



Contamination levels and seasonal variations of pesticides in suspended particles in the Bia, Comoe and Tanoe rivers (Côte d'Ivoire)

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Abstract: The agricultural industry and urban pesticide users are increasingly dependent on pesticides. However, little information is available on the residues of these substances at the mouths of aquatic systems. In Côte d'Ivoire, the agricultural sector has long been a driver of economic growth. In order to evaluate the concentrations of pesticides in watercourses, contamination levels and seasonal variations of pesticides in suspended particles were determined at the mouths of the Bia, Comoe and Tanoe rivers. Forty-five sediment samples from the South-Comoe region were analyzed by high-performance liquid chromatography (HPLC) combined with UV/visible detector. These pesticides are grouped into 8 families including triazines, triazines, phenylureas, organophosphates, carbamates, chloroacetanilides, dicarboximides and crimidine, which are regularly used in this area. Concentrations reached 423 $\mu\text{g.kg}^{-1}$ in Bia, 933.21 $\mu\text{g.kg}^{-1}$ in Comoe and 65 $\mu\text{g.kg}^{-1}$ in the Tanoe. In the rainy season, the levels reached 43.76 $\mu\text{g.kg}^{-1}$ with simazine in Bia, 933.21 $\mu\text{g.kg}^{-1}$ with fenuron in Comoe and 14.36 $\mu\text{g.kg}^{-1}$ with aldicarb in Tanoe. In the flood season, they reached 423 $\mu\text{g.kg}^{-1}$ with monuron in Bia, 611 $\mu\text{g.kg}^{-1}$ with fenuron in Comoe and 65 $\mu\text{g.kg}^{-1}$ with cyanazine in Tanoe. They reached 421 $\mu\text{g.kg}^{-1}$ with metamitron in Bia, 500 $\mu\text{g.kg}^{-1}$ with simazine in Comoe and 65 $\mu\text{g.kg}^{-1}$ with cyanazine in Tanoe in the dry season. In the Bia, cyanazine, desisopropylatrazine and chlorfenvinphos are the only pesticides detected in all seasons. At the Comoe River, cyanazine and fenuron are the only pesticides detected in all seasons. In the Tanoe River, propazine, chlorfenvinphos and parathion-ethyl are the pesticides detected in all seasons.

1. Introduction

Rapid growth in the world's population, particularly in Africa, has led an increasing demand for agricultural products. For reaching this requirement, pesticides are used to control pests (Schiffers, 2012; Li et al., 2006). However, after their application, they affect not only the targets but the entire environment (the atmosphere, soil, groundwater and surface water) through various processes (Nsibande et Forbes, 2016). Several studies on pesticides have been carried out around the world. In view of their capacity to harm the environment and the food chain, much work has been undertaken

on pesticides in several areas of the world, particularly in Europe (Ivanova *et al.*, 2021; Rusina *et al.*, 2019), in Asia (Kafilzadeh, 2015; Yang *et al.*, 2005) and in Africa (N'dohou *et al.*, 2023; Kone *et al.*, 2021; Kassegne *et al.*, 2020; Gnonsonoro *et al.*, 2016; Bazzi *et al.*, 2013; Salghi *et al.*, 2012). Once in the aquatic environment, due to their low solubility in water and high values of the n-octanol/water partition coefficient (K_{ow}), pesticides are adsorbed by sedimentary particles and are deposited at the end in the water bottom of water bodies (Barbieri *et al.*, 2019; Yang *et al.*, 2005). Coming from the deposition of suspended particles in the water body, sediments easily absorb substances in the water body, such as pesticides. As a result, they become a vector for the transfer of toxic components into the aquatic environment (DeMars *et al.*, 2018; Hall *et al.*, 2015; Zoumis *et al.*, 2001). However, such accumulation may be reversible over longer periods and promote the presence of these contaminants in the water column. In fact, Zhou *et al.* (2014) and Liu *et al.* (2016) found that pesticides can be remobilized in the water column due to turbulence and bioturbation (reworking sediments). Also, after reducing emissions relating to runoff from agricultural land, sediments become a source of water pollution, depending on the difference between the level of pollution in the water column and the sediments (Rusina *et al.*, 2019; Roberts, 2012; Zoumis *et al.*, 2001). Thus, they can pose a risk to non-target organisms due to their presence in water, their accumulation in sediments (Ccanccapa *et al.*, 2016; Terrado *et al.*, 2007). Therefore, the determination of pesticides in sedimenting particles gives an indication of the extent of aquatic contamination and the contamination profile which makes it possible to understand the behavior and fate of these chemicals (Kassegne *et al.*, 2020; Hall *et al.*, 2015; Kafilzadeh, 2015). In Côte d'Ivoire, the use of phytosanitary products becomes higher and higher and causes their presence in water bodies (Kone *et al.*, 2021; Soro *et al.*, 2018). The work of Kone *et al.* (2021) highlighted that the waters of the Bia presented a risk for children Which age is comprise between 0 and 11 years old. The waters of the Bia, Comoé and Tanoé rivers are used for consumption and various daily tasks by the local population (Kone *et al.*, 2021). Their work also showed that most pesticides transferred into river systems often reach levels above legal limits for drinking water. The Bia, Comoé and Tanoé rivers are tributaries of the Ebrié and Aby lagoons in Ivory Coast. They therefore represent a source of pollution of these lagoons. In the watershed part of these rivers, Kone *et al.*, (2021) noted the presence of agricultural activities using fertilizers and pesticides. These agricultural activities are therefore potential sources of water contamination by pesticides (Kone *et al.*, 2021; Curchod *et al.*, 2020). This study aims to evaluate the level of contamination of pesticide particles suspended in water at the mouths of the Comoé, Bia and Tanoé rivers. To do this, we determined the pesticide concentrations of suspended particles and studied seasonal variations. This information is essential for a better monitoring policy and the establishment of a database on the sources of contamination of these bodies of water by pesticides.

