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Geochemistry, mineralogy and nutrient concentrations of sediment of River Pampa in India during a massive flood event

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Abstract

Kerala, the southern state of India, was severely hit by a massive flood in August 2018 affecting millions of people causing loss to the state exchequer. The aim of this paper was to study the impacts of this flood on mineralogy, geochemistry (grain size, and heavy metal content) and nutrient content (organic carbon, total and available nitrogen, and phosphorus) of sediment of flood affected Pampa river, Kerala. The study indicates that this large-scale flood results in a considerable reduction in the heavy metals and nutrient concentration of sediment. Frequency histograms for most of the sediment particle size showed unimodal distribution curve with the dominance of sand particles which may be due to wash of fine size fraction like silt and clay during flood. FTIR study indicates that Pampa river sediment is dominant with quartz, orthoclase and microcline feldspar, and kaolinite, along with other trace minerals. SEM study also indicates that quartz is the common occurring mineral and its shape varies from highland to downstream due to transportation. Ratio of carbon to nitrogen and phosphorus particularly at downstream stations indicates the considerable influence of macrophyte which leads to accumulation of terrestrial organic matter. The cluster analysis results indicate that there were some similarity in origin and migration behaviour among these metals and nutrients of the sediments.

Keywords Sediment geochemistry . Nutrient concentrations . Kerala flood . Pampa river

Introduction

Pampa, the third longest river in the state of Kerala in India, was badly affected by a massive flood due to heavy rainfall during the monsoon in 2018. The Indian government had declared it as "calamity of severe nature" which affected one-sixth of the population. The importance of this river for drinking water purpose, irrigation, hydel power generation, fisheries, and

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recreational activities is immense. The river is 176 km long with a catchment area of 2235 km2 (Thella et al. [2018;](#page-17-0) Mayaja and Srinivasa [2017](#page-16-0)). It originates at Pulachimalai hill (Peerumedu, Idukki district) in the Western Ghats at an altitude of 1650 msl and flows westwards draining through Idukki, Pathanamthitta (major part), Kottayam, and Alappuzha districts. Average drainage density of Pampa basin is 2.96 km/km2 with an annual discharge rate of 3.9 km³/year (David et al. [2016](#page-15-0)). The river basin is influenced by two rainy seasons: southwest monsoon (mid-May/June to August) and northeast monsoon (October to December), respectively, with an average annual rainfall of 2276–4275 mm. The basin experienced severe floods during 15–18 August 2018 when Kerala received abnormally high rainfall from 1 June to 19 August 2018. Swaminathan Research Foundation has reported an increase in the intensity, frequency, and severity of floods in this region (Mayaja and Srinivasa [2017\)](#page-16-0). The 2018 flood drew the attention of both scientific fraternity and policymakers as it is supposed to be the century's worst flood (Mishra et al. [2018\)](#page-16-0).

During historical events like flood, sediments act as a valuable repository of various environmental parameters and providing very vital information (VonGunten et al. [1997;](#page-17-0) Renjith and Chandramohanakumar [2007\)](#page-16-0). Sediment is recognized as a carrier of nutrients and contaminants in aquatic systems which could affect the aquatic flora and fauna (Tessier et al. [1994\)](#page-17-0). Flood leads to the loss of sediment nutrients in several ways like (i) surface sediment depletion resulting in loss of organic matter and nutrients, (ii) leaching losses of nutrients particularly nitrogen to groundwater, (iii) induce saturated sediment environment which may increase the denitrification process and thus volatilization losses of nitrogen, and iv) reduce the populations of soil microorganisms and thus the nutrient cycling (Clark [2019](#page-15-0)). When flooding occurs, understanding the processes related to generation, transport, and deposition of sediment and its influence on the sediment particle size is fundamentally important in the perspective of nutrients and heavy metals (Walling and Moorehead [2004;](#page-17-0) Pacifico et al. [2007](#page-16-0)). Particle size controls hydrodynamic conditions and river morphology (Heitmuller and Hudson [2009\)](#page-15-0), as it holds important implications for sediment transport and river ecology (Henshaw et al. [2013](#page-15-0)). By studying the river bed sediment texture, studies on erosion, deposition, and sorting processes in different types of rivers has been explored (Xu [2000;](#page-17-0) Heitmuller and Hudson [2009](#page-15-0); Pan et al. [2015;](#page-16-0) Panwar et al. [2016](#page-16-0)). Additionally, the componentry of a deposit has been used to help distinguish the provenance of the sediment (Muhs et al. [1996;](#page-16-0) Martí et al. [2019](#page-16-0)). Analysis of deposit grain size distributions and componentry provide a direct record of at least some portion of the particles transported by currents and changes in the composition of deposits can be used to infer spatial or temporal changes in current behaviour and the ability, or lack thereof, of the current to transport particles (Andrews and Manga [2012](#page-15-0); Dufek and Bergantz [2007](#page-15-0); Martí et al. [2019\)](#page-16-0). Study of these sedimentological variations may help in developing sediment transport and erosion modelling (Martí et al. [2019\)](#page-16-0) and also help for investigations of the flux and storage of sedimentassociated substances in the channel and riparian zone (Walling and Woodward [2000\)](#page-17-0). Flood events may have a major impact on the course of the river, thus affecting the grain entrainment, transport, and deposition, and nutrient and metal concentrations in sediment is highly influenced by the particle size. Thus, appropriate monitoring of the sediment particle size may be useful in characterizing the flood event sequences with regard to its duration and enormity (Bridge [2009;](#page-15-0) Habersack et al. [2011](#page-15-0); Pacifico et al. [2007\)](#page-16-0).

Heavy metals are extensively investigated contaminants in fluvial processes. The prime source of heavy metal contamination is the flood-induced sediment pollution. There may be a decrease in the heavy metal concentrations in the post-flood period due to the dilution effect caused by non-contaminated sediment or large amount of flood water (Lecce and Pavlowsky [1997\)](#page-16-0). Magnitude of the flood and the extent of affected catchment area determine the level of heavy metal contamination in sediment. If the level of heavy metal contamination goes beyond the acceptable limits, it may affect the

growth and survival of the aquatic flora and fauna. To determine this, it is inevitable to evaluate the environmentally sensitive heavy metals, like Cu, Zn, Mn, Cd, and Pb in flooddeposited sediment.

