RESEARCH ARTICLE

CHARACTERIZATION OF THE RIVER BED SEDIMENT PROFILE AND EVALUATION OF URBANIZATION POLLUTANTS AT LUCKNOW CITY AREA.

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Manuscript Info

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Abstract

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Sediment profile has played a crucial character to control the river water pollution due to exchangeable processes take place between sediment and water. In present study three sediment samples were taken from up, mid and downstream of Gomti River, at Lucknow city during March 2016. Identification of physicochemical components, morphologic, functional groups, particle size, mineralogy and metallic contents were found out in sediment samples. For the characterization of river sediments samples instruments were used scanning electron microscope, (SEM-EDX), fourier transform infrared spectroscopy (FTIR), particle size distributor and atomic absorption spectrophotometer (AAS). The investigated results indicated an increase in organic matter content as a function of pollutants chelating with sediment, related to the specific surface area. Various hazardous elements like Cd, Pb, Cr, Mn, Ni, Cu, Zn, Mg, Co and Hg were also identified in samples, probably due to anthropogenic activity. The functional group shows the richness of elements in samples. The special finding was found out the enriched components pattern mid>down>upstream. The presence of Hg an anthropogenic occurring element was found, can cause a high toxicity/ risk for aquatic and human life around river city. The aim of study due to analyzed components play an important role in mobilization, water pollutants exchanges, surface area for binding pollutants, functional groups for the confirmation, metals for aquatic toxicity and minerals for the rock function.

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Introduction:-

The sediment of the rivers contaminated through naturally or anthropogenically has become one of the environmental issues. Both natural and human activities affect the composition of the sediment. Sediment can act as a major pollutant reservoir for heavy metals and others that will often bio accumulate through the food chain and

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directly affected by aquatic life and indirect to human life. The study performed of Gomti river alluvial zone at Lucknow city 2016.

The contaminant is introduced into the aquatic system as a result of weathering of rocks, volcanic eruptions and from a variety of human activities involving, domestic sewage, mining, dredging, processing and use of metals and/or substances containing metal and vehicles also (Zhang et al., 2011). Spatial distribution and concentration of heavy metals in sediments are affected by both natural environmental and anthropogenic factors (Bai et al., 2011). Bottom river sediments are not only the sink of heavy metals but also potential secondary sources of heavy metals in an aquatic system (Bing et al., 2011). Riverine sediments play an important role as pollutants and they reflect the history of the river pollution (Jain, 2004). Sediment transport depends on a number of factors, the most important of which are the amount of available water, precipitation (both average and peak), discharge (volume and velocity), topographical and environmental features of the terrain, basin geology, magnitude of human impact, and amount of sediment or load that the river or stream can carry (Richmond et al., 2003; Delpla et al., 2009; Alexander et al., 2010; Syvitski, 2011; Mouri et al., 2014).

The sediment is generally constituted dominate, and are called metals and metalloids. These contents in sediment are found in a coarse fraction of sediments such as particle size and percentage of clay, silt, and sand. The more dominate minerals which commonly occur in sediment along with their differentiating characteristics. Usually the dominant mineral of fine sand and coarse silt fraction of sediment it is occasionally found in clay fraction. The metals in surface sediment availability play a very important roll on human as well as ecological views. Bed - sediments are contaminated by trace elements, including As, Cd, Cu, Hg, Pb, and Zn. Concentrations of As, Cu, and Zn are greatest in sediments of the riverine reach upstream and concentrations of Cd, Pb, and Hg are greatest in reservoir sediments (Bortleson et al. 2001and Cox et al. 2004).

Potential influences on metal bioavailability in sediments include differences in the nature and proximity of metal sources (e.g., solid and liquid smelter wastes vs. historic mining activities), weathering and dilution of metal-contaminated particles within the river and reservoir, dewatering of sediments due to reservoir operations, and physical–chemical characteristics of bed sediments, notably concentrations of metal binding phases such as sulfides, organic matter, and iron/ manganese hydrous oxides (Ankley et al. 1996). The development of analytical microscopic technology has increased their usage in geosciences. Recent application of urban particles (Bibby and Webster-Brown, 2005) showed promising results to understand the binding phenomenon of pollutants. Although this type of technology demands a longer analysis and interpretation period, the results carry more information and understanding on the particles' past and composition. Electron microscopy has been used to study soils and sediments since the 1940's (Jackson, 1946).

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. As a major advantage, infrared spectroscopy permits the identification of the alternative method for acquiring quantitative mineralogy (Ravisankar, 2009). Several studies have presented geological applications of ATR FTIR for qualitative phase identification in sediments and cement (e.g., Herbert et al., 1992; Hughes et al., 1995; Besson and Drits, 1997; Vaculicova and Plevova, 2005; Kumar and Rajkumar, 2013).