2. Materiel and methods

2.1 Description of the sampling area

The study area is part of the South Comoe region which is one of the 19 administrative regions of Côte d'Ivoire located in the South-East of the country which covers an area of 800 km². The economy of the South Comoe region is dominated by agriculture. Oil palm plantations occupy 12,000 hectares (ha) and represent 25% of the palm industry's production (Lacina *et al.*, 2012; Zadou, 2011). We also note commercial crops such as cocoa, coffee, rubber, cashew, palm oil, pineapple, banana, mangoes and cotton. In the Ivorian part of the Comoe watershed, there are industrial plantations (banana, palm, pineapple) to the south and cotton fields to the north which require the use of

pesticides. These fields are generally located near surface waters (Lacina *et al.*, 2012). With an average annual flow of 104 m³/s and a basin of 9,650 Km², the Bia River has its source in Chremaso (Ghana) and empties into the Atlantic Ocean through the Aby lagoon. The Comoe River has its source in the Banfora region of Burkina Faso and travels 1,160 km in Ivory Coast and flows into the Ebrie lagoon in Grand-Bassam and into the Gulf of Guinea. It has an average annual flow of approximately 106 m³/s and a catchment area of 82,408 Km² (Kone *et al.*, 2021; Soro *et al.*, 2020). The Tanoé River with a catchment area of 16,000 Km² drains the Ashanti region (Ghana) and flows into the Aby Lagoon (Kone *et al.*, 2021).

Five sampling stations were selected at the estuary of each river to better capture the level of contamination. The stations for Bia are: Bia1, Bia2, Bia3, Bia3, Bia4 and Bia5. Those of Comoe are: Comoé1, Comoé2, Comoé3, Comoé4 and Comoé5. Those of Tanoé are: Tanoé1, Tanoé2, Tanoé3, Tanoé4 et Tanoé5 (Table 1) (Fig. 1)

Table 1: GPS locations of the sampling stations

Sampling stations	GPS coordinates	
Bia1	N 5°21.7414'	O 3°12.5187'
Bia2	N 5°21.7688'	O 3°12.1987'
Bia3	N 5°21.7017'	O 3°12.0387'
Bia4	N 5°21.5612'	O 3°12.0146'
Bia5	N 5°21.2479'	O 3°21.0795'
Comoé1	N 5°13.9591'	O 3°40.3433'
Comoé2	N 5°13.6199'	O 3°40.7452'
Comoé3	N 5°13.5401'	O 3°41.2016'
Comoé4	N 5°13.8516'	O 3°41.7911'
Comoé5	N 5°14.0553'	O 3°42.0220'
Tanoé1	N 5°07.3514'	O 2°55.2943'
Tanoé2	N 5°07.2939'	O 2°55.4551'
Tanoé3	N 5°07.2989'	O 2°55.6141'
Tanoé4	N 5°07.4001'	O 2°55.8485'
Tanoé5	N 5°07.5216'	O 2°56.3401'

