

Evaluation of Organochlorine Pesticides (OCPs) in Surface Water and Bed Sediment Samples from the River Nile at Rosetta Branch, Egypt

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Abstract: The aim of this study is to; investigate the occurrence of 17 OCPs (total DDTs, total HCHs, heptachlor, dieldrin, aldrin, endrin, endosulfan and methoxychlor) residues in surface water and bed sediment samples from Rosetta branch; their spatial distribution and concentration in different types of pollutant (industrial and agricultural drains outfalls) in order to evaluate the levels and possible sources of pollution, as well as a role of the long-range transport in contamination of Rosetta branch with OCPs. These pesticides are measured in surface water and bed sediment samples using Gas Chromatography- Electron Capture Detector (GC-ECD, 9001). Surface water and bed sediment samples have been collected from nine sampling locations; El Kanater Barrage, five drains outfalls and three industrial effluents discharge points in Kafr El Zayat area along Rosetta Branch. These samples are analysed for their organochlorine pesticides residues before, during and after winter closure periods (August 2007 - April 2008). The results showed that OCPs in surface water and bed sediment samples were below the detection limit i.e. $0.01 \mu\text{g l}^{-1}$ and $0.01 \mu\text{g kg}^{-1}$, respectively which are still within safety margins.

Key words: Organochlorine pesticides, surface water; bed sediment; winter closure period; Rosetta Branch

INTRODUCTION

Rosetta branch, starting from Delta Barrage receives relatively high concentrations of organic compounds, nutrients and oil & grease. Major sources of pollution are El-Rahawy drain (which receives part of Greater Cairo wastes), Sabal drain, El-Tahrer drain, Zawiet El-Bahr drain and Tala drain. At Kafr El-Zayat, Rosetta branch receives wastewater from Soda, El-Malia and Kafr El-Zayat pesticides production companies.

Organochlorine pesticides (OCPs) are a common name of a group of pesticides consisting of benzene and chlorine. Some OCPs belong to the Persistent Organic Pollutants (POPs) that are semi-volatile, environmental persistent and toxic. OCPs have bioaccumulation potential in organisms and long-term adverse effect on ecosystems (surface water and bed sediment) and human health.^[1,2,3] Considering their harmful effects on human and ecosystem, during the last 30 years, many international agreements were initiated to reduce the environmental burden by reducing or withdrawing the registered usage of OCPs, for example, aldrin, dieldrin, endrin, methoxychlor, etc. although most of the world

nations agreed some of OCPs, such as lindane (pure -HCH), are still used in some of countries. In Egypt, 1,2,3,4,5,6-hexachlorocyclohexane (HCHs) and dichlorodiphenyltrichloroethane (DDTs) are extensively used as pesticides for agricultural activities. Hua and San;^[4] Li et al.^[5] stated that during 1960s to 1983, HCHs and DDTs accounting for about 78% of total pesticide production and usage. OCPs have become essential components of modern agricultural systems and in public health programmes. Their use has been considered to be vital in reducing crop losses and controlling vectors of human and livestock diseases. However, OCPs as DDT and aldrin, which have been extensively used in agriculture and public health programmes, are very persistent in nature. Their persistence and lipid solubility make them major environmental pollutants. The accumulation of low concentrations of these pesticides in the body fat of mammals might pose potential hazards on the long run.^[6] Although most of OCPs have been banned in many countries because of mutagenic and carcinogenic effects according to Van der Hoff and Van Zoonen. OCPs^[7] OCPs and their metabolites are still present in the environment, especially in sediment, owing to their

persistence and lipophilic properties.^[8,9] Currently, pesticide residue analyses for sediment samples are under investigation. This investigation aims at the developing analytical method, which permit simultaneous determination of environmentally significant pesticides^[10].

This current study aims at the evaluation of organochlorine pesticides residues (total DDTs, total HCHs, lindane, aldrin, dieldrin, heptacholr, endrin, endosulfan and methoxychlor) and to monitor its impact on water quality of the River Nile water at Rosetta Branch.

MATERIALS AND METHODS

Reagents: All the chemicals and solvents were special grade for pesticide residue analysis and purchased from Sigma-Aldrich (St. Louis, MI, USA). Deionized water was used throughout the study. Stock solutions of standard were prepared in n-hexane and stored in a refrigerator (2-8°C) in glass bottles with PTFE-faced screw caps. All other chemicals (analytical grade) were bought from different commercial sources.

