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Water and Sediments Contamination by Pesticides in Sassandra River at Guessabo Area (Central-Western of Ivory Coast)

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ABSTRACT

Background and Objective: Agriculture is very often practiced in rural areas and uses pesticides to improve yields. The aquatic environment is thus regularly exposed to pesticides from agricultural activity. This study aimed to assess the contamination of water and sediments of the Sassandra River by pesticides in the Guessabo area. **Materials and Methods:** Water and sediment samples were taken from Guessabo Lake during the rainy season at ten stations. These samples were analyzed for some pesticide actives ingredients as well as the physicochemical parameters of water. **Results:** The temperature and pH of the water are almost constant. The average values of temperature, dissolved oxygen, pH, conductivity and transparency were 26.82°C, 4.97 mg L^{-1}, 6.82, 93.84 μS cm^{-1} and 0.95 m, respectively. It was found that the water and sediments are contaminated by pesticides. The results showed that the mean values in water were 0.0052, 0.0055, 0.635, 0.0129 and 0.0109 μg L^{-1} for Imidacloprid, Deltamethrin, Lambda-Cyhalothrin, Cypermethrin and Acetamiprid, respectively. These pesticides were found at higher concentrations in sediments than in water. The mean values in sediment were 0.01910, 0.1139, 3.8543, 0.0044 and 1.0626 mg kg^{-1} for Imidacloprid, Deltamethrin, Lambda-cyhalothrin, Cypermethrin and Acetamiprid, respectively. Lambda-Cyhalothrin was also found to be the most dominant substance in water and sediment. **Conclusion:** The Sassandra River was therefore mainly contaminated by pyrethroids. This presence of pyrethroids was due to the important agricultural activities that take place along the river. The organisms of this aquatic ecosystem are then exposed to the toxicity of these compounds.

KEYWORDS

Pesticides, pollution, surface waters, sediments, Sassandra River, Guessabo Lake

INTRODUCTION

In the quest for food self-sufficiency and sustainable development, humanity has put in place plant protection systems. Thus, for several decades most modern methods of crop protection have been based on the use of phytosanitary products. This has encouraged the significant use of pesticides to increase agricultural production[1,2]. Pesticides are widely used in most sectors of agricultural production to prevent or reduce losses by pests and thus can improve yield as well as the quality of the products, even in terms

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of cosmetic appeal, which is often important to consumers[3,4]. There are also many other kinds of benefits that may be attributed to pesticides, but these benefits often go unnoticed by the general public[5,6]. Because of their popularity and extensive use, pesticides have serious concerns about health risks arising from the exposure of farmers when mixing and applying pesticides[4,7]. According to these authors, pesticide residues can be found in food and drinking water. They also represent real dangers in terms of their toxicity for users and consumers of agricultural products[8,9] as well as for the pollution of the environment and particularly of surface waters and soils[10,11]. In developing countries, farmers face great risks of exposure due to the use of toxic chemicals that are banned or restricted in other countries, incorrect application techniques, poorly maintained or inappropriate spraying equipment, inadequate storage practices and often the reuse of old pesticide containers for food and water storage[12,13]. The effects of pesticides are well documented and constitute a major problem that raises many questions at the national, regional and global levels. In Côte d'Ivoire, diagnoses carried out by doctors from the University Hospital Center of Yopougon (Abidjan) revealed the presence of clinical signs due to exposure to phytosanitary products[14]. In addition, many watersheds of rivers in Côte d'Ivoire are used by the population for cash crops and food crops. The watershed of Sassandra River is a heavily agricultural area that is intensely used for these agricultural activities. Indeed, in Guessabo, around the Sassandra River, several agricultural activities are carried out because of the presence of water all year round[15]. Pesticides are used at all stages of carrying out these agricultural works. Our study aimed to assess the contamination of water and sediments of the Sassandra River by pesticides in the Guessabo area.