2.2 Sampling

Better understand the seasonal variations of associated pesticides, sampling was carried out in May to August (wet season), October (flood season) and December to February (dry season). The sampling sites begin at the edge of the mouth. The cylindrical sediment traps were deployed at five stations (Figure 1) along the mouth, in a less frequented area using the method described by Botwe *et al.* (2017). These traps were immersed at a maximum of 1 m in order to minimize the impact of the water current and to give the settling particles time to settle. The sediment traps were plugged before recovery to keep the trapped materials intact. A total of 45 samples were collected during the study period. After recovery, the trapped sediments were transported, stored in a freezer at -20°C for processing and analysis.

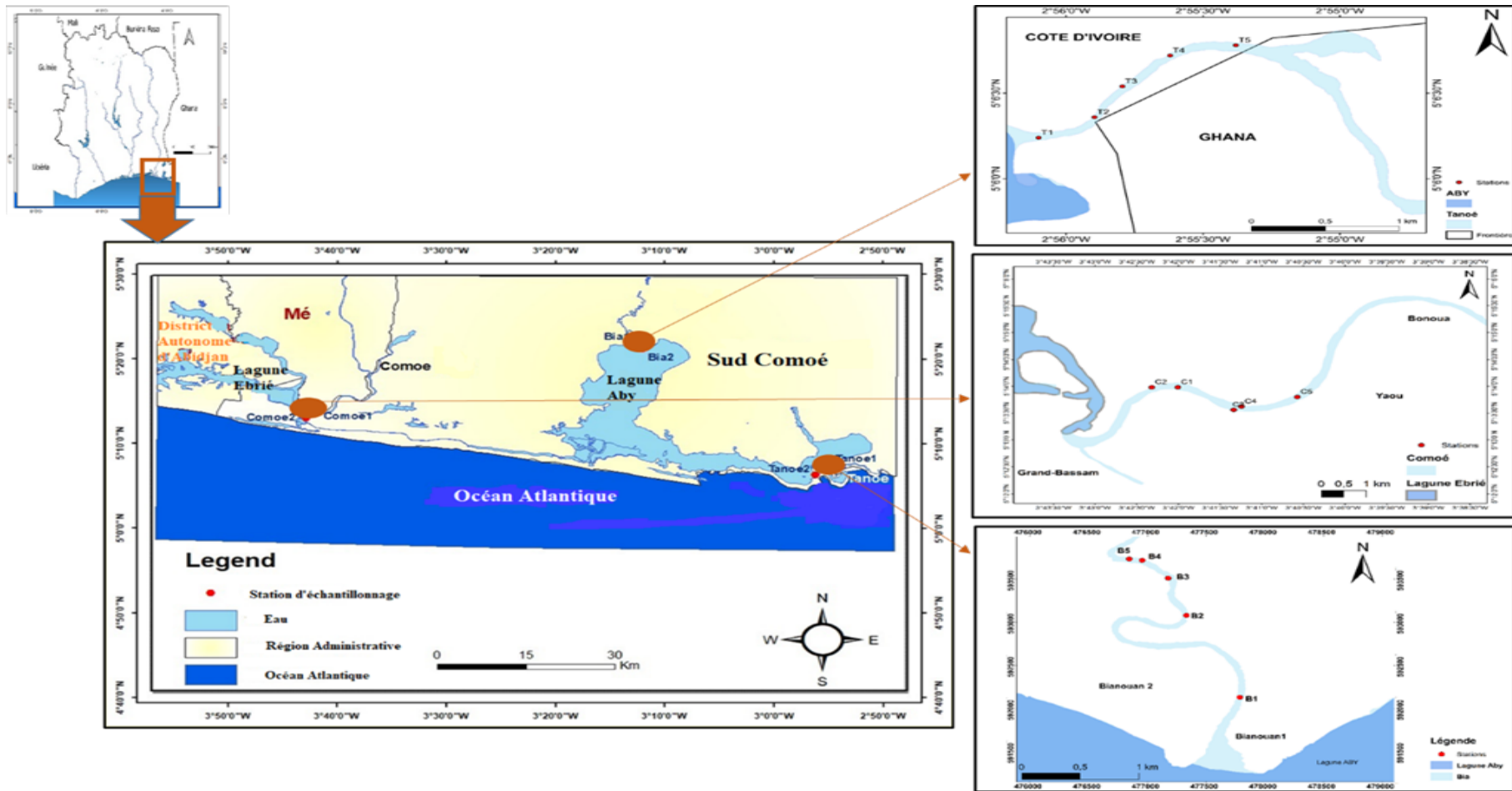


Fig. 1. Location of sampling stations in the Bia, Comoe and Tanoe

2.3 Chemicals and reagents

Analytical grade solvents were used for HPLC extraction and injection. Solid phase extraction (SPE) cartridges (Agilent Bond Elut Mega BE-C18, 2 g 2 ml, 20/pk (Agilent Technologie, USA) were purchased from MAERCK (Morristown NJ, USA). Hexane and methanol were obtained from SCHARLAU. Aldicarb, Atrazine, Buturon, Chlorfenvinphos, Chlorpropham, Chlortoluron, Crimidine, Cyanazine, Desethylatrazine, Desisopropylatrazine, Diuron, Fenuron, Hexazinone, Isoproturon, Linuron, Metamitron, Metazachlor, Methabenzthiazuron, Metobromuron, Metolachlor, Metoxuron, Metribuzine, Monolinuron, Monuron, Parathion-ethyl, Parathion-methyl, Prometryn, Propazine, Simazine, Terbutylazine, Terbutryn, and Vinclozolin. dichloromethane, ethyl acetate, acetone, and acetonitrile were purchased from PROLABO, France.

2.4 Sample extraction

Pesticides in the sediment samples were extracted by solid-liquid extraction (SLE) according to the method described by [Henry and Kishimba \(2003\)](#). First, 10 g of sediment previously freeze-dried, crushed in an agate mortar and filtered were mixed with anhydrous sodium sulfate (Na_2SO_4) (10g) and reduced to a homogeneous powder. The extraction was then carried out successively with 50 mL, then with 3 x 20 mL of a cyclohexane/acetone mixture (1:1 v/v) by mechanical stirring for approximately 5 minutes