Samples: For the current study, sampling is carried out before, during and after winter closure period, (August 2007- April 2008). The area of investigation is Delta Barrage as reference point (RP), five drains outfalls are El-Rahawy, Sabal, El-Tahreer, Zawiet El-Bahr and Tala (D1, D2, D3, D4 and D5), respectively and three industrial outfalls are El-Malyia, Soda and Kafr El-Zayat pesticides production companies (C1, C2 and C3), respectively are chosen along Rosetta branch. Figs. (1,2) show the selected points.

Surface water: Water samples are collected from the surface water in Van Dorn plastic bottles (1.5 liter capacity) and kept in 50 ml pre-cleaned polyethylene bottles then freeze in an ice box.

Bed Sediment: Sediment samples are collected from depths (0 - 20cm) using pre-cleaned stainless steel sediment sampler from the selective sites. Samples are taken in polyethylene bags and delivered immediately to the laboratory. The samples are air dried at room temperature (25°C±2), crushed and finely ground, sieved through (0.2 mm) sieve.

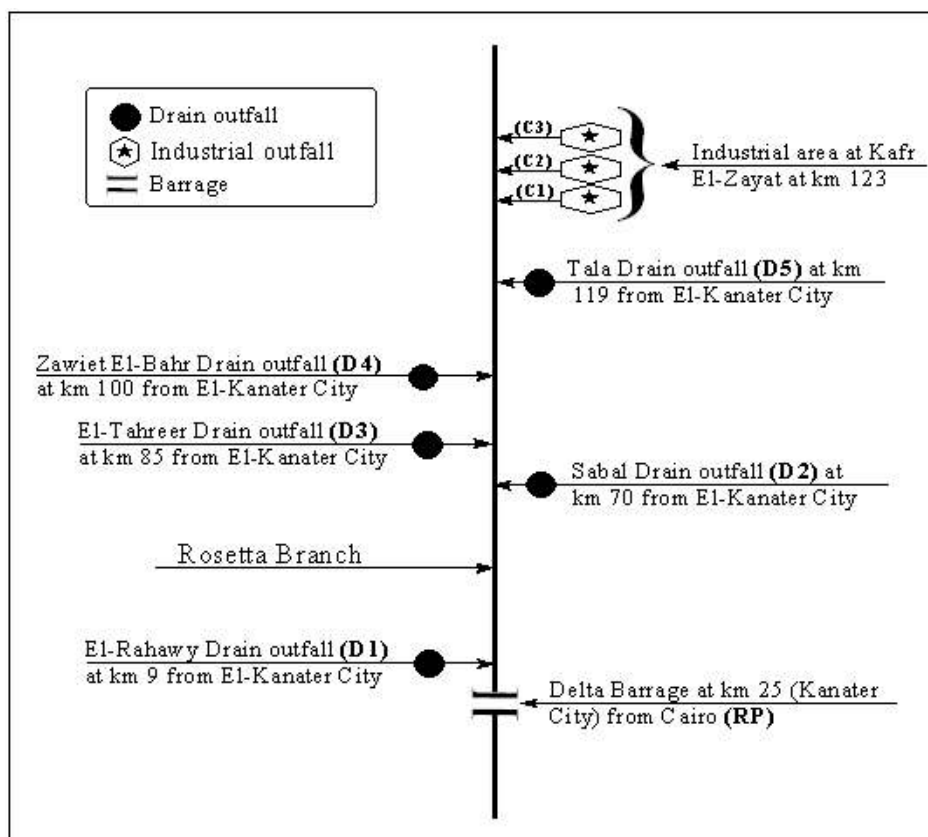


Fig. 1: Monitoring sites along Rosetta Branch.