Earlier researchers have documented biological effects associated with metal-contaminated with sediments, including elevated metal concentrations in aquatic biota and toxic effects of sediment and pour water (Era and Serdar, 2001). The hydrology that affects depositional processes in aquatic pond converts them in dynamic environments with variable characteristics such as pH, salinity, sediment type, biological habitats, localized depositional and transport processes and water level and, because of that there is a great interest in their analytical control (EPA, 1992).

The objective of present study is to examine the possible participation of effluents originating from urban centers and industrial wastes as pollution sources of the Gomti River by determining the (i) levels of trace metals including, Cd, Pb, Hg, Cr, Cu, Ni, Mn, Mg and Zn through AAS, (ii) the morphology was carried out of polluted sediment by SEM visualized image, (iii) the identification of mineralogy from SEM-EDX chromatogram and also trace metals were carried out and (iv) functional groups were identified by FTIR analysis.

Materials and methods:-
Study area:-
Lucknow city is situated (26.8467° N, 80.9462° E) after 250 km flowing river from the origin point. The river serves as one of the major source of drinking water at the Lucknow city surrounding and helped by the river in a different way. The study area covers three different locations river up to downstream viz. site-1(upstream- ghaila bridge), site-2 (midstream –gomtibairraj) and site-3 (downstream- saheed path) the river spread over about 15 km stretch flowing the Lucknow city (Figure 1).
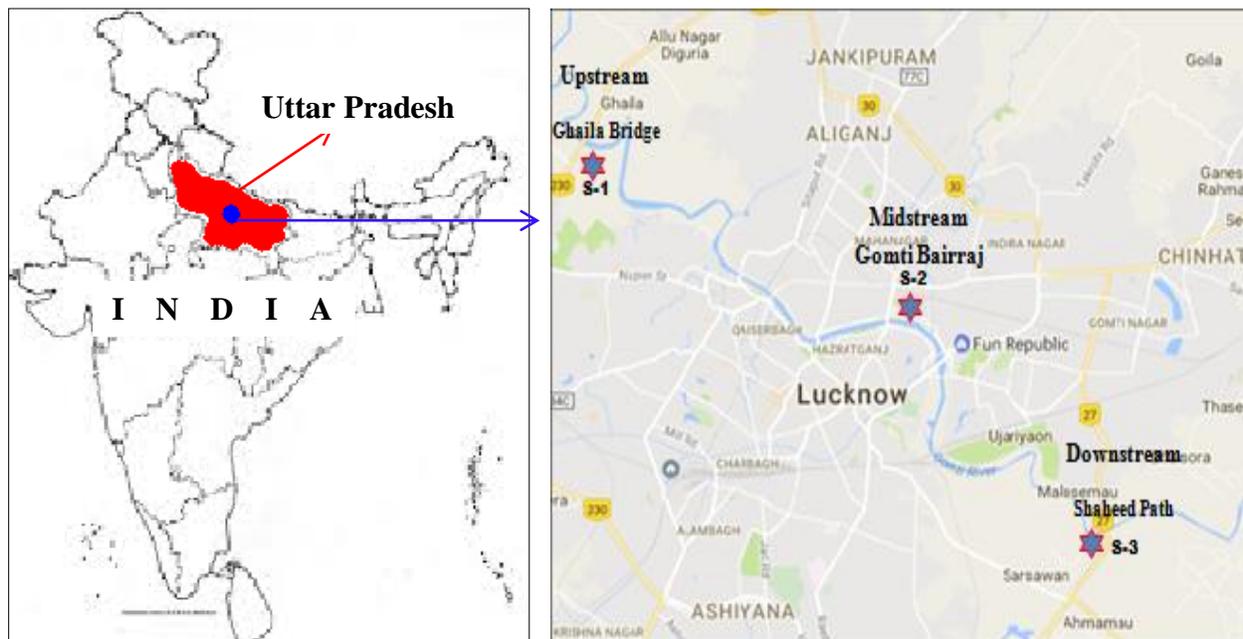

Fig. 1:- Map of the study area and showing the locations in Gomti River Lucknow

Collection and preparation of sediments:-
Bottom sediment samples were collected about 5.0 km separately, one from a depth of 25-30 cm of surface bottom sediment at three points (1-up, 2-mid and 3-downstream) along the Gomti River at Lucknow city total 15 km distance during winter season 2016.The samples are representative of the course of the Gomti River from this urban area until its mouth and end. The samples were identified, stored in plastic bags, and packed in boxes until arrival at the laboratory in frozen condition. The samples were air dried before being pulverized and homogenized with a mortar and pestle. All samples packed in power form without moisture condition and send for identification to instrumentation laboratory.

Quality assurance:-
Reagents and calibration standards for physic-chemical analysis were prepared using milliqui distilled water. Chemicals were used throughout the study analytical grade (AR) chemicals (Merck, Germany) without any further purification or disturbance. The glass wares were washed with dilute nitric acid (1.15 N) followed by several portions of distilled water. The quality assurance measures included meticulous infectivity control (stringent washing/cleaning procedures), a solvent for blank, equipment and other materials. All analyses were carried out in duplicate.