The sediment geochemistry may help in understanding the source and distribution of the metal elements as well as the existing sediment environment prevailing in the vicinity of the river. The sediment mineralogical profile also indicates the history of geological transport and sorting process. Various authors (Chakrapani and Subramanian [1990;](#page-15-0) Saikia et al. [2016;](#page-16-0) Ramasamy et al. [2006\)](#page-16-0) have reported the geochemistry of different Indian rivers. Fourier transform infrared (FTIR) spectroscopy (Saikia et al. [2016](#page-16-0); Ramasamy et al. [2006](#page-16-0)) and scanning electron microscope (SEM) (Plumlee et al. [2005\)](#page-16-0) analysis provide necessary information on the mineralogical composition of sediments. In comparison to the traditional method, where acidic dissolution is necessary for determination of mineralogical composition of the sediments, FTIR approach is simple and requires only a few steps for sample analysis. In order to make the environmental interpretations of the flood deposits, Pampa river sediment has been examined with SEM.

The present study aims to assess the impacts of a major flooding event on the mineralogy, geochemistry (grain size, and heavy metal content), and nutrient content (organic carbon, total and available nitrogen and phosphorus) of sediment taken from the Pampa river in Kerala.

Materials and methods

Study area and habitat characteristics

Seven sampling stations (Fig. [1\)](#page-2-0) on River Pampa were selected to study the impacts of the 2018 Kerala flood on its sediment. Coordinates of each location are given in Table [1](#page-2-0) and a brief description of each station is given below.

Ranni: It is middle stream site of Pampa river and the renowned Hindu temple, Sabarimala is located in this taluk. It is the largest rubber-producing taluk in Kerala and the economy is primarily dependent on agriculture. Here, water level has gone above 22 ft from the ground during the flood.

Aranmula: It is the temple town situated on the middle stream site. It is a global heritage site enlisted by the United Nations and is famous for the "Vallam kali" (Snakeboat regatta). The water level during the floods was above 20 ft from the ground.

Kadapra: It is the middle stream site of Pampa river where water level has gone above 6 ft from the ground during the flood.

Veeyapuram: It is the lower stream station where Achankovil river meets and merges with Pampa river in

Fig. 1 GIS map depicting the sampling stations on River Pampa

Alappuzha district. It is under Kuttanad ("the rice bowl of Kerala") sector and the water level from the ground was recorded above 6 ft during the flood.

Karuvatta: It is the lower stream station where river Pampa debouches in to the Arabian sea. At this point, discharge from the river is regulated by the Thottappally spillway. The major attractions of the region are the paddy fields, coconut lagoons, and back waters. The level of water above the ground was recorded at about 4 ft.

Thakazhi: It is a lower stream station in the Kuttanad region bound by backwaters on the banks of river Pampa. It is entirely an agricultural village and there are no industries, other than cottage industries, making bamboo articles, bricks, etc. prevailing. Here, the water level during the flood was above 5 ft from ground level.

Table 1 GPS coordinates of the sampling stations in Pampa river

Sl. no.	Stations	Latitude	Longitude
	Ranni	9° 22' 35" N	76° 46' 44" E
2	Aranmula	9° 19' 58" N	76° 41' 52" E
\mathcal{F}	Kadapra	9° 19' 55" N	76° 32' 05" E
$\overline{4}$	Veeyapuram	9° 19' 36" N	76° 27' 41" E
5	Karuvatta	9° 19' 51" N	76° 25' 07" E
6	Thakazhi	9° 22' 09" N	76° 25' 38" E
7	Kainakary	9° 29' 30" N	76° 23' 04" E

Kainakary: It is also in the lower stretch of the river where five rivers originating from the Western Ghats, including Pampa, drain into the Vembanad lake. The major income source is agriculture and fishing, while tourism (house boats) is also emerging. The height of water level was beyond 4 ft from the ground level during the flood.

Sediment sampling and analysis

Sediment samples were collected with a dredge, properly labeled, and transported to the laboratory. It was then air-dried and grounded. The ground sediments were then passed through 10 and 80 mesh sieves to prepare samples for analyzing the physico-chemical parameters and trace metals, respectively. The physicochemical parameters viz., pH, specific conductance, organic carbon, total and available phosphorus, total and available nitrogen, and calcium carbonate content were studied following methods described by Jackson [\(1967\)](#page-15-0). The heavy metals viz., Cd, Cu, Mn, Pb, and Zn were estimated from 1-g samples taken in 100-mL digestion flasks. To this, tri-acid mixture (14 mL $HNO₃:2$ mL $H₂SO₄:2$ mL $HClO₄$) was added and digested till it became white (partially modified from Samanta et al. [2007\)](#page-16-0). The cooled content was then passed through Whatman® 42 filter paper and washed with 2% HNO₃ solution to make up the final volume to 50 mL. Analytical blanks were prepared with the glass double distilled water after treating with the same reagent. The metal contents were then estimated with flame AAS (GBC 932 B Plus) and expressed in mg kg^{-1} of dry sediment.

Mineralogical analysis through Fourier Transform Infrared Spectroscopy (FTIR)

A few milligrams (30–50 mg) of homogenous sediment samples were powdered by adding 20–25 drops of ethanol in an agate mortar. Further, the samples were dried at 120 °C to avoid a broad spectral peak as the presence of -OH would affect the interpretation of the spectrum. This powder was mixed with KBr in the ratio of 1:20 at which the mixture gives the maximum transmittance. The pellet was then subjected to FTIR spectrophotometry (Shimadzu Corpn., Japan, IR-Prestige 21) in the wave number range of 400–4000 cm⁻¹ with a scanning rate of 4 cm^{-1} .

Surface morphology

The sediment samples were analyzed using SEM (JEOL, Japan, JSM-6390 LV) to determine the surface microstructure of riverbed sediment. Prior to SEM analysis, the dried samples were coated with platinum-palladium (JFC 1600) to neutralize the surface charge of the grain during electron beam scanning.