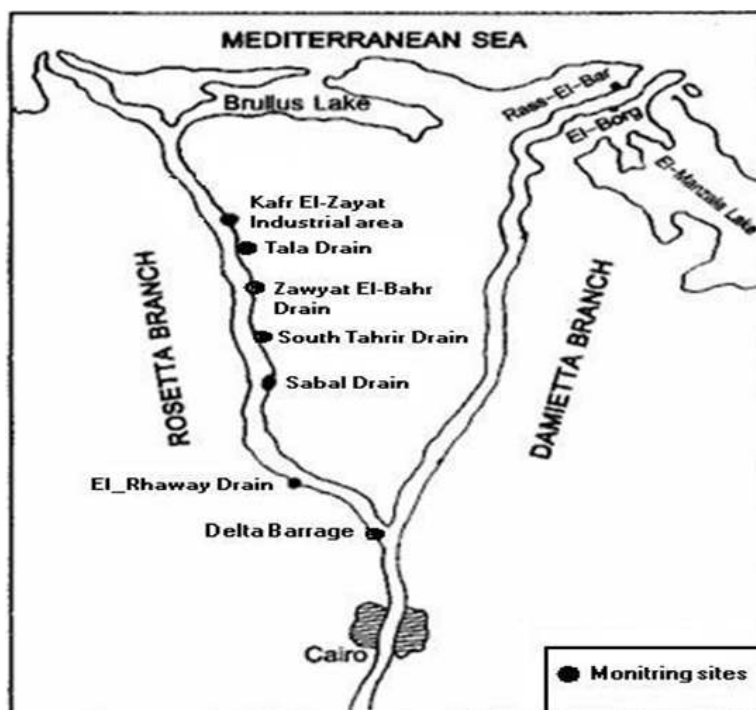


Fig. 2: Map of sampling locations along Rosetta Branch.

Extraction procedure

Extraction of residues from surface water: Extraction of organochlorine pesticide residues from water samples procedure as describe by US.EPA,^[11] is used. One liter of water sample is taken in a separatory funnel and mixed with a solvent of CH_2Cl_2 . Samples extracts are combined and concentrated by rotary evaporating to approximately 5 ml, add 50 ml of n-hexane and concentrate extract to approximately 2 ml.

Extraction of residues from bed sediment : Extraction of organochlorine pesticide residues from bed sediment samples procedure, as described by US.EPA,^[11] is used. Air-dried bed sediment (10 gm) with anhydrous sodium sulphate is taken to the extraction cell. Extract the vessel with a mixture of hexane and acetone. When the extraction is complete transfer the contents into separatory funnel with adding 200 ml of die-ionized water. Samples extracts are combined and concentrated by rotary evaporating to approximately 5 ml, add 50 ml of n-hexane and concentrate extract to approximately 2 ml.

Analytical procedure: Organochlorine pesticide residues are measured by subjecting samples to Finnigan Gas Chromatography (GC 9001), equipped with an Electron Capture Detector (ECD), injection system (Split/ splitless mode 200 °C) and a capillary column RTX-5 Restek

Corporation fused silica column (60 m x 0.25 mm), film thickness 0.25 μm (5% diphenyl, 95% dimethyl polysiloxane). The carrier gas is helium flowing at 1.3 ml/min. The oven temperature is programmed from 120- 300°C, changing at a rate of 9°C/min and maintain at 300°C for 10 min.

RESULTS AND DISCUSSION

The results obtained from a comprehensive study of 17 OCPs residue in water samples collected along Rosetta branch, drains outfall and industrial outfalls to detect the levels of organic contaminants and represent an attempt to improve our understanding of pollution from non-point sources. As a result, the following interpretation and discussion focused on OCPs residue in surface water are shown in table (1) and illustrated in fig (4). Note worthy that chromatogram of OCP residues in the standard sample is illustrated in fig (3).

The minimum detection limits of the methods used for extraction of OCPs residue from water is 0.01 $\mu\text{g/l}$. In all analyzed water samples, none OCPs are detected (below the method detection limit 0.01 $\mu\text{g l}^{-1}$), although they are widely used in agricultural purposes. This can be attributed to the fast rate of degradation of this class of pesticides that was accelerated through the variation of climatic conditions in the study area. OCPs, especially

Table 1: Continued

Endosulfan Sulf.	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Dieldrin	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Heptachlor	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Heptachlor epoxide	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Methoxychlor	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01

BWCP: Before winter closure period.

DWCP: During winter closure period.

AWCP: After winter closure period.

