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# Heavy metals and metalloids in soils and groundwater contamination in Fatehpur Sikri and Sikandra area of Agra district (India)

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**Abstract**
Assessment of heavy metal and metalloids pollution in soils and groundwater was carried out at the two key sites in Fatehpur sikri and Sikandra area of Agra district of UP. (India). The geological structure, hydrogeological conditions and contamination of soils and groundwater were studied at the key sites and contaminants migration in the vadoze zone and groundwater was simulated. The results of statistical analysis prove that at the key site in Agra was elevated concentrations of some chemical elements leading to soil pollution with heavy metals as: Cd, Cu, Pb and Zn are related to technogenic and industrial activities. The modeling of ground- and surface water contamination showed that the area of sewage influence on groundwater is limited and that there is no hazard of river water contamination in the long term perspective. The fill ground and ancient alluvium at the key site in Agra district (India) the multi element (Pb, Cu, Zn, Ni, Cd, Mn, Cr, As, oil products) contamination of soil, which is substantially variable both by depth and area. The modeling results permitted assessing the hazard of contaminated soils as the secondary long acting source of groundwater contamination. The geological structure and hydrogeological differences between the key sites determined the use of different models for the investigation of heavy metals migration in the aquifers.

**Keywords:** heavy metals, metalloids soils and ground water, Agra district

## Introduction
Rural and Urban areas with sources of different contamination in types and scales which provide the ingress of various contaminants and pose hazards to groundwater and soils in Agra district. Agra popularly known as the Taj city (27 10 $N^0$, 7802 $E^0$) is located in the North central park of India. It is bounded by the arid Thar desert of Rajasthan on two third of its periphery. Tha Taj city is famous for its Petha and leather industry all over the world. The research of soils and aquifers contamination by heavy metals and metalloids was performed in the framework of Agra district for Basic Research. The investigations have been carried out at key sites at Fatehpur sikri and Sikandra Agra district (India), where soil media plays a pivot role in assessing the quality of water. Present investigation were carried out for the geological structure, hydrogeological conditions and contamination of heavy metals in soils and groundwater were studied time to time by various Scientist [1, 2, 3, 4]. The second stage the contaminants of heavy metals migration in the granite aquifer and groundwater was stimulated.

## Materials and Methods
The key site is located within the area of former disposal fields, which were put into operation in the reclamation of disposal fields has started. Sludge was partially removed, and partially it remained on the treatment pond bottom. Uncontrolled dumps of domestic and industrial waste appeared somewhere within the former disposal fields. Borehole cores showed interlayers of organic municipal waste in the fill profile. The fill ground is underlain by ancient alluvial sandy deposits. The main aquifers are the following: the aquifer in quaternary sand and the rocky, red stone and granite aquifer in middle carboniferous limestone. The above-lime, rocky red stone and granite aquifer appear to be closely connected within the so-called hydrogeological windows. The rapid transfer of contaminants from the above-limestone to rocky red stone and granite aquifer is supposed. The key site Fatehpur sikri and Sikandra area of Agra district of UP. (India) in 2018-19. Consist of one major rock formation of medium to coarse grained granite. The aquifer represents a water bearing confined unconfined aquifer composed of fractured granites and the weathering layer developed on their surface. The stream is fed by the area infiltration and also by the inflow from the high watershed in the northwest of the region. High fractured granites are underlain by low fractured granites, with very insignificant groundwater movement in the latter.