MATERIALS AND METHODS

Study area: Guessabo Lake is located between 6°57' and 7°2' and 5°30' North Latitude and between 6°45' and 6°46' West Longitude. This permanent watercourse is located upstream of the dam of Buyo built on the Sassandra River in Central-Western of Ivory Coast. The depth of this Lake varies from 0.5 to 20 m. It undergoes the successive influence of the pluviometric regimes of the tropical transition climate and the equatorial transition climate. The region enjoys a humid tropical climate with a dry season and a rainy season. The shores of the lake are lined with cocoa plantations, rubber trees, forests and livestock farms. Medium-fertility ferritic soils are favorable for the development of agriculture in this zone. This regional advantage makes forests prone to human aggression during the dry season due to extensive agricultural practices. The rural population of this locality is estimated at 36302 inhabitants. Sampling was carried out from April, 2021 to October, 2021 during the rainy season.

Sampling: The sampling stations were chosen according to their specificities due to the surrounding anthropogenic influences (proximity of agricultural activities, fishing places) and their accessibility. The water and sediment samples were taken during the rainy season at ten (10) stations numbered S1, S2, S3, S4, S5, S6, S7, S8, S9 and S10.

The water samples were collected using a Niskin Hydrological bottle. The water collected is transferred to 1 L bottle and then stored at -4°C to be transported as soon as possible to the laboratory for analysis. The sediment samples were collected using a stainless steel Van Veen grab. These samples were placed directly in a glass container. They are then kept at low temperatures (4°C) before being transported to the laboratory. During sampling, temperature, pH, dissolved oxygen and conductivity were measured using a multi-parameter. The transparency of the water was also measured using the Secchi disk.

Sample preparation and extraction: Before extraction, the samples were filtered under a vacuum through filter paper to remove the particles. Each sample was returned to its original sampling container. The principle of SPE (Sample preparation and extraction) is to allow a volume of 10 mL of sample to pass through a plastic cartridge containing octadecyl (C18). Before use, the cartridges were preconditioned with

4 mL of methanol and then 4 mL of distilled water. The water samples were loaded onto the cartridges at a rate of 5 mL min^{-1}. After sample percolating, the cartridges were aerated by pumping air and the retained solutes were eluted with 5 mL of ethyl acetate:methanol mixture followed by 4 mL of hexane, leaving to soak for 30 min. The combined eluate was evaporated to dryness and the residue was dissolved in 100 µL of ethyl acetate. Once the extraction process is complete, the next step is the analysis consisting of the separation, identification and determination of the isolated substances. In the case of the pesticides in this study, the technique used is that of gas chromatography (GC) coupled with mass spectrometry.

For the analysis of sediment, the sample was dried below 60°C using an Oven. Ten milliliters hexane and 10 mL acetone were added into 4 g of sample crushed and allowed to mix using a microwave digester (UV) for about 45 min. The samples were stored at +4°C and extraction was performed within 48 hrs.

Sample analysis: For the analysis of the molecules in this study, it was coupled with several types of detectors such as the NPD detector and the LC-20AT HPLC mass spectrometer SHIMADZU made in Japan. The apparatus used is a Varian® 431-GC chromatograph equipped with an automatic sample changer coupled to a Varian® 210-MS mass spectrometer operating with a charge-trapping analyzer. A mass spectrometer was used in full scan mode. The whole is controlled by a computer equipped with software allowing the acquisition and exploitation of the data. A sample volume of 2 µL is injected using the autosampler to obtain a good reproducibility of the injection. The pesticides were identified by comparing the retention times obtained by analyzing a standard mixed working solution at 500 ppb and by interrogating the software's mass spectra library. The pesticide contents contained in the samples are calculated by comparing the areas of the peaks of the products in the sample with the areas obtained with standard solutions of known concentrations.

Statistical analysis: In this study, the Kruskal-Wallis test was performed to test the variability of pesticide concentrations at stations. If this test showed a significant difference, the differences were then located by the Mann-Whitney. Differences were considered statistically at $p<0.05$. Finally, the spatial variation of the pesticides was represented by boxplots which present the extreme values, the mean values and the standard deviations. All statistical analyses were performed with STATISTICA 7.1 software.

RESULTS

A summary of mean, maximum and minimum values of temperature, dissolved oxygen, pH, conductivity and transparency are shown in Table 1. The temperature and the pH of the water are almost constant. The mean values are 26.75°C for temperature and 6.76 for pH. The pH of water is slightly acidic. The dissolved oxygen concentrations also vary little in the medium with a mean value of 4.97 mg L^{-1}. Conductivity values are between 75 and 125 µS cm^{-1}. The water studied is not very transparent. The mean value of transparency is 0.95 m.