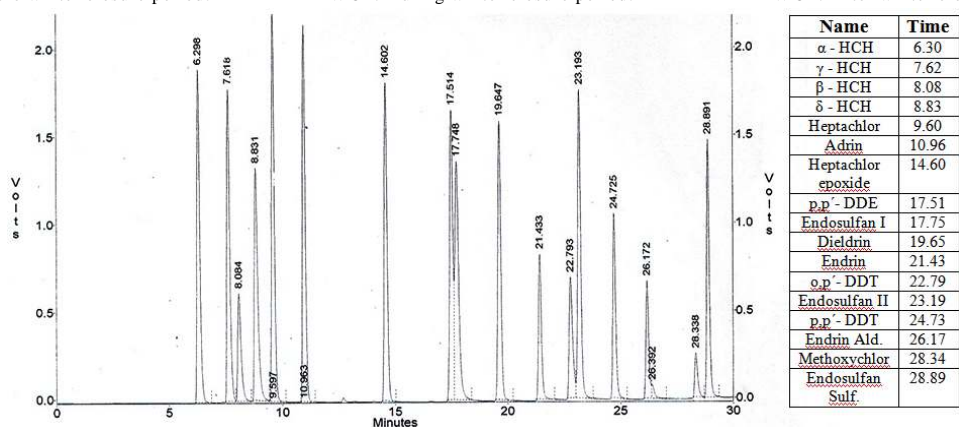


Fig. 3: Chromatograms of OCP residues in the standard sample.

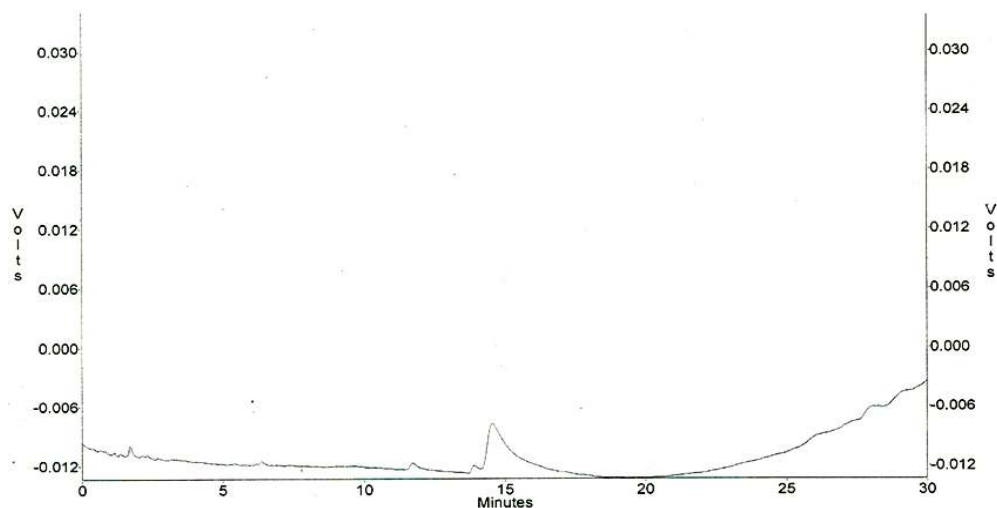


Fig. 4: Chromatograms of OCP residues in surface water sample.

Table 2: Continued

Endosulfan Sulf.	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Dieldrin	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Heptachlor	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Heptachlor epoxide	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
Methoxychlor	BWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	DWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
	AWCP	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01

BWCP: Before winter closure period.

DWCP: During winter closure period.

AWCP: After winter closure period.

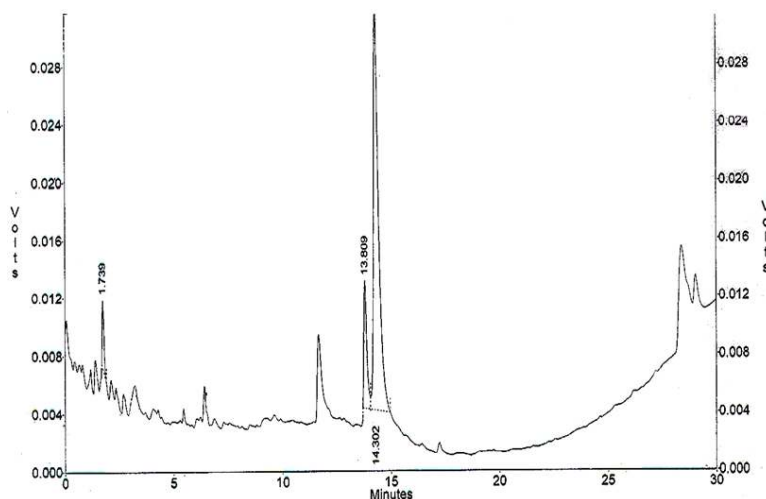


Fig. 5: Chromatograms of OCP residues in bed sediment sample.