and by ultrasonic bath for 5 minutes. Finally, the extract is filtered through glass wool containing approximately 15 g of anhydrous sodium sulfate in order to eliminate all traces of water and transferred to a separating funnel. The flask containing the extract is rinsed with 5 mL of the cyclohexane/acetone mixture (1:1 v/v), the rinsing extract is filtered through glass wool containing anhydrous sodium sulfate and added to the filtrate in the separating funnel. 200 mL of saturated sodium chloride are then mixed with the filtrate from the separatory funnel. The organic phase containing the pesticides is extracted with 50 mL of a dichloromethane: cyclohexane mixture (15:85 v: v) and filtered through glass wool containing approximately 5 g of anhydrous sodium sulfate. The extract is then concentrated in a rotary evaporator equipped with a water bath at a temperature of around 50°C and the solvent changed to cyclohexane. The volume of cyclohexane is adjusted to approximately 2 mL with ethyl acetate at a 1:1 (v/v) ratio. The extract concentrated to 2 mL on the rotary evaporator (Buchi) is fractionated on the SPE cartridge. The appropriate fraction, containing the pesticides, is evaporated and dissolved in a cyclohexane: acetone mixture (9:1 v/v) of approximately 2 mL and introduced into a vial for HPLC analysis ([Henry and Kishimba, 2003](#)).

2.5 Chemical and Statistical analysis

A SHIMADZU model LC-20AT type HPLC equipped with a DGU-20A5 degasser, a SHIMADZU model SPD-20A UV/Visible detector and a SIL-20A injector model was used to carry out the analyses. The separation was carried out on a VP-ODS type analytical column, 154 mm in length and 4.6 mm in internal diameter with a pre-guard column of 10 x 4.6 mm. The mobile phase used consists of a mixture of ultra-pure water (E) and acetonitrile (A) (acetonitrile/water 20/80) at a flow rate of 1 mL/min. The column temperature was 40°C. The injections were performed automatically with a volume of 20 μL .

All statistical tests used to process data (minimum concentration, maximum concentration and average) were made using Microsoft Excel 2016.

2.6 Limits of detection (LOD) and limits of quantification (LOQ)

The different values of limits of detection and limits of quantification are presented in **Table 2**.