Sediment grain size analysis

To determine the sediment grain texture, samples were analyzed by Laser Diffraction Particle Size Analyzer (Beckman Coulter, USA, LS 13320). The sediment samples (0.5 g) were suspended in the Milli-Q water and added drop by drop into the sample cuvette until the Polarization Intensity Differential Scattering (PIDS) detector indicator reached the saturation point. Percentage of clay $(< 2 \mu m)$, silt $(2-63 \mu m)$, and sand ($> 63 \mu m$) and grain size of 10th (d₁₀), 50th (d₅₀), and 90th (d₉₀) percentile particles were determined with a Gradistat spreadsheet (Blott and Pye [2001\)](#page-15-0) as described by Folk and Ward [\(1957](#page-15-0)).

Statistical analysis

The results of all the sediment parameters are expressed as the mean of three replicates. SPSS version 20.0 was used for the analysis of variance (ANOVA). For statistical comparison between the sediment parameters of different stations, Duncan's Multiple Range Test (DMRT) was done at $p < 0.05$. Bivariate statistical technique like correlation and multivariate techniques like cluster analysis (CA) and factor analysis (FA) were used to interpret the sediment quality.

Results and discussion

Sediment organic carbon (OC)

OC is a measure of the oxidizable carbon content within soil organic matter and its content depends on various factors like supply and deposition of organic matter in the sediment, their decomposition rate, and sediment granulometric composition (Robertson et al. [1992](#page-16-0); Woodroffe [1992](#page-17-0); Koshy [2002\)](#page-16-0). It has a crucial role in maintaining biological productivity of a river ecosystem. The required organic carbon in the bottom sediment to support fish production is about 1.5 to 2.5%. OC content of Pampa river sediments ranged from 0.33 to 3.8% d.w. (Table [2\)](#page-4-0). All the stations except Kainakary exhibited a homogeneous and stable OC content. Kainakary is a tourist spot and the urban runoff during the flood would have resulted in higher deposition of domestic waste from the streets and sidewalks leading to a higher value for OC (3.8%). Nutrients released from this untreated sewage, as well as the station being at the river mouth with the deposits of riverine sediment would also have resulted in the high OC content. Being a part of Kuttanad, vast paddy fields make up the major part of Kainakary which also have role in higher OC content. A comparatively higher OC (1.66%) at Veeyapuram may also be contributed by the paddy cultivation in the region.

Statistical analysis revealed a negative correlation of organic carbon with sand content, while a positive correlation with silt and clay contents (Table [3](#page-5-0)). When fresh organic matter gets added into the sediment, initially, it get decomposed by the microbial community and remain in coarse fraction. With passing of time, the decomposed organic matter will get trapped in the small pores of finer particles. Due to large surface area, finer particles of sediment can adsorb colloidal size fraction of dissolved organic matter by forming sedentary complexes and thus organic carbon remains in finer fraction like silt and clay rather than coarser fraction (Daka and Moslen [2013](#page-15-0); Adesuyi et al. [2016](#page-15-0)). Joseph and Chacko [\(2007\)](#page-16-0) reported the OC content in sediments of Chitrapuzha river, Kerala ranges from 0.13 to 9.02%. Relatively lower value of OC in the sediment attributed to the sandy characteristics of the sediment in most of the stations.

Sediment pH and specific conductance (EC)

Sediment pH is a measure of the hydrogen (H⁺) ion activity and it regulates the availability of nutrients and metals, both in sediment and water. It determines the health of the habitat for congenial growth and survival of biotic communities including fish. EC gives a clear-cut understanding on the presence of soluble salt in sediment and assesses the current carrying capacity of the system. In this study, pH of Pampa river sediment was slightly acidic to neutral in the range of 5.0 to 7.2 with an average value of 6.5. Sediment from Veeyapuram (5.0) and Kainakary (5.60)

Table 2

Sediment quality parameters of Pampa river

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were acidic in nature (Table 2) and were close to neutral at Ranni (7.2). Moderate values ($< 200 \mu S \text{ cm}^{-1}$) of EC were found at most of the stations except Veeyapuram (690 μ S cm⁻¹) and Kainakary (1310 μ S cm⁻¹). Low pH at Kainakary site, a tourist spot, may be due to discharge of effluents (sewage, commercial wastes, and other solid wastes) from the surroundings (Marathe et al. [2011](#page-16-0)). Pampa and Manimala rivers join at Veeyapuram before meeting the Achancovil river and these rivers influx at the station would have reduced the sediment pH. This low pH definitely poses a severe risk to aquatic organisms. In the present study, sediment of Veeyapuram and Kainakary with low pH also had comparatively high concentration of organic carbon which indicates high organic loading that led to low pH. Chandran and Natarajan [\(2014](#page-15-0)) and Prasad and Ramanathan [\(2005](#page-16-0)) also observed acidic pH in the sediments of Karamana and Achankovil rivers in Kerala, respectively, which is in conjunction with our results. The high values of EC at Veeyapuram and Kainakary may be due to higher organic matter accumulation at the bottom (Das et al. [2017\)](#page-15-0). Sediment pH showed a strong negative relation with EC (Table [3\)](#page-5-0). Numerous factors like soil mineralogy, porosity, texture of sediment, moisture content, and temperature affects the specific conductance (Mohd-Aizat et al. [2014\)](#page-16-0).

Sediment available nitrogen

Nitrogen content in the river sediment has a profound influence on the quality of overlaying waters, its biodiversity, and productivity (Kumar et al. [2012\)](#page-16-0). Available nitrogen in sediment is an indication of presence of easily oxidizable form of total nitrogen and is highly influenced by the sediment organic carbon content (Sugunan and Bhattacharya [2000\)](#page-17-0). Sediment of Pampa river contains moderate level of available nitrogen (mg 100 g^{-1} soil) in the range of 2.94–10.64 (av. 5.88) (Table 2) and its content among the different stations varied significantly. Low content of available nitrogen at middle stretch region like Ranni, Aranmula, and Kadapra may be attributed to its relatively elevated altitude that led to less deposits of material during the flood. Relatively higher value of available nitrogen during post-flood period at downstream of the river (Kainakary) could be due to agricultural fertilizer run off from Kuttanad rice field. Veeyapuram station also showed a slightly higher content of available nitrogen which may be due to high nutrient influx, as it is the meeting point of Pampa with Manimala and Achancovil rivers. It may also be due to the nutrient run-off from Kuttanad rice fields. Correlation between sediment available nitrogen and organic carbon content was positive and found significant (Table [3](#page-5-0)).