DDT, were used intensively during past years; therefore, it is still detected with its metabolites (DDE and DDD) in irrigation, drainage canals and in low concentrations in the River Nile and its branches. This can be related to the currently flushing processes, its use during the past years, low rate of application and attachment to the sediments along their flow as they are associated with solid phase or due to its low solubility and low photo-oxidation^[12]. The HCHs concentrations have lower values than DDTs' in water. Because of their differences in physico-chemical and biological properties, having HCHs a higher water solubility, vapor pressure, biodegradability, lower lipophilicity and particle affinity as compared to DDTs properties^[13].

Pesticide residues seep from the soil into drains, irrigation water and finally into the Nile and pose serious environmental and health risks. It is worth mentioning that, this phenomenon could also happen even under controlled application methods, which is not always the case in Egypt. This leaching mainly depends on the type of pesticide, soil characteristics, hydrogeological conditions, climatic factors, agro-technical factors and human factors. In 1995, a condensed monitoring program was carried out by the Ministry of Public Work and Water Recourses (MPWWR) to analyze water samples along the River Nile. - HCH, lindane, aldrin, dieldrin, heptachlor, endrin, p,p -DDT and its analogous were detected. The highest detected level of DDTs was at Aswan Dam,

Table 3: Concentration of organochlorine pesticides residue in water and bed sediment according to CWQGs (2005) and CSQGs (2002).

OCPs	CWQGs ($\mu\text{g l}^{-1}$)		CSQGs ($\mu\text{g kg}^{-1}$)	
	Irrigation water	Fresh water	ISQG	PEL
Total HCHs	-	0.01 ?0.01	0.94	1.38
Total DDE	-	0.001	1.42	6.75
Total DDD	-	-	3.54	8.51
Total DDT	-	-	1.19	4.77
Aldrin	-	0.004	-	-
Endrin	-	0.0023	2.67	62.4
Endosulfan	-	0.02	-	-
Dieldrin	-	0.004	2.85	6.67
Heptachlor	-	0.01	0.6	2.74
Methoxychlor	-	-	-	-

CWQGs: Canadian water quality guidelines for the protection of agricultural water uses. CSQGs: Canadian sediment quality guidelines for the protection of aquatic life.

ISQGs: Interim freshwater sediment quality guidelines (dry weight).

PELs: probable effect levels (dry weight).

): No guideline availabl.

reaching $0.048 \mu\text{g l}^{-1}$. The results are considered slightly below Canadian water quality guidelines^[14] and not exceed $1 \mu\text{g l}^{-1}$ in Egyptian guidelines for Health Ministry^[15].

In general, the levels of OCPs in the studied area from the River Nile are still within safety margins compared to the permissible limits for irrigation water.

The results of bed sediment sample analyses for the same study regions are shown in table (2) and illustrated in fig. (5). The minimum detection limits of the methods used for extraction of OCPs residue from bed sediment is $0.01 \mu\text{g kg}^{-1}$. In all analyzed bed sediment samples, none OCPs are detected (below the method detection limit $0.01 \mu\text{g kg}^{-1}$).

In general, the levels of OCPs in bed sediment are still within safety margins compared to the permissible limits for Canadian sediment quality guidelines¹⁶ shown in table (3).

It is worth mentioning that, fig. (5) has three peaks at 1.739, 13.809 and 14.302 min that could be characterized due to the lack of having no standard solution to detect these peaks.

CONCLUSION

Assessment of the available data indicates the following: Organochlorine pesticide residues in surface water and bed sediment samples collected from Rosetta branch at the reference point, drains outfall and industrial outfalls are found below the detection limit i.e. $0.01 \mu\text{g l}^{-1}$ and $0.01 \mu\text{g kg}^{-1}$ for water and bed sediment, respectively.

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