Analysis of physicochemical parameters and metals in sediment samples:-
Physicochemical analysis has also carried out for sediment pH, chloride, nitrate, sulphate and phosphate through APHA, 2012. The total organic carbon content of the sediment was determined using back titration method (Walkley and Black, 1934).The sediment sample for metal analysis was dried at100^{o}C grind to below 100-mesh size. The analysis of metal concentration through Atomic Absorption Spectroscopy (AAS, Model GBC Avanta-Sigma, Australia) instrument. Hollow cathode lamps (Varian) for respective metals were used at a working current ranging from 5-30 mA with 213.9- 357.9 nm spectral line.

Analysis of SEM (scanning electron microscopy) and EDX:-
Samples were analyzed using a scanning electron microscope (SEM) JEOL JSM- 840 coupled with an X-Ray micro analysis system from princeton gamma tech (PGT). A ray of generated electrons of the size of a few angstroms is scanned over a randomly located field. A numerical image is produced from the backscattered electron beam with particles ranging from 0.2 to 20 µm. X-ray spectrum generated from these particles are then acquired using a high purity Germanium (HPGe) detector and digital pulse processing from PGT. Hundreds of spectrums of particles per sample were analyzed automatically to assure that results are qualitatively representative.

The spectrum is analyzed by the energy dispersive spectrometer (EDX) and then classed according to the pre-defined sediment, as well as metal phases. Pre-defined sediment phases included various iron and manganese oxides, calcium, SiO_2, pyrite and barite. These sediment phases were chosen according to the capability of the SEM-EDX to identify particles and analyze spectra. Organic matter and amorphous iron oxide are not defined since these phases cannot be detected by the SEM. On the other hand, metal classes consisted of zinc, lead, chrome, copper, and vanadium. These metals were chosen due to their high quantity, which allows them to be detected by the spectrometer.

Analysis of FTIR:-
The attenuated total reflectance-fourier transform infrared (ATR-FTIR) spectra of sediment were recorded in spectral range 4000-550 cm^{-1} on a Nicolet, iS5, (Thermo Fischer, USA) IR spectrometer. The samples were placed directly under the probe of ATR and spectra were recorded at a rate of 16 scans/min.

Analysis of particle size in sediment:-
The sediments were kept in oven 100±4ºC for 24 h. The dried samples were grounded to powder and sieved with sieve set containing 25 µm to 300 µm sieves. The powder passing with different sieves having size range 25 µm to 300µmand thereafter collected and stored in the plastic bottle for further study.

Results and discussion:-
The elemental composition, determined using SEM-EDX, showed that each particle is composed of different elements, however, the analysis general showed the presence of Al, Si, Cl, K, Ca, Fe, Cu and O in sediment samples.

Characterization of sediment: SEM-EDX, particle size analyzer and FTIR:-
The Scanning electron microscope-SEM (Model ZEISS, EVO, Germany) equipped with an Oxford link INCA, Penta FET$_{X3}$ Energy Dispersive X-ray (EDX) was used for the surface morphology and chemical composition using EDX. The operational voltage of SEM was 20 kv. Particle size analyzer (CILAS 1190, France) was used for measurement of the particle size distribution of sediment samples. The FTIR spectrum (Perkin Elmer Spectrum Version 10.03.06) study was carried out to identify the functional groups present in samples. The FTIR technique was employed to find out the degree of contamination in sediment samples. Using electron microscopy and chemical microanalysis techniques, information can be obtained about the size, shape, surface texture and elemental composition of individual particles which may be as small as 3 mm or less (Pye, 2007).

The characterized the sediment samples by scanning electron microscopy (SEM) because sediment particle size less than 0.2 microns cannot be resolved under the ordinary microscope and hence cannot be seen. In the river, sediment particle sizes play a big role in river flowing, ground water recharge, river contamination and other application. Figure 2show the microscopy of typical clay particles size from different sediments, which indicated the difference between up, mid and upstream sediment samples particle size. The large particle size (sand) was found in upstream compared to mid and downstream sediment river sample.

The SEM chromatograms clearly indicate the presence of minerals highest in midstream compared to up and downstream. This analysis clearly reveals that some of the value of the parameter has been found to be higher. This analysis also supports the presence of detected minerals. Identified minerals were highest such as Na, Mg, Al, Kr, Si, K, Ca, Ti, Fe, Co and Pt in midstream, minerals present in downstream same as midstream but comparatively less (Table 1). Other minerals found in upstream lower than other than both locations. The chromatograms peaks were showing in the Figure 3a, b & c for up, mid and downstream minerals composition and clear differences of city contribution.

Results of minerals in all location analyzed by SEM instrument and identified the composition and percentage of components. In upstream of a river is an entry point of the river in the city so less number of elements present and lowest and highest percentage like K-1.38 % and Si-84.72 % (Table 1a). These results have due to the anthropogenically contribution of cities wastage in the river.