Total nitrogen

Different letter within the same column indicate that they are statistically different

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The concentration of total nitrogen (mg 100 g^{-1} soil) in Pampa river sediment varied from 32.7 to 61.25 (Av. 45.3) which is

Parameters pH		EC	OC	$CaCO3$ AN		AP	TN	TP	C: N	C: P	Sand	Silt	Clay Cu		Zn	Mn
pH																
EC	-0.820^{\degree}	1.000														
OC	-0.733	$0.983***$	1.000													
CaCO ₃	0.310	-0.171	-0.150	1.000												
AN	-0.823	$0.944***$	$0.937***$	0.004	1.000											
AP	0.503	-0.412	-0.332	0.754	-0.144	1.000										
TN	-0.436	0.556	0.557	-0.436	0.560	-0.142	1.000									
TP	0.188	-0.534	-0.493	-0.339	-0.394	0.185	-0.092	1.000								
C: N	-0.756^*	0.977 **	$0.991***$	-0.092	0.946	-0.313	0.461	-0.481	1.000							
C: P	-0.474	$0.887**$	$0.941***$	-0.109	0.790	-0.281		$0.516 - 0.588$	$0.913***$	1.000						
Sand	0.843	-0.873 [*]	-0.818^{\degree}	-0.062	-0.946 ^{**}	0.111	-0.599	0.444	-0.820^{\degree}	-0.632	1.000					
Silt	-0.839 [*]	0.869^{*}	0.815^*	0.071	$0.945***$	-0.101	0.597	-0.444	0.817^{*}	0.629	-1.000	1.000				
Clay	-0.883 [*]	$0.910***$	$0.854*$	-0.043	$0.955***$	-0.215	0.627	-0.432	0.851^{\degree}		$0.668 -0.993$ **	0.992	1.000			
Cu	-0.566	0.606	0.624	0.223	0.701	0.055	0.000	-0.226	0.702		$0.486 - 0.600$	0.602	0.584	1.000		
Zn	-0.452	0.594	0.641	0.339	0.806°	0.447	0.502	-0.149	0.652	0.532	-0.772 [*]	0.776^*	0.725	0.665	1.000	
Mn	-0.355	0.440	0.455	0.550	0.686	0.583	0.394	-0.202	0.469		$0.335 -0.738$	0.743			0.664 0.506 $0.937**$ 1	

Table 3 Correlation matrix for different sediment quality parameters of Pampa river

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

EC electrical conductivity, OC organic carbon, TN total nitrogen, AN available nitrogen, TP total phosphorus, AP available phosphorus, Cu copper, Zn zinc, Mn manganese

very low as compared to temperate rivers (Table [2\)](#page-4-0). Varughese et al. [\(2009](#page-17-0)) also observed a low value of sediment total nitrogen of Meenachil river, Kerala which ranged between 5.6 and 140 mg kg−¹ . In Pampa river, sediment total nitrogen was highest at the downstream station, Kainakary. In the middle stretch, Aranmula and Kadapra also showed higher values like Kainakary. Point sources may be the cause of higher value at Aranmula, as it is a famous tourist attraction spot. Bibliographic comparison also indicates that these values are low when compared to total nitrogen content of a riverine system in China $(1890-4750 \text{ mg kg}^{-1})$ (Huang et al. [2007](#page-15-0)) and river Po, Italy $(590–7200 \text{ mg kg}^{-1})$ (Davide et al. [2003\)](#page-15-0). However, the values for total nitrogen in the present study were comparatively higher than the values (Total N 20–280 mg kg^{-1}) reported by Koshy ([2002\)](#page-16-0) for Pampa river sediment. This can be attributed to the increased anthropogenic activities in the recent past. Also, nutrient loads from agricultural estates brought by the flood may be another reason. Information on sediment quality guidelines based on total nitrogen for aquatic environments is limited. Ontario sediment quality guidelines state that sediment will be considered as heavily polluted if total Kjeldahl nitrogen of bulk sediment is at or above 4800 mg kg^{-1} (Persaud et al. [1993](#page-16-0)) which is likely to affect the health of organisms dwelling in the sediment.

Available phosphorus

The available phosphorus was found to be low in all stations especially in the downstream. Ranni showed the highest content of available phosphorus (2.77 mg 100 g⁻¹ soil) followed by Aranmula (1.39 mg 100 g⁻¹ soil) (Table [2\)](#page-4-0). Higher levels of available phosphorus in highlands (particularly in Ranni) may be due to the contribution of leachate from extensive rubber plantations (Hindu [2007](#page-15-0); Kumar [2005](#page-16-0)) which led to this amplification (Chen and Lin [2016\)](#page-15-0). Downstream catchments of Pampa river, especially Kuttanad area, is famous for "low land rice cultivation." However, low available phosphorus content in this area during the study period may be due to the removal of top layer of sediment by heavy flood and deposition of sand. It may also be due to subsiding of phosphorus that leached out from the paddy fields around these stations after the heavy flood. Phosphate and nitrate showed positive correlation with $r = 0.566$ (Table 3).

Total phosphorous

Total phosphorous displayed significant spatial variations compared to the available phosphorus and were comparatively higher in highland area like Ranni, Aranmula, Kadapra, and Veeyapuram (Table [2\)](#page-4-0). Differences in geography and geomorphology could have attributed to this variation. This also indicates that phosphate-trapping mechanism and its retaining capacity vary among the different river sediments. Presence of clayey/silty sediment in highland stations facilitates trapping of nutrients (Resmi et al. [2016\)](#page-16-0). The present study shows that the P fraction in available form was quite low as compared to the total form. Phosphorus adsorption and speedy diffusion of available P into the water column may be the reason (Froelich et al. [1979](#page-15-0)).