Table.2 Limits of detection, and limits of quantification of the pesticides

Pesticides family	LOD ($\mu\text{g}/\text{kg}$)	LOQ ($\mu\text{g}/\text{kg}$)
Substituted ureas	0.006	0.018
Triazines	0.008	0.025
Triazinone and crimidine	0.1	0.350
Carbamates	0.006	0.018
Organophosphates	0.004	0.01
chloro acétanilide	0.003	0.009

3. Results and Discussion

3.1 Evaluation of pesticide levels

The concentrations of these pesticides in the settling particles are given in **Tables 3, 4 and 5** respectively for the Bia, Comoe and Tanoe rivers. Among all these 32 pesticides searched for in our samples nine (9) pesticides (chlorpropham, crimidine, diuron, fenuron, methabenzthiazuron, metolachlor, metoxuron, metribuzin, terbuthylazine) were not detected in the Bia River (**Table 3**). Nine (9) pesticides were not detected in the Comoe River (**Table 4**). These pesticides are atrazine, chlorpropham, chlortoluron, crimidine, hexazinone, methabenzthiazuron, metoxuron, metribuzin, monolinuron. In the Tanoe River, thirteen (13) were not detected (**Table 5**) including buturon, chlorfenvinphos, diuron, hexazinone, isoproturon, linuron, methabenzthiazuron, metobromuron, metolachlor, metoxuron, metribuzin, terbuthylazine, crimidine. The pesticide concentrations obtained in our study varied from $0.023 \mu\text{g}\cdot\text{kg}^{-1}$ (vinclozolin) to $423 \mu\text{g}\cdot\text{kg}^{-1}$ (monuron) in the Bia River. They varied from $0.023 \mu\text{g}\cdot\text{kg}^{-1}$ (linuron) to $933.21 \mu\text{g}\cdot\text{kg}^{-1}$ (fénuuron) in Comoe and $0.043 \mu\text{g}\cdot\text{kg}^{-1}$ (prométryn, triazine) to $65 \mu\text{g}\cdot\text{kg}^{-1}$ (cyanazine) in the Tanoe River. Overall, among the three rivers, the pesticides vinclozolin and linuron have presented the lowest quantifiable levels of $0.023 \mu\text{g}\cdot\text{kg}^{-1}$ in Bia and Comoe while the pesticide fenuron gave the highest concentration of $933.21 \mu\text{g}\cdot\text{kg}^{-1}$ in the Comoe river. The pesticides aldicarb, chlorfenvinphos, cyanazine, desethylatrazine, desisopropylatrazine, metamitron, metazachlor, monuron, parathion-ethyl, parathion-methyl, prometryn, propazine, simazine, terbutryn, vinclozolin detected in these three rivers suggest a possible use of pesticides in agriculture along these waters. After treatment of agricultural surfaces, pesticides can be adsorbed on soil particles. Thus, the entrainment of these particles by runoff during rainy events leads in the presence of these pesticides in the particulate phase of the water. According to [Hall et al. \(2015\)](#), the transport of sediments in watercourses is associated with the transport of contaminants.

3.2 Seasonal variation of pesticides

Seasonal variations are presented in **Table 3, 4 and 5**. These tables show differences in pesticide concentrations during different seasons. During the rainy season, 16 pesticides were detected in the Bia River, 17 in the Comoe River and 13 in the Tanoe. In flood season, 14 pesticides were found in the Bia River, 8 pesticides in the Comoe River and 8 pesticides in the Tanoe River.

Table 3. Concentrations ($\mu\text{g.kg}^{-1}$) of pesticides measured in particles sedimenting in the Bia River