The concentrations of pesticides in water are presented in Table 2. The concentrations of Imidacloprid in water are between 0.0024 and 0.0116 µg L^{-1} with a mean value of 0.0052 µg L. This molecule could not be detected at station S6, its value at this station being below the detection limit measuring equipment. Concerning Deltamethrin, the levels in the water vary from 0.0023 to 0.0380 µg L^{-1}. The mean value is 0.0055 µg L^{-1}. The concentrations of Lambda-Cyhalothrin and Cypermethrin are between 0.0303 and 2.7330 µg L^{-1} and between 0.0002 and 0.1213 µg L^{-1} for Lambda-Cyhalothrin and Cypermethrin, respectively. It is important to note that Cypermethrin was not detected at four stations (S5, S6, S7 and S8). In contrast, Acetamiprid, Deltamethrin and Lambda-Cyhalothrin were detected at all stations. The mean value for Acetamiprid is 0.0109 µg L^{-1}.

Table 1: Some physicochemical characteristics of Sassandra River

	Maximum	Minimum	Mean value
Temperature (°C)	28.30	25.30	26.75
Dissolved oxygen (mg L^{-1})	7.74	4.05	5.17
pH	7.15	6.30	6.76
Conductivity (µS cm^{-1})	125.00	75.00	93.84
Transparency (m)	1.10	0.80	0.95

Table 2: Concentrations of pesticides in water (µg L^{-1})

Stations	Imidacloprid	Deltamethrin	Lambda-cyhalothrin	Cypermethrin	Acetamiprid
S1	0.0116	0.0380	2.7330	0.007	0.112
S2	0.0024	0.0112	0.0303	0.1213	0.01
S3	0.0074	0.0039	0.0781	0.0005	0.0121
S4	0.0073	0.0104	0.0576	0.0052	0.0113
S5	0.0063	0.0094	0.0579	nd	0.0105
S6	nd	0.0046	0.08	nd	0.0116
S7	0.0071	0.0019	0.0667	nd	0.0103
S8	0.0062	0.0025	0.0617	nd	0.0115
S9	0.062	0.0023	0.0743	0.0007	0.0113
S10	0.0041	0.0056	0.0474	0.0002	0.0097
Mean values	0.0052±0.0028	0.0055±0.0035	0.635±0.0161	0.0129±0.0383	0.0109±0.0008

nd: No detected

Table 3: Concentrations of pesticides in sediments (mg kg^{-1})

Stations	Imidacloprid	Deltamethrin	Lambda-cyhalothrin	Cypermethrin	Acetamiprid
S1	0.0116	0.0380	2.7330	nd	0.3296
S2	0.332	0.0166	3.1876	nd	0.5347
S3	0.1913	0.0318	1.4289	nd	0.4940
S4	0.1832	0.0278	5.0346	nd	1.2862
S5	0.0817	0.0987	4.7223	nd	0.2795
S6	nd	0.074	0.8520	0.0108	0.3756
S7	0.0641	0.1242	1.7243	0.0117	0.8109
S8	0.005	0.1892	3.0291	0.0079	0.6044
S9	0.8336	0.3698	9.4781	nd	5.3109
S10	0.0628	0.1652	6.3592	0.0133	0.0600
Mean values	0.01910±0.243	0.1139±0.1079	3.8549±2.6218	0.0044±0.0058	1.0626±1.5206

nd: No detected

The comparison of the concentrations of pesticides showed that the content of Lambda-Cyhalothrin is highest in water. There is a significant difference ($p<0.05$) between the concentration of Lambda-Cyhalothrin and that of other substances shown in Fig. 1. The concentration of Lambda-Cyhalothrin in water is more than 10 times higher than that of Acetamiprid, Cypermethrin, Deltamethrin and Imidacloprid concentrations, respectively.

The results of the analyses of pesticides in sediments of the study area was given in Table 3. The results revealed that the Imidacloprid concentrations vary from 0.005 to 0.8336 mg kg^{-1} at stations S8 and S9, respectively with an average value of 0.1910 mg kg^{-1}. Lambda-Cyhalothrin has the highest concentrations in both sediment and water. Its mean value in sediments is 3.8549 mg kg^{-1}. In the case of Cypermethrin, the concentrations are between 0.0079 and 0.0133 mg kg^{-1}. The average value is 0.0040 mg kg^{-1}. Moreover, Cypermethrin was only detected on four stations among the ten stations sampled. For Acetamiprid, the highest and lowest concentrations are 5.3109 and 0.2795 mg kg^{-1}, respectively. The average value is 1.0626 mg kg^{-1}.