Sediment CaCO₃

Calcium carbonate $(CaCO₃)$ content of surface sediment gives the base line for paleoclimatic, and paleo-sedimentologic

studies (Biscaye et al. [1976](#page-15-0)). In general, content of $CaCO₃$ in the Pampa river sediment was low and it varied from 1.5– 10.5% with an average of 3.8% (Table [2\)](#page-4-0). Except the station Ranni, all other stations contain almost similar quantity of CaCO₃ but in low content. High content of sand may be the reason for this low value of $CaCO₃$ (Raju et al. [2011](#page-16-0)). In addition, flow of waste water from industry, municipal, and commercial places bring the non-carbonated materials which may reduce the content of $CaCO₃$. Low accumulation of $CaCO₃$ also indicates that the biogenic activity is not supported by the Pampa river sediment (Jonathan et al. [2004](#page-16-0)). Low non-significant positive correlations (Table [3](#page-5-0)) were observed between $CaCO₃$ content and Cu, Zn, and Mn which indicates the partial association of these elements with carbonates.

Carbon:nitrogen (C/N) and carbon:phosphorus (C/P) ratio

Source of organic matter can be identified by carbon-nitrogen ratio. High sediment C/N ratio was observed for all the stations and it spatially varied between 10.17 and 68.99 (Table [2](#page-4-0)). Lithology and prevalent agricultural activities are responsible for higher value of sediment C/N ratio. Highland, Ranni and lowland, Thakazhi and Kainakary showed C/N ratio more than 15 which indicates that the aquatic system is being controlled by terrestrial organic matter (Meyers [1994\)](#page-16-0). Recent fluvial deposits (George and Joseph [2017\)](#page-15-0) due to heavy rain in August 2018 during Kerala flood may have increased the carbon concentrations and, hence, the high C/N ratio. Sudden increase in C/N ratio, particularly at downstream Thakazhi and Kainakary may be due to terrestrial macrophytes. Mat-like root systems of invasive plants may interact with the sediment as influenced by macrophyte bloom. During the study period, occurrence of the macrophyte, particularly, water hyacinth (Eichhornia crassipes) was extensively found at downstream Thakazhi and Kainakary stations (Fig. 2). Sand-Jensen [\(1998](#page-16-0)) reported

that macrophytes can retain almost 80% sediment transported in eutrophic Danish streams. High C/N ratio as influenced by macrophyte was also found in downstream region of Meenachil river, Kerala particularly during monsoon season (George and Joseph [2017\)](#page-15-0).

The high-sediment C:P indicates the terrestrial interference as organic matter deposition during flood may increase the carbon concentration (Table [2\)](#page-4-0). However, very high C:P ratios in downstream Kainakary station may be well correlated with the macrophyte (Fig. 2) influence due to its abundance in this region (Marinho et al. [2010\)](#page-16-0).

Sediment texture

Grain size distribution or particle size analysis is a basic step to understand the sedimentology and it gives necessary order of information about the composition and environmental deposition of sediment. Since natural sediment contains different sized particles, on the basis of average diameter of sediment particles, several class intervals are suggested to identify the different size groups. The most widely used sediment particles grading based on particle size classes is $\lt 2$ μ m: clay, 2–63 μm: silt, and > 63 μm: sand. Table [4](#page-7-0) shows the size distribution of bottom sediment particles of Pampa river as determined by laser diffraction particle size analyzer (Beckman Coulter, USA, LS 13320). Pampa river sediments contain more of sand particles in most of the stations with a minimum value of 54.85% at Kainakary and a maximum value of 99.27% at Karuvatta station. The next dominant size class was silt $(0.33-41.5\%)$ followed by clay $(0.57-3.6\%)$. One of the most common and best methods for graphical representation of sand, silt, and clay composition is drawing the triangular diagrams (Shepard [1954\)](#page-16-0) to determine sediment class type. The study reveals that the river sediments of Pampa fall under fine sand (Aranmula, Karuvatta and Thakazhi), loamy fine sand (Ranni and Kadapra), and sandy loam (Veeyapuram and Kainakary) category (Table [4\)](#page-7-0). Figure [3](#page-7-0) represents the ternary diagram of each one of the sediment sample from these three different textural classes.

Figure [4](#page-8-0) represents the frequency histograms for the size distribution of the Pampa river sediment particles. These figures showed that size distribution of most of the sediment particles are unimodal with a few exceptions. Bi-modal distribution curves were found in Ranni and Veeyapuram sediment samples. Though the sediment samples of Kadapra and Kainakary shows unimodal distribution, their frequency diagram is extended. This is due to the presence of particles of different size ranges. Unimodal distribution with sharp peak towards the coarser particle size fraction of Aranmula, Karuvatta, and Thakazhi sediment samples indicates the dominance of sand particles. During the flood, the sediment layer exposed to strong current which washed off the fine materials Fig. 2 Kainakary station showing macrophytic bloom like silt and clay; hence, only the coarser materials, like sand,

Table 4 Particle size distribution of the bottom sediment of studied locations

will remain on the sediment surface. Thus, grain size distributions are unimodal in most of the cases with sharp peak at coarser size fraction. The high content of sand in sediment has some positive effect on flora and fauna and also on the environment. On the other hand, sediment will be less toxic as all the heavy metals will not get bounded to the sediment and get escaped from the river ecosystem. However, chances of nutrient leaching will be also more as sand will not be able to hold the nutrients and organic matter. A gradual but noncontinuous downstream decrement in sand content was observed in Pampa river sediment indicating textural maturity of the sediments which is universal for alluvial streams. Contrary to this finding, the stations Aranmula, Karuvatta, and Thakazhi showed higher values for sand indicating its deposition following heavy rainfall during August 2018 Kerala flood. Prasad et al. [\(2006\)](#page-16-0) revealed that the sediments of Achankovil river, Kerala, composed of relatively higher percentage of sand irrespective of season. This was in contrast to the findings of Maya [\(2005\)](#page-16-0) who found that sediment of Periyar and Chalakudy rivers of Kerala exhibiting a wide spectrum of particle sizes, ranging from pebbles to mud. Except Aranmula, Karuvatta, and Thakazhi, d_{10} (μ m) value decreased from upper stretch to lower stretch which also indicates that the fineness increased from upper to lower stretches (Table [5](#page-9-0)). However, opposite trend was for d_{90} (μ m) values where this parameter increased from upstream to downstream with the exception of Kadapra, Veeyapuram, and Kainakary.