In midstream is the middle areas of river and city which play a significant role in a city because river water used in the city as a drinking and domestic purposes. In midstream have present minerals maximum compared to other location due to an addition of extra wastage of cities. The lowest and highest minerals were K-0.45 and Si-47.79% (Table 1b). Finding of minerals in downstream were also highest from upstream. The lowest and highest minerals were in river sediments like P-1.14 and Si-63.34% (Table 1c). The best information about the shape, internal structure and chemical composition of individual particles is often obtained if the particles are embedded in resin, sectioned, polished and imaged in the SEM using the backscattered electron mode (Krinsley, 1998). Quantitative image analysis can be performed to characterize the particle form and internal micro-fabric, and techniques such as electron microprobe analysis used to obtain information about chemical composition (Reed, 1996 and Goldstein, 2003). The Computer-controlled elemental analysis in the SEM or microprobe can provide compositional information for thousands of particles, and allow estimates of relative mineral abundances to be made if the particle types are classified in terms of defined categories based on elemental composition (Pirrie, 2004).
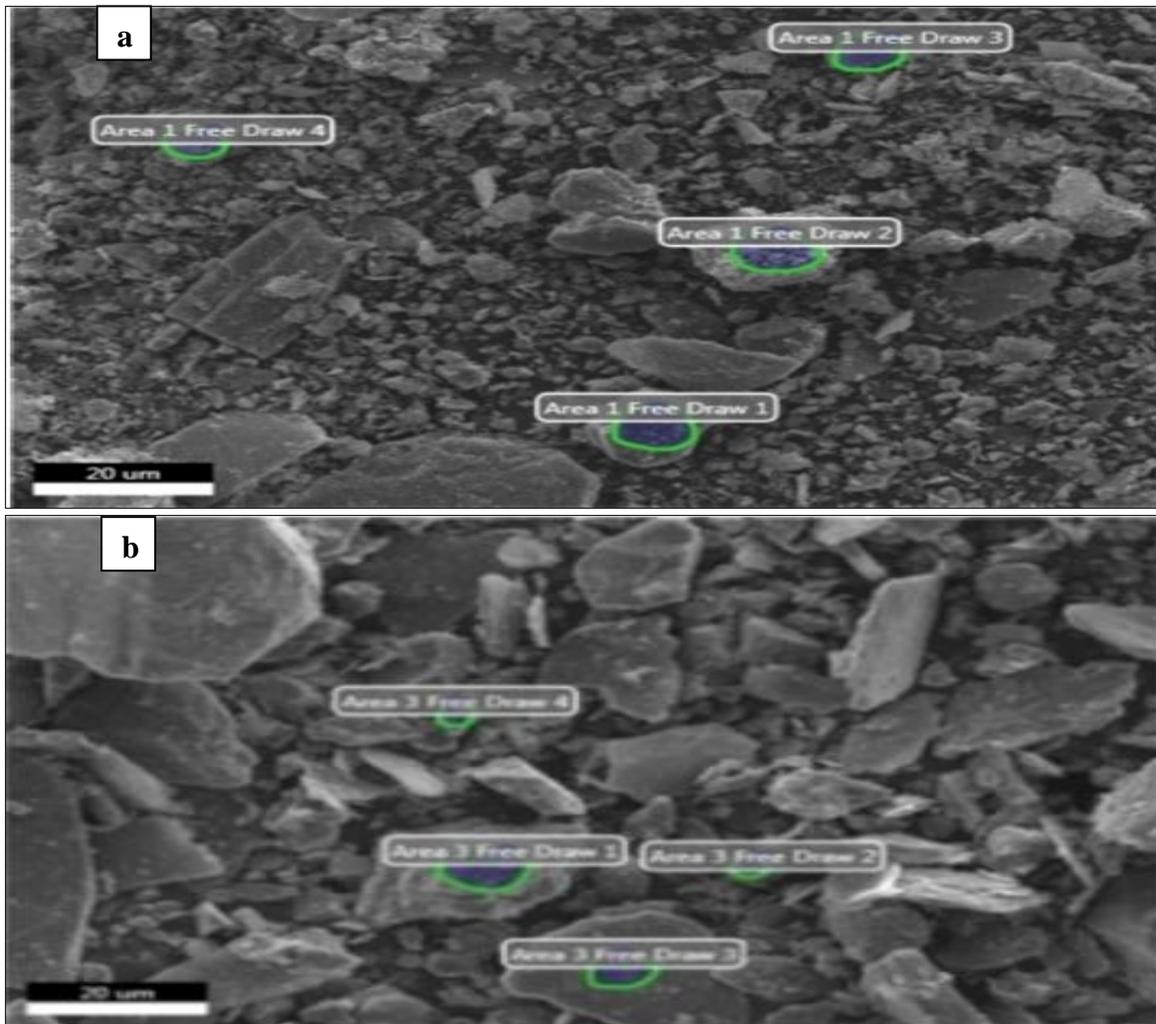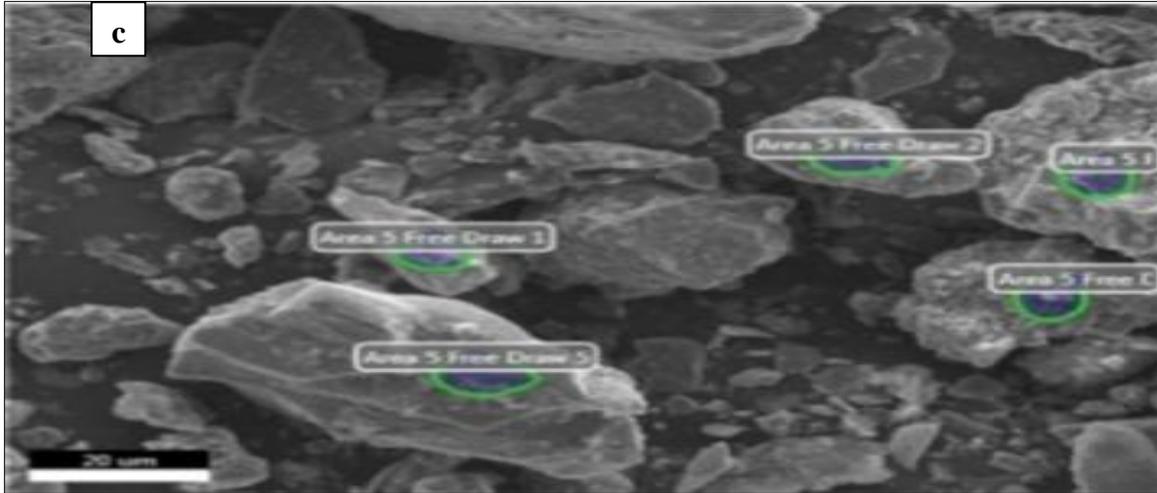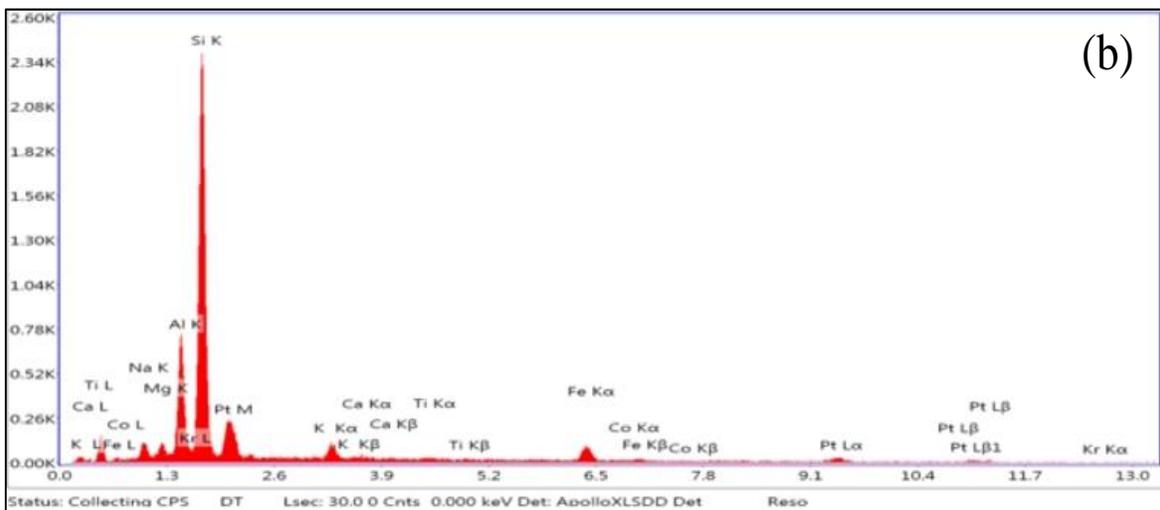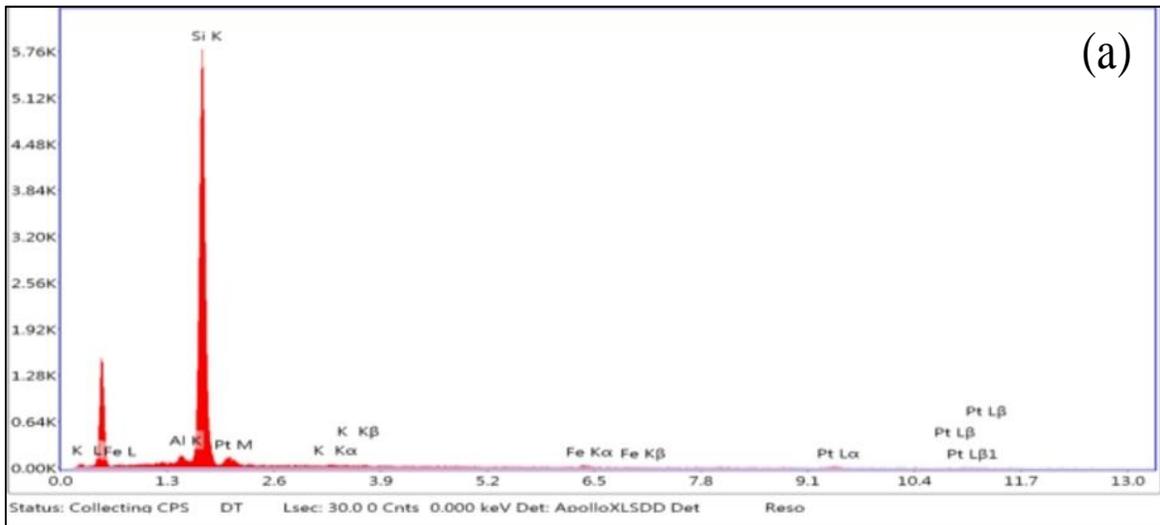
Fig. 2:- SEM microphotographs of (a- upstream, b- midstream and c- downstream) river Gomti sediments samples.
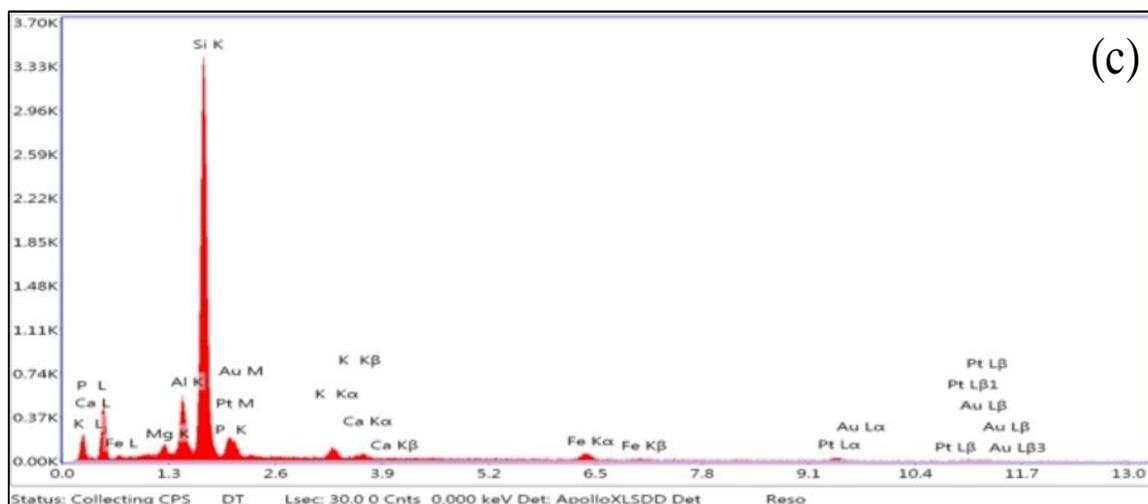
Fig.3:- EDX elemental chromatograph speaks of (a- upstream, b- midstream and c- downstream) river Gomti sediments samples