PESTICIDES	Chemical family	Rainy Season			Flood Season			Dry Season		
		Minimum	Maximum	Moyenne	Minimum	Maximum	Moyenne	Minimum	Maximum	Moyenne
HERBICIDES										
Atrazine	Triazines	0.23	2.22	1.225	<0.008	0.45	0.45	nd	nd	nd
Buturon	Substituted ureas	nd	nd	nd	<0.006	2.3	2.3	nd	nd	nd
Chlorpropham	Carbamates	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlortoluron	Substituted ureas	<0.006	0.865	0.865	nd	nd	nd	nd	nd	nd
Cyanazine	Triazines	<0.008	1.68	1.68	<0.008	0.93	0.93	<0.006	41.2	41.2
Desethylatrazine	Triazines	nd	nd	nd	3.78	3.78	3.78	nd	nd	nd
Desisopropylatrazine	Triazines	<0.008	19.91	19.91	2.6	4	3.3	3	5	4
Diuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fenuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Hexazinone	Triazinones	nd	nd	nd	nd	nd	nd	<0.1	2.1	2.1
Isoproturon	Substituted ureas	nd	nd	nd	<0.006	0.21	0.21	nd	nd	nd
Linuron	Substituted ureas	<0.006	0.88	0.88	nd	nd	nd	nd	nd	nd
Metamitron	Triazinones	<0.1	0.6	0.6	nd	nd	nd	3	421	149
Metazachlor	Chloroacetanilides	0.39	7.9	3.111	nd	nd	nd	nd	nd	nd
Methabenzthiazuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metobromuron	Substituted ureas	nd	nd	nd	nd	nd	nd	<0.006	7.2	7.2
Metolachlor	Chloroacetanilides	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metoxuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metribuzine	Triazinones	nd	nd	nd	nd	nd	nd	nd	nd	nd
Monolinuron	Substituted ureas	<0.006	0.49	0.49	nd	nd	nd	2	20	11
Monuron	Substituted ureas	nd	nd	nd	<0.006	423	423	4.2	42	23.1
Prometryn	Triazines	<0.008	0.043	0.043	<0.008	0.31	0.31	nd	nd	nd
Propazine	Triazines	<0.008	0.64	0.64	0.83	2.09	1.46	nd	nd	nd
Simazine	Triazines	1.041	43.76	16.327	1.37	4.91	3.14	nd	nd	nd
Terbuthylazine	Triazines	nd	nd	nd	nd	nd	nd	nd	nd	nd
Terbutryne	Triazines	<0.008	0.39	0.39	<0.008	0.42	0.42	nd	nd	nd
INSECTICIDES										
Aldicarb	Carbamates	nd	nd	nd	nd	nd	nd	2	2.1	2.05
Chlorfenvinphos	Organophosphates	0.78	0.79	0.785	<0.004	0.79	0.79	<0.004	2.2	2.2
Parathion-ethyl	Organophosphates	0.28	1.3	0.874	0.86	1.28	1.07	nd	nd	nd
Parathion-methyl	Organophosphates	<0.004	2.04	2.04	nd	nd	nd	nd	nd	nd
FUNGICIDES										
Vinclozolin	Dicarboximides	0.023	0.46	0.258	<0.01	0.43	0.43	nd	nd	nd
RODENTICIDES										
Crimidine	Pyrimidines	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table.4 Concentrations ($\mu\text{g.kg}^{-1}$) of pesticides measured in particles sedimenting in the Comoe River

PESTICIDES	Chemical family	Rainy Season			Flood Season			Dry Season		
		Minimum	Maximum	average	Minimum	Maximum	average	Minimum	Maximum	average
HERBICIDES										
Atrazine	Triazines	nd	nd	nd	nd	nd	nd	nd	nd	nd
Buturon	Substituted ureas	nd	nd	nd	nd	nd	nd	<0.006	2.4	2.4
Chlorpropham	Carbamates	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlortoluron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cyanazine	Triazines	1.094	25.1	9.378	12.1	28	20.05	<0.008	19	19
Desethylatrazine	Triazines	<0.008	2.043	2.043	nd	nd	nd	nd	nd	nd
Desisopropylatrazine	Triazines	nd	nd	nd	2,5	10	6,25	<0.008	6	6
Diuron	Substituted ureas	nd	nd	nd	<0,006	4	4	2.9	3	2.95
Fenuron	Substituted ureas	<0.006	933.21	933.21	<0.006	611	611	<0.006	61.2	61.2
Hexazinone	Triazinones	nd	nd	nd	nd	nd	nd	nd	nd	nd
Isoproturon	Substituted ureas	<0.006	16.4	16.4	nd	nd	nd	nd	nd	nd
Linuron	Substituted ureas	<0.006	0.023	0.023	nd	nd	nd	nd	nd	nd
Metamitron	Triazinones	<0.1	26.4	26.4	nd	nd	nd	<0.01	28	28
Metazachlor	Chloroacetanilides	0.042	0.975	0.5085	nd	nd	nd	nd	nd	nd
Methabenzthiazuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metobromuron	Substituted ureas	<0.006	0.965	0.965	<0.006	3	3	nd	nd	nd
Metolachlor	Chloroacetanilides	<0.003	1.453	1.453	nd	nd	nd	<0.003	3	3
Metoxuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metribuzine	Triazinones	nd	nd	nd	nd	nd	nd	nd	nd	nd
Monolinuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Monuron	Substituted ureas	nd	nd	nd	8	24	16	3	34	18.5
Prometryn	Triazines	<0.008	0.26	0.26	nd	nd	nd	nd	nd	nd
Propazine	Triazines	<0.008	0.6	0.6	nd	nd	nd	<0.008	12.1	12.1
Simazine	Triazines	nd	nd	nd	<0.008	5.6	5.6	<0.008	500	500
Terbuthylazine	Triazines	<0.008	0.65	0.65	nd	nd	nd	nd	nd	nd
Terbutryne	Triazines	<0.008	1.042	1.042	nd	nd	nd	nd	nd	nd
INSECTICIDES										
Aldicarb	Carbamates	<0.006	15.26	15.26	nd	nd	nd	<0.006	3.1	3.1
Chlorfenvinphos	Organophosphates	<0.004	1.024	1.024	nd	nd	nd	nd	nd	nd
Parathion-ethyl	Organophosphates	0.345	0.742	0.544	nd	nd	nd	nd	nd	nd
Parathion-methyl	Organophosphates	nd	nd	nd	<0.004	7	7	<0.004	4	4
FUNGICIDES										
Vinclozolin	Dicarboximides	0.432	2.106	1.113	nd	nd	nd	nd	nd	nd
RODENTICIDES										
Crimidine	Pyrimidines	nd	Nd	nd	nd	nd	nd	nd	nd	nd