Lambda-Cyhalothrin has the highest concentration in sediment, followed by Acetamiprid. As in water, the comparison of the different concentrations shows a significant difference ($p<0.05$) between the concentration of Lambda-Cyhalothrin and that of the other substances was shown in Fig. 2. The concentration of Lambda-Cyhalothrin in sediments is more than 3 times higher than that of Acetamiprid concentration which is also more than 10 times higher than the other three substances.

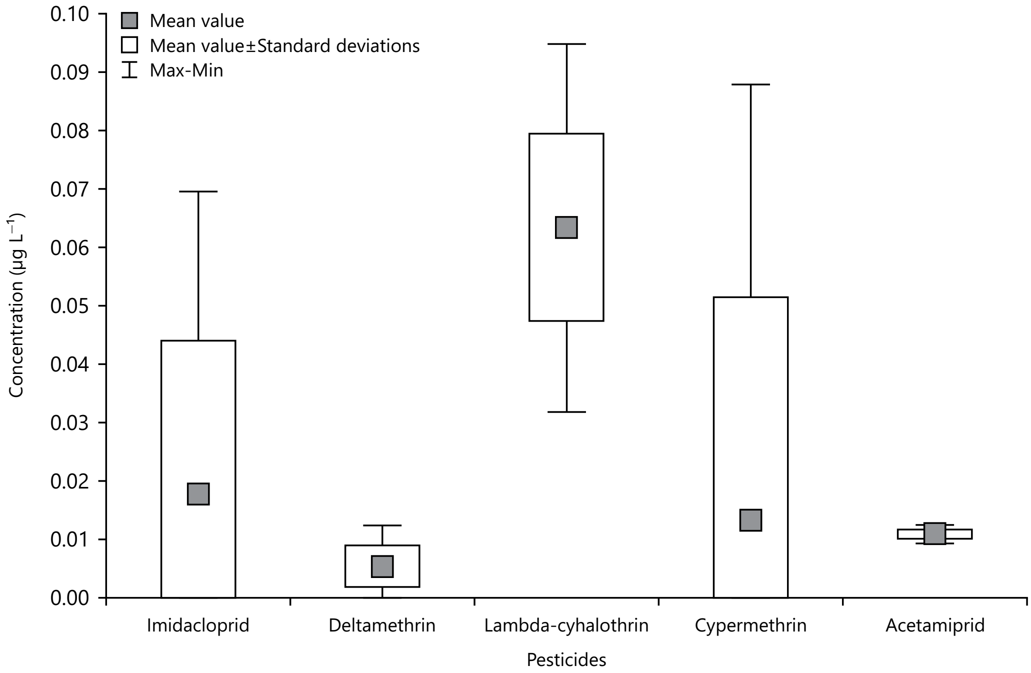

Fig. 1: Comparison of pesticides concentrations in water

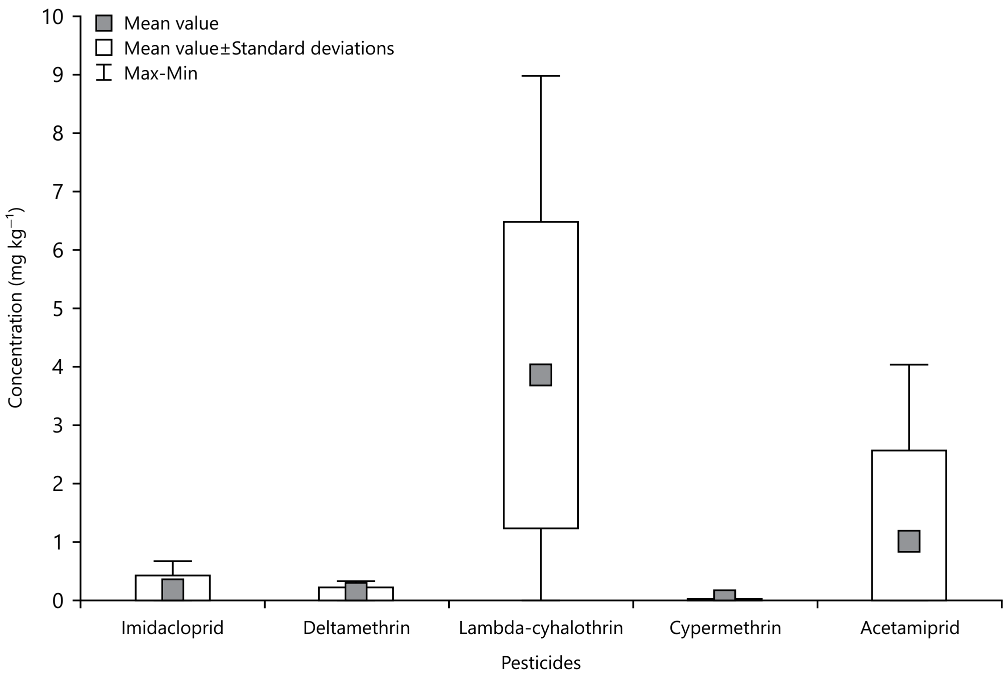

Fig. 2: Comparison of pesticide concentrations in sediments

DISCUSSION

The study of waters and sediments of the Sassandra River contamination by pesticides in the area of Guessabo required the determination of some physicochemical parameters before pesticides. The results show that the spatial distribution of the values of temperature, pH, dissolved oxygen, conductivity and transparency of the medium do not vary significantly from one station to another. The lowest temperature is 25.31°C and the highest value is 28.80°C. These results are under WHO standards for surface water quality. These values are similar to those obtained by N'dri *et al.*[16], who carried out studies on the physicochemical characterization of the Sassandra River. The average value of pH is 6.82, reflecting a slight acidity of the water. This value of pH obtained in the Sassandra River was within the range of the WHO standard ($6.5<pH<8.5$) for animal life in the aquatic environment. In contrast, the Sassandra River is weakly mineralized. The average conductivity of 93.84 µS cm^{-1} of the water is low reflecting a very low dissolution of minerals in the watershed[17]. For dissolved oxygen, the values vary from 4.05 to 6 mg L^{-1} against 5 to 8 mg L^{-1} as recommended by the WHO. The results obtained showed that the waters of the river are deficient in dissolved oxygen. These low dissolved oxygen levels could be linked to the significant inputs of organic matter from domestic waste, as reported by Hamid *et al.*[15] in studies on the Ebrie Lagoon. Transparency is an important visual descriptor of the body of water. The average transparency value is 0.95 m. The low values of transparency obtained also reflect the presence of undissolved materials in the medium. Our results were similar to those obtained in Lake Buyo where low transparency values were attributed to domestic wastewater inputs[17].

