating the assessment of pesticides known to underlie cancer development in humans. The use of organochlorine pesticides, parathion-ethyl and methamidophos (Stockholm and Rotterdam Convention), which are also on the priority lists of the United States Environmental Protection Agency (US EPA) and EU to control insect pests of crops, including cocoa, a major foreign earning commodity in Ghana, was banned by the Environmental Protection Agency of Ghana (EPA Ghana) in 1985 (EPA Ghana, 1994; Ghana NIP, 2007; Stockholm convention, 2004).

The Ankobra River Basin (8400 km^2), which is part of the southwestern river systems and located in the western region of Ghana, is a major water resource and of vital economic importance to Ghana. The river basin has a groundwater potential of 45.82×10^9 m^3 and a recoverable groundwater storage of 29.39×10^9 m^3 (Nyarkoh, 2011). The basin has agricultural catchments dominated by cocoa crops. Although imidacloprid, bifenthrin, and thiamethoxam are the government-recommended chemicals for insect pest control of the cocoa crops in Ghana, recent studies indicate that organochlorine pesticides, methamidophos, and parathion-ethyl, as well as some non-banned pesticides consisting of synthetic pyrethroids and organophosphorus pesticides, exist in cocoa-cultivating soils (Adu-Acheampong et al., 2014; Dankyi et al., 2014). Thus, despite the official ban of these pesticides, their release into the environment has not ceased. Furthermore, anecdotal evidence from the agricultural catchments of the basin corroborated by Bateman (2015), indicates that poor pesticide management practices by farmers exacerbates the pesticide contamination in the water sources. In addition, the persistence of organochlorine pesticides coupled with the extensive application of synthetic pyrethroids and organophosphorus pesticides to crops indicate that these pesticides can exist in the environment for a long time via enrichment processes (AERU, 2017). The high rainfall pattern and porous geology of the Ankobra River Basin indicate that organochlorine pesticides (Log K_{ow}: 3.20–6.91), organophosphorus pesticides (Log K_{ow}: −0.79–3.69) and synthetic pyrethroids (Log K_{ow}: 4.6–6.8) may leach from the nearby cocoa-cultivating soils via run-off into surrounding water sources consumed by the human population (Vryzas et al., 2009). Additionally, lipophilic pesticides bound to sediments and suspended particulate matter can be remobilized into the water compartment under various interconnecting factors that includes varying pH and water turbulence conditions. These processes can result in long-term contamination of the aquatic environment, posing a threat to human health and aquatic organisms (AERU, 2017; Montory et al., 2017). Various studies indicate that aquifers that underlie land that undergoes pesticide applications can also be contaminated during groundwater recharge either by direct infiltration or through surface water-groundwater interactions (Mechen et al., 2017; Wang et al., 2015).

More than half of the rural human population (55,773) in the eighth district of the agricultural catchment of Ankobra Basin consumes these water sources likely contaminated with these pesticides without any prior treatment (GSS, 2014). Nevertheless, the ecotoxicological and human health risks of these pesticides via these water sources have been given less attention than the pesticides in water resources in urban communities in Ghana (Darko et al., 2008; Kuranchi-Mensah et al., 2012; Ntow, 2005), Ethiopia (Mekonen et al., 2016), Lebanon (Kouzayha et al., 2013), Egypt (Dahshan et al., 2016), and the US (Kolpin et al., 1998). Thus, it is imperative to know the exposure levels of these pesticides and the risk that they pose to human health (especially in the development of cancers) and aquatic organisms in the water sources in this agricultural catchment (Shukla and George, 2011). The specific aims of this study were to 1) screen for banned pesticides, non-banned pesticides and their metabolites in the groundwater and surface water sources in the agricultural catchment of Ankobra Basin, 2) identify the origin of the pesticides in the water sources, 3) determine the various hydrochemical facies of the water sources and its relationship to pesticide occurrence in the water medium, 4) conduct a health risk assessment of these pesticides for humans via the oral ingestion pathway and a probabilistic ecotoxicological risk assessment of these pesticides for non-target organisms inhabiting the surface water, and 5) recommend water resource management measures to mitigate pesticide contamination in these water sources.

2. Materials and methods

2.1. Study area

The agricultural catchment (Fig. 1) is located between latitude 5° 12′ 0″ and 5° 33′ 0″ N and between longitude 1° 49′30″ and 1° 58′30″ W and lies within the forest ecological zone of the Ankobra River Basin in the Western Region of Ghana. This basin was selected because of its economic importance to Ghana, its high average annual tonnage of cocoa production (equivalent to 28% of the average yearly tonnage (427,441 tons) for the western region of Ghana), its high rainfall (annual precipitation of 1500–2150 mm) and the porosity of its geological bedrock (Yidana et al., 2008; COCOBOD, 2017). Subsequently, 11 rural communities, namely, Asanteayer, Boakrom, Larbikrom, Nyamebekyere, Obengkrom, Obisikrom, Pemeso, Tettehkrom, Wassa Akwapim, Yawkrom, and Yawmensahkrom, were randomly selected based on the high average annual tonnage of cocoa production (equivalent to 11% of the average yearly tonnage (165,806 tons) of the basin), land elevation (61–198 m above sea level), and accessibility and availability of publicly used boreholes and surface water. The Peme River (16 km) and Ben River (13 km), which drain the agricultural catchment, merge with the Oppon River, which flows into the Ankobra River and then into the Gulf of Guinea. The cassava, plantain and maize found in the catchment are cultivated as household food and therefore not intentionally sprayed with pesticides. Organochlorine pesticides (α-, γ-, δ-, β-HCH, heptachlor, aldrin, γ-chlordane, α-, β-endosulfan, p,p′-DDT, p,p′-DDD, p,p′-DDE, dieldrin, endrin, and methoxychlor), parathion-ethyl and methamidophos were selected based on the Stockholm and Rotterdam Conventions and the priority lists of the US EPA, EU and the EPA of Ghana. Subsequently, the non-banned pesticides, consisting of allethrin, fenpropathrin, L-cyhalothrin, permethrin, cyfluthrin, cypermethrin, deltamethrin, dimethoate, ethropophos, profenofos, pirimiphos-methyl, fonofos, malathion, chlorpyrifos, diazinon, chlorfevinphos, fenvalerate and fenitrothion, were selected based on literature indicating their occurrence in cocoa soils in Ghana (Adu-Acheampong et al., 2014).