Table.5 Concentrations ($\mu\text{g.kg}^{-1}$) of pesticides measured in particles sedimenting in the Tanoé River

PESTICIDES	Chemical family	Rainy Season			Flood Season			Dry Season		
		Minimum	Maximum	average	Minimum	Maximum	average	Minimum	Maximum	average
HERBICIDES										
Atrazine	Triazines	<0.008	0.502	0.502	nd	nd	nd	nd	nd	nd
Buturon	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpropham	Carbamates	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlortoluron	Substituted ureas	<0.006	0.705	0.705	nd	nd	nd	nd	nd	nd
Cyanazine	Triazines	nd	nd	nd	<0.008	65	65	4.3	42	23.15
Desethylatrazine	Triazines	nd	nd	nd	3	10.2	6.6	nd	nd	nd
Desisopropylatrazine	Triazines	nd	nd	nd	nd	nd	nd	0.3	0.3	0.3
Diuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fenuron	Substituted ureas	<0.006	8.951	8.951	nd	nd	nd	nd	nd	nd
Hexazinone	Triazinones	nd	nd	nd	nd	nd	nd	nd	nd	nd
Isoproturon	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Linuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Métamitron	Triazinones	nd	nd	nd	34	53.4	43.7	31	31	31
Metazachlor	Chloroacetanilides	0.842	0.842	0.842	nd	nd	nd	nd	nd	nd
Methabenzthiazuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metobromuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metolachlor	Chloroacetanilides	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metoxuron	Substituted ureas	nd	nd	nd	nd	nd	nd	nd	nd	nd
Metribuzine	Triazinones	nd	nd	nd	nd	nd	nd	nd	nd	nd
Monolinuron	Substituted ureas	nd	nd	nd	1.2	1.3	1.25	<0.006	2.4	2.4
Monuron	Substituted ureas	nd	nd	nd	2	3.2	2.4	<0.006	1.9	1.9
Prométryn	Triazines	0.043	0.402	0.223	nd	nd	nd	nd	nd	nd
Propazine	Triazines	0.5	0.95	0.725	3.1	42	19.133	3.1	29.1	16.1
Simazine	Triazines	1.03	2.09	1.56	nd	nd	nd	nd	nd	nd
Terbuthylazine	Triazines	nd	nd	nd	nd	nd	nd	nd	nd	nd
Terbutryne	Triazines	<0.008	0.987	0.987	nd	nd	nd	nd	nd	nd
INSECTICIDES										
Aldicarb	Carbamates	<0.006	14.36	14.36	nd	nd	nd	<0.006	2.8	2.8
Chlorfenvinphos	Organophosphates	<0.004	0.956	0.956	<0.004	20	20	1	20.1	10.55
Parathion-ethyl	Organophosphates	0.294	0.965	0.620	<0.004	22	22	1.2	29	15.1
Parathion-methyl	Organophosphates	1.33	1.33	1.33	nd	nd	nd	nd	nd	nd
FUNGICIDES										
Vinclozolin	Dicarboximides	0.063	0.66	0.348	nd	nd	nd	nd	nd	nd
RODENTICIDES										
Crimidine	Pyrimidines	nd	nd	nd	nd	nd	nd	nd	nd	nd