Table 1:= Elemental composition & % of (a-up, b-mid and c-downstream) of river sediment

a – Upstream sediment sample

Elements	Weight %	Atomic %	Net Int.	Net Int. Error
Al	1.88	2.17	37.97	0.06
Si	84.72	93.99	1671.06	0.00
K	1.38	1.10	12.83	0.14
Fe	2.05	1.14	9.81	0.24
Pt	9.97	1.59	7.63	0.41

b – Midstream sediment sample

Na	2.41	3.81	18.21	0.11
Mg	1.28	1.91	16.42	0.1
Al	12.79	17.19	194.35	0.02
Kr	0.45	0.19	3.28	0.67
Si	47.54	61.38	695.87	0.01
K	4.13	3.83	38.65	0.1
Ca	1.07	0.97	9.08	0.24
Ti	1.25	0.94	9.82	0.3
Fe	8.51	5.52	40.97	0.1
Co	1.0	0.62	4.14	0.58
Pt	19.57	3.64	15.26	0.28

c – Downstream sediment sample

Mg	1.49	2.04	20.94	0.1
Al	8.6	10.64	139.44	0.02
Si	63.34	75.28	995.16	0.01
P	1.14	1.22	8.42	0.22
K	4.12	3.51	36.36	0.11
Ca	1.9	1.58	15.17	0.18
Fe	5.64	3.37	25.38	0.12
Pt	12.56	2.15	9.1	0.35
Au	1.22	0.21	0.76	0.59