During flood, carrying capacity of river has been reduced due to higher turbidity and high carrying power as well as flow rate. In addition, due to reduction of flow capacity, there is a reduction in supply and carry of fine- to medium-sized particle, however, the power of flow carrying capacity increased which led to coarse sediment passing all along the riverbed through rotating and rolling forms (Wang et al. [2011\)](#page-17-0). This led to higher transportation of coarse-grained sandy sediment at lower stretches during the co-occurrence of extreme flood flows and rainfall (Kheirfam and Sadeghi [2017](#page-16-0)).

Mineral characterization through FTIR analysis

For mineralogical description of the Pampa river sediments, FTIR spectrophotometric analysis was carried out. Minerals corresponding to wave numbers $(cm⁻¹)$ are given in Table [6.](#page-11-0) Wave numbers obtained in this study were compared with available bibliographic source (Ramasamy et al. [2009;](#page-16-0) Russell [1987;](#page-16-0) Ramasamy et al. [2004](#page-16-0)) which indicates that Pampa river sediment contains minerals like quartz, orthoclase and microcline feldspar, kaolinite, calcite, and gibbsite. The major dominating minerals are quartz, orthoclase and microcline feldspar, and kaolinite, along with others in trace as indicated by the intensities of their corresponding peaks. FTIR spectrum of sediment of different stations of Pampa river is shown in Fig. [5](#page-10-0).

Fig. 3 Representative ternary diagrams of Pampa river sediment. a Ranni, b Aranmula, and c Veeyapuram

Fig. 4 Frequency histograms showing particle size distributions measured by Laser Diffraction Particle Size Analyzer: a Ranni, b Aranmula, c Kadapra, d Veeyapuram, e Karuvatta, f Thakazhi, g Kainakary

Table 5 The average values of the sediment characteristic diameters d_{10} , d_{50} , and d_{90} (μ m) during the flood

Stations	d_{10} (μ m)	d_{50} (μ m)	d_{90} (μ m)	Mean	Median
Ranni	45.78	125.7	351.7	161.1	125.7
Aranmula	132.9	325.5	545.5	334.4	325.5
Kadapra	36.9	163.3	343.7	179.1	163.3
Veeyapuram	11.49	93.76	248.3	119.6	93.76
Karuvatta	240.2	420.1	646.6	432.4	420.1
Thakazhi	194.4	376.9	610.7	389.6	376.9
Kainakary	7.999	82.96	330.9	131.9	82.96

Non-clay-mineral quartz was consistently present in all the samples. The presence of Si-O asymmetrical (460–470 cm⁻¹) and symmetrical (690–695 cm^{-1}) bending vibrations, Si-O symmetrical (790 cm^{-1}) and asymmetrical stretching (1030 cm−¹) confirmed the occurrence of quartz. Presence of quartz was also confirmed by the distinct noticeable peaks at around 514 and 1870 cm−¹ . These observations showed that all the sediment samples from different sites contain quartz. Frequent presence of quartz in sediments is due to its chemical structure as well as hardness which make it unwitherable and not easy to erode.

Feldspar is an important constituent of natural sediments. Among the different feldspars, orthoclase, microcline, and sanidine are the most common. From Table [6,](#page-11-0) the observed frequencies at 425–435 cm⁻¹ and 535–540 cm⁻¹ confirmed the presence of feldspars (Ramasamy et al. [2006](#page-16-0); Ravisankar [2009\)](#page-16-0). Presence of Si-O group associated asymmetrical bending vibration at about 535– 540 cm^{-1} (Ramaswamy and Venkatachalapathy [1992\)](#page-16-0) confirmed the presence of orthoclase. The peak at around 420–435 cm^{-1} indicates the presence of microcline feldspars (Chandrasekaran et al. [2013\)](#page-15-0).

Clay mineral kaolinite $[AI_2Si_2O_5(OH)_4]$ is composed of one tetrahedral sheet connected to one alumina octahedral sheet through oxygen molecules. The creation of kaolinite clay is through chemical weathering of feldspar minerals. Kaolinite is extremely fine in nature and thus can easily mix with water and transported as liquid slurry. Band at around 3690, 3620, 3400, 1100, and 920 cm⁻¹ indicates the presence of kaolinite clay (Ramasamy et al. [2004](#page-16-0); Ramasamy et al. [2011](#page-16-0)). A series of absorption band in the range of 3700–3600 cm^{-1} is shown by kaolinite which is associated with the stretching vibrations of inner surface OHs (3696 cm⁻¹). Presence of these peaks in the collected sediment confirms the presence of kaolinite. It was also observed that weak sharp doublet at 3697 and 3620 cm−¹ are present in all the samples. Peak around 3400 cm^{-1} is present in all the samples except from Ranni. However, the band intensity differs from sample

to sample which is due to the presence of different quantities of clay. Bands at 920 cm⁻¹ were present in the sediment at the stations Ranni, Aranmula, Veeyapuram, and Kainakary. Bands at 1100 cm^{-1} were present at the stations Kadapra and Karuvatta. According to Russell [\(1987\)](#page-16-0), kaolinite is in ordered state if four peaks can be seen in the region $3697-3620$ cm⁻¹. However, in this study, bands at around 3697 and 3620 cm^{-1} , only three peaks were observed which suggests the disordered state of kaolinite.

Among the carbonate minerals, calcite is the most frequently found in sediments. From Table [6](#page-11-0), the IR absorption bands at around 1420 and 1790–1800 cm^{-1} was due to calcite (Sivakumar et al. [2012;](#page-17-0) Sajitha et al. [2017\)](#page-16-0) which was present in all the stations except Aranmula and Thakazhi. Absence of calcite minerals in some samples may be due to the interference of silicate minerals or particle size of the minerals (Ramasamy et al. [2004](#page-16-0)). However, Aranmula and Thakazhi showed peak for carbonate mineral at around 1520 cm^{-1} (Saikia et al. [2016](#page-16-0)). Aragonite is identified in some of the samples by the FTIR at $1770-1785$ cm⁻¹ (Aranmula, Veeyapuram, and Thakazhi) (Sivakumar et al. [2012](#page-17-0)). The existence of a peak near 1630–1680 cm⁻¹ and 3527 cm⁻¹ indicates the presence of palygorskite and gibbsite (Ramasamy et al. [2004\)](#page-16-0) while organic carbon can be identified by weak absorption band present at $2100-2200$ cm⁻¹ and strong absorption band 2800–3000 cm⁻¹. Some more peaks are also observed in some samples (Table [6\)](#page-11-0) which were not identifiable and may have arises due to interaction with other functional groups.