During the dry season, 9 pesticides were detected in the Bia River, 12 pesticides in the Comoe River and 9 pesticides in the Tanoe River. These results show that the presence of pesticides in these rivers is linked to the seasons. The large number of different pesticides detected in settling particles during the rainy season can be explained by the contribution of these particles by runoff from the first rains. Pesticide concentrations in sediments can be affected seasonally due to variable precipitation. This precipitation can transport pesticide-containing materials to the downstream area (Nguyen et al., 2019). This precipitation can also wash weakly adsorbed pesticides from the particles, thereby reducing their presence on these particles. This fact could explain the low number obtained after the rainy season. In the rainy season, the water current is stronger than in the dry season. This intensity of the water current during the rainy season further favors the transport of pesticides to the lower reaches and causes an increase in their concentration in the rainy season compared to the dry season (Md Pauzi et al., 2015; Barasa et al., 2007).

These results show the relationships between flow and transport of pesticides associated with suspended sediments. In the sedimenting particles of the Bia River, cyanazine, desisopropylatrazine and chlorfenvinphos are the only pesticides detected in all seasons (rainy season, flood season and dry season) (Table 3) with the seasonal average concentrations of 1.68; 0.93 and 41.2 $\mu\text{g.kg}^{-1}$ for cyanazine; 19.91; 3.3 and 4 $\mu\text{g.kg}^{-1}$ for désisopropylatrazine, and 0.785; 0.79 and 2.2 $\mu\text{g.kg}^{-1}$ for chlorfenvinphos. At the Comoe River, cyanazine and fenuron are the only pesticides detected in all seasons (Table 4) with the seasonal average concentrations of 9.378 $\mu\text{g.kg}^{-1}$; 20.05 $\mu\text{g.kg}^{-1}$ et 19 $\mu\text{g.kg}^{-1}$ for cyanazine and 933.21 $\mu\text{g.kg}^{-1}$; 611 $\mu\text{g.kg}^{-1}$ and 61.2 $\mu\text{g.kg}^{-1}$ for fénuron. In the Tanoe River, propazine, chlorfenvinphos and parathion-ethyl are the pesticides detected in all seasons (Table 5) with the seasonal average concentrations of 0.725 $\mu\text{g.kg}^{-1}$; 19.133 $\mu\text{g.kg}^{-1}$; 16.1 $\mu\text{g.kg}^{-1}$ for propazine, 0.956 $\mu\text{g.kg}^{-1}$; 20 $\mu\text{g.kg}^{-1}$; 10.55 $\mu\text{g.kg}^{-1}$ for chlorfenvinphos and 0.620 $\mu\text{g.kg}^{-1}$; 22 $\mu\text{g.kg}^{-1}$; 15.1 $\mu\text{g.kg}^{-1}$ for parathion-éthyl. These results show that the presence of pesticides in settling particles depends on the seasons and the characteristics of each contaminant. El Azzi et al. (2016) showed that pesticides with low solubility were mainly transported via surface runoff where suspended matter is concentrated.

Conclusion

This study showed that pesticides accumulate on suspended particles. Over all three seasons, 23 different pesticides were detected in the Bia River, 23 in the Comoe River and 19 in the Tanoe River. The pesticides vinclozolin and linuron presented the lowest concentration 0.023 $\mu\text{g.kg}^{-1}$ in Bia and Comoe while the pesticide fenuron presented the highest concentration value 933.21 $\mu\text{g.kg}^{-1}$ in Comoe. The seasonal comparison showed that these molecules were more present in the rainy season and less in the dry season. In the Bia River, the highest content was recorded in the rainy season with simazine (43.76 $\mu\text{g.kg}^{-1}$). In the Comoe River, it was obtained with fenuron (933.21 $\mu\text{g.kg}^{-1}$) in the rainy season and in the Tanoe River in the flood season with metamitron (53.4 $\mu\text{g.kg}^{-1}$). These results showed that the presence of pesticides in settling particles is linked to the seasons. The large number of pesticide molecules in the settling particles was detected in the rainy season due to the entrainment of these particles by runoff water from the first rains, the intensity and volume runoff. Our results provide comprehensive information on the level of sediment contamination by pesticides at the mouths of the Bia, Comoe and Tanoe rivers. They could contribute to strengthening the policy put in place within the framework of water protection and the ban on certain pesticides.

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