FTIR of study for sediment samples:-

The FTIR spectra of sediment analyzed and find out in all locations (up, mid and downstream) are shown in Figure 4. The peaks of the different range were observed in sediment spectrum via 1- upstream, 2- midstream and 3- downstream. Upon analysis spectral peak, at 3685.38, at 3400 cm^{-1} indicates the O-H stretching. The peaks at 3019.46 cm^{-1} are due to C-H stretching of aliphatic groups. The peaks denote at 2400 cm^{-1} shows the presence of C≡N (cyano) functional group. The broad band peak at 1629.4 cm^{-1} refers to C=O (aromatic amide or amine)

functional group. The weak band at 1522.42 represents N=O (nitroso) groups. The shoulder range between 1404.38 to 1328.44 cm^{-1} is designated for the S=O (sulfate and sulfone) functional group. The sharp shoulder at 1215.51 P=O (phosphoramide) and 928.66 cm^{-1} P-OR (esters) are for the phosphorus groups. The IR peak at 1025.25 cm^{-1} denotes for Si-OR (silicon) group (OCW, 2008). All the functional groups were described in image clear that richness of sediment river quality.

The qualitative and quantitative analysis of metals present in sediment by the EDX and AAS are in accordance with the FTIR spectra which also confirms by the shoulders obtained in the region 450-750 cm^{-1}. This FTIR study confirms that surrounding sediment of a river is contaminated with metallic toxicants come from the neighboring city. In Figure 4 showing the chromatogram that was peck 1 - up stream peck 2 - midstream and peck 3 - downstream.
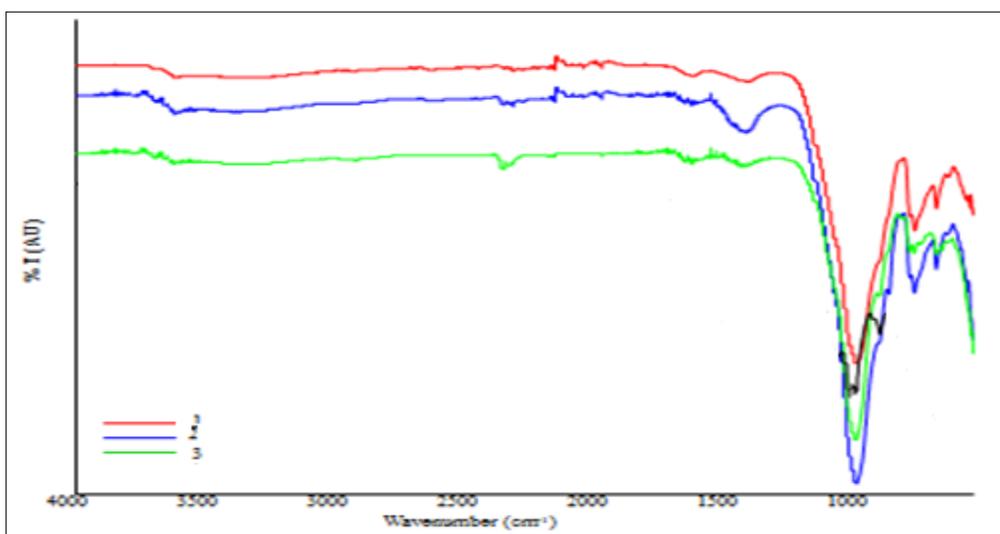

Fig. 4:- ATR-FTIR spectra of sediment

Grain size of river sediment:-

The granule size identified in selected locations (up, mid and downstream) of sediments sample and results indicate that size of particles of upstream has smaller than midstream and downstream. These changes in particle size were due to adding on the organic matter substances by domestically in the river. This organic matter effect also percolation of river water to ground water. The particle size results showing in Figure 5. The small particle sizes more in midstream of sediment because more organic matters are mixing by surrounding Lucknow city, which are affected the sediment compositions. Whereas, more than 250-micron size particles have found in midstream because concrete of city surrounding accumulated in the river.
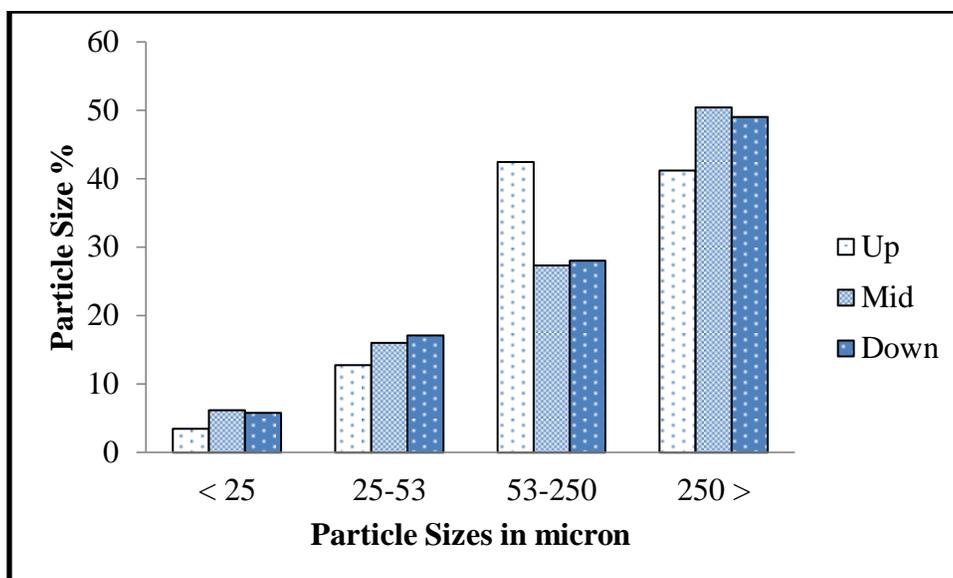
Fig.5:- Particle size percentage in river bed sediment quality