Scanning electron microscope (SEM) investigation of Pampa river sediment

The use of SEM to decipher different sedimentary environment is well established. It provides an insight into the history of transportation and deposition of clastic particles (Ying and Deonarine [1985](#page-17-0); Chen et al. [2019](#page-15-0)). There have been no detailed SEM studies of the Pampa river sediment and thus no details are known so far about the mineralogical variation. The study reveals a marked variation in the surface morphological patterns of these sediments with quartz as the common occurring mineral in all the samples (Fig. [6\)](#page-12-0). In samples from Aranmula, Karuvatta, and Thakazhi, quartz is the only dominating mineral as seen from Fig. [6.](#page-12-0) However, the shape of quartz of Aranmula and Karuvatta is different from and quartz of Thakazhi station. The quartz grains of Aranmula and Karuvatta show the angular outline with straight steps which indicates the short-range transport and rapid deposition of the sediments. Whereas in the quartz of Thakazhi, the angular outline is gradually decreased due to transportation which led to downstream rounding (Nagendra and Elango [2015\)](#page-16-0). Thakazhi station is near to estuary and perfect rounding of

Fig. 5 FTIR spectrum of sample of A Ranni, B Aranmula, C Kadapra, D Veeyapuram, E Karuvatta, F Thakazhi, G Kainakary

the estuarine quartz grain with bulbous projections, pitted surfaces, and other un-oriented etch pits results from mechanical and chemical activities, distinctly indicate subaqueous impact and agitation due to water flow along with long-term chemical activity and extended dwelling time under which the grains were subjected to. Sediment of Ranni, Kadapra, Veeyapuram, and Kainakary stations indicates a composite structure. Sediment of Kadapra (Fig. [6\)](#page-12-0) showed a large composite

 ϵ

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Fig. 6 Scanning electron micrograms of Pampa river sediment at different stations

particle, the dense core of this composite particle represents a massive quartz particle, bounded to sheet-like clay minerals along with silt-sized particles and organic matter. Sediment of Ranni and Veeyapuram (Fig. 6) is generally composed of sand and silt grains with intermittent clay deposits. However, angular quartz particle of Ranni is due to the highland position of this station. Sediment of Kainakary indicates a medium composite in nature with adhered clay platelets to the corner of a larger sand/silt particle as clay content was highest in this station.

Heavy metal contamination in Pampa river sediment

Sediment quality guideline as proposed by the United States Environmental Protection Agency (US EPA) was used to evaluate the level of heavy metal contamination in Pampa river sediment. These evaluation criteria are given in Table 7. Moderate values of copper (Cu) were observed at stations Ranni, Veeyapuram, Thakazhi, and Kainakary, while in all other stations, it was below detection level (Table [8\)](#page-13-0). Average value of Cu in Pampa river sediments also indicates moderate level of pollution. Concentration of Zn was less than the average shale value (95 mg kg^{-1}) in all sampling stations (Table [8\)](#page-13-0).

Table 7 EPA Guidelines for sediments (mg kg⁻¹ dry weight) (Iqbal and Shah [2014](#page-15-0))

Not polluted	Moderately polluted	Heavily polluted		
< 25	$25 - 50$	> 50		
${}_{< 90}$	$90 - 200$	> 200		
		> 6		
< 40	$40 - 60$	> 60		
${}_{<} 300$	$300 - 500$	> 500		

Concentration of Mn varied from 100.3 to 613.8 mg kg⁻¹ and the average concentration was below the shale value (900 mg kg⁻¹) (Table [8\)](#page-13-0). In sediments of all stations, toxic elements Cd and Pb were below detection level (BDL). On an average, the metals showed a declining order of Mn > Zn > Cu.

Metal pollution status of Pampa river sediment was also calculated by using different indices like contamination factor (C_f) , degree of contamination (C_d) , and pollution load index (PLI).

The level of toxic metal contamination in sediment according to C_f^i , and C_d value is given in Table [9](#page-13-0) and their calculation is as follows:

$$
C^i_{f}=C^i_{0-1}/C^i_{n}
$$

and

$$
C_d = \Sigma^n_{i} = _1C^i_{\;f},
$$

Where C_{0-1}^i denotes the mean content of the metal;

 C_n is the reference shale value for that particular metal.

The value of C_f and C_d indicates the level of metal contamination in sediment.

Degree of contamination (C_d) is expressed as sum of all the contamination factors.

PLI was calculated using the following formula:

PLI = $(C_f_1 \times C_f_2 \times C_f_3 \times \dots C_{fn})^{1/n}$, where, C_f denotes the contamination factor, n is the number of metals, and shale value of an element is taken as a background value. For each sampling stations, PLI was calculated. If value of PLI is > 1 , it indicates that the sediment is polluted, while values < 1 indicate non-polluted sediment (Shiji et al. [2015\)](#page-16-0).

As shown in Table [10](#page-13-0), based on PLI, C_f and C_d , low degree of metal contamination was observed in all sediment samples of Pampa river. This low level of metal contamination may be

Stations	Metals $(mg kg^{-1})$						
	Cu	Zn	Cd	Pb	Mn		
Ranni	26.1	71.5	BDL	BDL	613.8		
Aranmula	BDL	39.2	BDL	BDL	317.5		
Kadapra	BDL	47.0	BDL	BDL	397.2		
Veeyapuram	27.5	55.9	BDL	BDL	464.1		
Karuvatta	BDL	BDL	BDL	BDL	100.3		
Thakazhi	27.8	34.1	BDL	BDL	189.6		
Kainakary	33.4	78.0	BDL	BDL	506.5		
Average (contamination status)	28.7 (moderately polluted 25–50)	54.3 non-polluted (< 90)			369.9 (moderately polluted 300–500)		
Average shale value	45	95	0.3	20	900		

Table 8 Heavy metal distribution in Pampa river sediment

BDL below detection limit

due to erosion of the contaminated sediments from the river channel (Ciszewski [2001\)](#page-15-0) during flood. Also, chemical adsorption or desorption of the metals in the sediment particles as influenced by the flood which may certainly have a role in manipulating the changes in the metal fraction. However, further studies are required to reach any valid conclusion. This preliminary study indicates that the high-magnitude flood may cause a substantial decrement in the average heavy metal level in the river sediment of Pampa. However, the results are only a short-term depiction and in general, the actual metal pollution level in river sediment is likely to be restored in 1–2 years.