Quantification of some pesticides in water and sediment has shown the presence of Imidacloprid, Acetamiprid, Deltamethrin, Lambda-Cyhalothrin and Cypermethrin. The concentration of these substances in water and sediments vary from one station to another. Among these substances, Imidacloprid and Acetamiprid are from the neonicotinoids family, while Deltamethrin, Lambda-Cyhalothrin and Cypermethrin are from the pyrethroids family. The highest concentrations of neonicotinoids are recorded at station S3 and those of pyrethroids are obtained at stations S1 and S2. Acetamiprid is present in all stations and Imidacloprid in nine of the ten stations sampled. This result is similar to that obtained by Tuo *et al.*[18] in the United States in California. This author showed that Imidacloprid was detected in 89% of the sites sampled. This is believed to be due to the water solubility of this substance. However, the recorded values are very low compared to the standard values of 0.1 µg L^{-1} for surface water quality[19]. These low concentrations showed that it was difficult to detect Imidacloprid in the Sassandra River. According to Crayton *et al.*[20], Imidacloprid was easily detectable only at levels greater than 0.02 µg L^{-1}. Analysis of Acetamiprid gives a maximum concentration of 0.1120 µg L^{-1} and a mean value of 0.0109 µg L^{-1}. Acetamiprid, like Imidacloprid, has a concentration below the threshold recommended by WHO but Acetamiprid remains the majority representative of neonicotinoids in the Sassandra River. The significant presence of neonicotinoid at station S3 could be explained by its position. Indeed, this station is near Guessabo city. Domestic activities would therefore be the factor increasing its water concentrations. Despite having low concentrations, neonicotinoids appear to have enormous negative impacts on the environment in general and on the aquatic system in particular[21]. These pesticides have the property of being propagated in all the compartments of aquatic plants. The mean concentrations of synthetic pyrethroids detected in water samples are 0.0055, 0.0635 and 0.0129 µg L^{-1} for Deltamethrin, Lambda-Cyhalothrin and Cypermethrin, respectively. Compared to WHO standards, these mean values are low. However, Cypermethrin concentrations at station S2 exceed the WHO standard of 0.1 µg L^{-1}. However, this substance was not detected at stations S5, S6, S7 and S8. This could be explained by the fact that Cypermethrin is poorly soluble in water and it would be difficult for it to disperse thereafter application[22]. A study carried out on the Abu Ali River in Liban showed that Cypermethrin concentrations were up to 0.496 µg L^{-1} [23]. These authors attributed the high concentrations of pyrethroids to their high use. In addition, Cypermethrin is very toxic to fish, crustaceans, amphibians and reptiles by blocking ion channels and causing paralysis of the victims[24,25]. The results of the sediment analysis showed that pesticides present in water were also present in sediments. The concentrations of these pesticides in the sediments also vary from station to station. In the neonicotinoid family, the Acetamiprid content is the highest. Regarding pyrethroids, the concentration of Lambda-Cyhalothrin is dominant. Apart from Cypermethrin which could only be detected in four stations, the other substances were detected in the ten stations sampled. The mean values are 0.1919 mg kg^{-1}, 1.0626 mg kg^{-1}, 3.8549 mg g^{-1} and 0.1139 mg kg^{-1} for Imidacloprid, Acetamiprid, Lambda-Cyhalothrin and Deltamethrin, respectively. The significant presence of pyrethroids can be explained by the hydrophobic character of these substances. Being poorly soluble in water, they will converge towards the sediments which have the property of absorbing them as quickly as possible[26,27] and become sinks for these compounds[26,27]. Once in the sediments, pyrethroids become potential threats to benthic invertebrates in the water. This statement was supported by Toumi *et al.*[27]. In addition, pyrethroids have a great affinity for sedimentary particles. They tend to accumulate there rather than disperse in the water column[28]. This presence of pyrethroids is due to the important agricultural activities that take place along the river. In the United States, pyrethroids have been detected in the water and in the sediments of environments located in agricultural areas[29]. The concentrations of neonicotinoids obtained at the stations attest to the use of these products in the study area. The organisms of the aquatic ecosystem are then exposed to the toxicity of these compounds[29]. In general, pesticides are more concentrated in sediment than in water.

The results of this study reveal that the cumulative effects of different molecules of pesticides in the aquatic environment require special attention because they could cause health risks. However, additional studies could be considered in order to know the contamination of fish in the environment by pesticides. Additional studies on the contamination of the Sassandra River and fish by pesticides will make it possible to control this process of contamination and to be able to find mechanisms for its reduction. Thus, speciation of the different forms of active ingredients in the environment would also make it possible to understand the contamination of aquatic organisms and to monitor their health effect on the upper consumer. However, the sensitization of farmers to the harmful effects of the contamination of rivers by pesticides handled in their surroundings is essential.

CONCLUSION

This study enabled us to assess the contamination of the waters and sediments of the Sassandra River by pesticides. The pH, conductivity, dissolved oxygen and transparency values reflect the degradation of the quality of the Sassandra River. These waters are slightly acidic, turbid and loaded with suspended matter. Laboratory analyses of water and sediment have found Imidacloprid, Acetamiprid, Deltamethrin, Lambda-Cyhalothrin and Cypermethrin at higher concentrations in sediment than in water. Lambda-Cyhalothrin is also found to be the most dominant substance in water and sediment. The Sassandra River is therefore mainly contaminated by pyrethroids.

SIGNIFICANCE STATEMENT

The potential and flow of agricultural contamination of surface water by pesticides depend on many parameters, including agricultural practices and the physicochemical properties of phytosanitary products. This study discovered the level of contamination of Sassandra River waters and sediments in Guéssabo by pesticides. It constitutes an important database in search of the sources of this contamination.

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