Physicochemical characteristics of sediment samples:-
The results of physicochemical characteristics in sediment average values of up, mid and downstream 8.10, 7.88 and 7.95 for the pH, 36.04, 56.06 and 38.10 mg/kg for chloride, 23.07, 27.84 and 24.80 mg/kg for sulphate, 0.79, 0.26 and 1.01 mg/kg for phosphate, 0.56, 0.69 and 1.00 mg/kg for OC and 0.96, 1.19 and 1.72 mg/kg for OM respectively (Table 2a). Both sediments and soils frequently contain aggregates composed of mixtures of mineral and organic matter which remain stable during transport in water and in an air (Edwards, 1967 and Tisdall, 1982).

The metal analysis of sediment sample also finds out in up, mid and downstream samples. Total 11 metals determine such as Cd, Pb, Cr, Co, Mn, Ni, Cu, Fe, Zn, Mg and Hg. The results of metals in sediment via. up, mid and downstream like 2.3, 9.7 and 3.6 for Cd mg/kg, 5.3, 13.5 and 9.9 for Pb mg/kg, 7.7, 10.7 and 8.4 for Cr mg/kg, 1.2, 4.4 and 3.7 for Co mg/kg, 78.4, 94.9 and 77.3 for Mn mg/kg, 10.3, 15.7 and 8.7 for Ni mg/kg, 30.6, 44.3 and 41.3 for Cu mg/kg, 698, 1459 and 1769 for Fe mg/kg, 63.7, 91.7 and 88.4 for Zn mg/kg and 1265, 1925 and 1532 for Mg mg/kg respectively (Table 2b). In a case of mercury results find out like upstream 0.011, midstream 0.035 and downstream 0.023 µg/kg for Hg respectively. The values of metals compared to prescribe standard by USEPA, non-polluted guidelines for classifying sediment quality criteria (µg/kg, dw). The value was compared and find out that Cd, Co, Cu value is higher than a standard in river other values were found out under than the prescribed limit.

Table 2:- Sediment results of physicochemical characteristics and b- metal concentration a- Sediment physicochemical characteristics results

Sample	pH	Chloride	Sulphate	Phosphate	OC	OM(%)	
Upstream	8.10	36.04	23.07	0.79	0.56	0.96	
Midstream	7.88	56.06	27.84	0.26	0.69	1.19	
Downstream	7.95	38.10	24.80	1.01	1.00	1.72	

b- Sediment metal concentration (mg/kg) and standard values given in µg/kg

Sites	Cd	Pb	Cr	Co	Mn	Ni	Cu	Fe	Zn	Mg	Hg
Upstream	2.3	5.3	7.7	1.2	78.4	10.3	30.6	698	63.7	1265	0.011
Midstream	9.7	13.5	10.7	4.4	94.9	15.7	44.3	1459	91.6	1925	0.035
Downstream	3.6	9.9	8.4	3.7	77.3	8.7	41.3	1769	88.4	1532	0.023
Criteria*0.0	<40	<25	NA	<300	<20	<25	<17000	<90	-	<1	

*USEPA, Non-polluted guidelines for classifying sediment quality criteria (µg/kg, dry weight).

Conclusion:-
The pollution episodes around urban regions, where rivers are affected by anthropogenically activities, the Gomati River in Lucknow, present a good example that can be used to compare and contrast the effect of urbanization on the sediment profile and elemental compositions. The disturbances in sediment characteristics (physically, morphology,

chemically, mineralogy and particle sized) have drastically changed due to extra activities in a river system. The changing of sediment structures are interference in many ways via. flow rate, adsorption/ absorbing of minerals, exchange and chelating of compounds. Present finding heavy metals concentration found higher than the standard and Hg found below the standard but Hg is a very toxic for aquatic as well as human being in the river system. It is evident from the present study that the urbanization process has a great influence on transportation and accumulation of these toxic heavy metals in the Gomati River. The present study can provide useful information for river sediment structural/ morphology condition, pollution control strategies and urban environmental planning in Lucknow, city as well as other and River system.

Acknowledgments:-

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