Cluster analysis

Cluster analysis (CA) was used to group the similar sampling stations (spatial variability) and to indicate areas with a specific contamination (Varol and Şen [2012](#page-17-0); Sundaray et al. [2011](#page-17-0); Singh et al. [2017](#page-17-0)). Standard methods like Squared Euclidean Distance and Ward's linkage method were used for CA (Singh et al. [2017](#page-17-0)). Spatially, CA provides a dendrogram (Fig. [7](#page-14-0)) where all seven sampling stations of Pampa river were categorized into statistically different clusters. Cluster 1 consisted of five sites (Ranni, Aranmula, Kadapra, Karuvatta,

Table 9 Contamination and their description (Shiji et.al. [2015](#page-16-0))

C_f^i	C_d	Description
C_f^i < 1	$C_d < 7$	Low degree of contamination
$1 < C_f^i < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f^i < 6$	$14 < C_d < 28$	Considerable degree of contamination
$C_f^i > 6$	$C_4 > 28$	Very high degree of contamination

and Thakazhi) and Veeyapuram and Kainakary stations belong to cluster 2 and cluster 3, respectively. This clusteringbased grouping gives indication that sources/level of pollution in some stations are similar. Similarity in pollution status among the different sites may be due to geomorphology, or industries and agriculture activities. Veeyapuram is the middle stream station of Pampa river where Achancovil river meets and merges with Pampa river and this may be the reason of high metal content. Pampa drain into the Vembanad lake at the tip of Kainakary station which is under cluster 3. Due to the closeness of this site to the estuary, this station contains higher level of metal while tourism (house boats) may be another reason. High clay content in the sediment of Veeyapuram and Kainakary stations may be differentiating them from all other stations. Ranni shows distinct difference from other stations of cluster 1, as already mentioned that the cultivation, particularly rubber plantation, may have influenced the some of the sediment parameters.

Table 10 Contamination factor (C_j) , degree of contamination (C_d) , and pollution load index (PLI) of Pampa river sediment

Stations	C_f^l					C_d	PLI
	Cu	Zn	Cd	Ph	Mn		
Ranni	0.58	0.75	BDL	BDL	0.68	2.0	0.67
Aranmula	BDL	0.41	BDL	BDL	0.35	0.8	0.38
Kadapra	BDL	0.49	BDL	BDL	0.44	0.9	0.61
Veeyapuram	0.61	0.59	BDL	BDL	0.52	1.7	0.57
Karuvatta	BDL	BDL	BDL	BDL	0.11	0.1	0.11
Thakazhi	0.62	0.36	BDL	BDL	0.21	1.2	0.36
Kainakary	0.74	0.82	BDL	BDL	0.56	2.1	0.70

Fig. 7 Dendrogram showing clustering of sediment sampling sites on the Pampa river

Factor analysis

Factor analysis (FA) reduces the large number parameters into a smaller, more convenient number of factors. Thus, it helps in determining the parameter's patterns and clustering of interrelated variables into factors. In general, the principal components with Eigen values more than one are considered important in the principal component analysis (PCA). With reference to the

Table 11 Factor loading (Varimax) of Pampa river sediment

EC electrical conductivity, OC organic carbon, TN total nitrogen, AN available nitrogen, TP total phosphorus, AP available phosphorus, Cu copper, Zn zinc, Mn manganese, Pb lead, Cd Cadmium

accumulated percentages of the total variances, the first two components are responsible for 80% of the variances of the original data (Table 11). This indicates that total variances of the original data are explained by two extracted components. 60% of the variances are explained by Factor 1 (F1) (Table 11) which is attributed by silt, clay, EC, OC, and available nitrogen. F1 is negatively correlated with sand and pH and categorized as "organic pollution factor." This indicates the accumulation of OC and available nitrogen in the silt/clay fraction of the river sediment. Negative correlation of sand and pH in F1 indicates that this will increase the availability of heavy metals. Factor 2 (F2) indicates that $CaCO₃$, available phosphorus, and Mn contribute to 20% of the variance. F2 is categorized as "metal and organic pollution factor." However, the frequency of detection and concentration of Mn in the sediment samples of Pampa river is higher as Mn is an essential nutritional element found in every kind of plants and animals. It also occurs in great variety of minerals widely scattered over the earth. Mn is also considered as a mobile element because it can be exchanged between sediment and water as result of changes in temperature and pH and may became more prevalent in available form.

Conclusion

The magnitude of the flood and the nature of the affected catchment area, made it essential to evaluate sediment quality of Pampa river system. The results show that the sediment is suitable to support the fisheries of the riverine system. The lack of pre-flood data for comparison was the main constraint for determining the impact of the flood on the riverine system. Hence, the present study may serve as baseline information on the sediment quality of river Pampa after the flood event. The unimodal nature of the frequency histogram of sediment particles indicates that the sediment is dominated by sand particles which may be due to the flushing of finer particles during flood. The reduced concentration of nutrients and metals in the sediment may be due to the dilution effect by flood water. River Pampa harbors a variety of ornamental and food fishes and also supports the tourism activities of the state. Hence, the results of the present study could be effectively used to develop management plans.

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Authors' contributions Ajoy Saha: Corresponding author, sample collection, data analysis, manuscript preparation. Sibina Mol S: Sample collection, manuscript preparation. Deepa Sudheesan: Sample collection, formal analysis. Vettath Raghavan Suresh: Coordination of the work. Subir Kumar Nag: Heavy metal analysis. Preetha Panikkar: Writing—review and editing. Thankam Theresa Paul: Manuscript preparation and editing. Rani Palaniswamy: Coordination for sampling. Basanta Kumar Das: Overall guidance. Arnab Roy Chowdhury: SEM, FTIR, and particle size analysis.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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