## Results and Discussion
The key site in Fatehpur sikri and Sikandra area of Agra district of UP. (India) among heavy metals the total highest concentrations were registered for Mn, Pb, Cu and Zn (7727, 4480, 2982, and 1157 mg/kg,). In general, the geochemical associations that show the technogenic contamination may be represented as and index on the right of the chemical element symbol designates the maximal value and the ratio of actual component content to its baseline concentration in Fatehpur sikri Agra district: in the fill ground - $Pb_{112}$ $Cu_{60}$ $Cd_{11}$ $Ni_{6,\ 4}$ $Hg_{5,\ 7}$ $Zn_{4,\ 8}$ $Mn_{1,\ 8}$ and in the alluvial deposits-$Hg_{77}Pb_{29}Cu_{9}$,$3Cd_{3,5}Zn_{3}Mo_{2,6}Sb_{2,6}$ $Ni_{2,3}$ $Mn_{2}$,1. High contrast anomalies were observed for Hg, Pb, Cu, Ni, Cd, Zn, which is associated with the specific use of

the study area. The highest concentrations of elements were found in the fill ground as shown in Table -1 and the bulk of the territory shows the trend to decreasing the element concentration with the depth. Based on eigen values and varimax rotation 4 factors explained 69.6 % of total variance in fill dump soils. Factor 1 as the main factor (33.2 %) has loadings on Pb, Cd, Cu, Co. This association is considered to represent ground contamination by the industrial sewage sludge. Three factors explained 67.4 % of total variance in alluvial deposits. Factor 1 as the main factor (43.5 %) has loadings on As, Sb and Co.

Groundwater in above-lime stone aquifer present pH in the range of 7.12-7.35: and a dry residue value between 308 and 862.0 mg/l. The Indian standards for the main components are exceeded mainly for oil products, NH +, Fe, Mn and Cd. Polluting elements Pb, Cu, Zn and Ni in the concentration of which in grounds exceeds MPC significantly appear to be present in the groundwater [5] in amounts lower than MPC, which is explained by the high adsorption capacity of ground.

Soils in Sikandra area of Agra and study area were found to contain a high concentration of heavy metal as compared to their normal distribution. The soil samples has maximum concentrations for As, Co, Cr, Cu, Mo, Ni, Pb, Se, Th, U and Zn and result are given in Table-1. High levels of these elements are observed in some pockets only close to some of the industries manufacturing steel and chemicals, as well as oil refinery and steel plant. Based on the values and varimax rotation 4 factors explained 91.06% of total variance. Factor -1, has loadings on Ba, Co, Cr, Cu, Mo and Ni. This element association is considered to represent the lithology of the study area, natural or anthropogenic input. Factor 2 has loadings on As, Cd and Pb; it indicates the anthropogenic activity in agriculture due to spray of pesticides. Factor loading > 0.75 for Uranium and Thorium indicates geogenic source from the surrounding Granitic Terrains. Factor 3 - Se and Zn > 0, 70. Factor loading indicates the anthropogenic influence due to deposition and absorption by clay minerals and calcareous soils formed due to weathering of parent granite rocks.

**Table 1:** Minimal, maximal and average concentrations of chemical elements (mg/kg) at the key (1-«Fatehpur sikri», fill ground, 2-«Fatehpur sikri», alluvial deposits, 3-«Sikandra », soils)

| Element | Min | | | Max | | | Mean | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Pb | 43.4 | 7.8 | 42.9 | 4480.0 | 1169.2 | 106.0 | 326.0 | 134.3 | 65.5 |
| Cd | 0.2 | 0.2 | 0.3 | 10.9 | 4.3 | 0.70 | 1.5 | 1.2 | 0.5 |
| Cu | 23.4 | 14.8 | 8.8 | 2981.7 | 463.2 | 42.9 | 252.3 | 1.2.2 | 220.2 |
| Zn | 56.9 | 17.9 | 58.1 | 1157.2 | 626.7 | 161.0 | 281.7 | 117.3 | 81.6 |
| Ni | 14.4 | 8.2 | 18.9 | 746.2 | 227.1 | 54.6 | 96.0 | 60.3 | 30.9 |
| Co | 1.2 | 0.3 | 5.6 | 10.7 | 3.3 | 22.9 | 1.8 | 1.4 | 10.2 |
| Mo | 0.05 | 0.01 | 0.6 | 6.5 | 7.90 | 2.2 | 1.4 | 0.7 | 1.4 |
| Cr | 2.7 | 2.4 | 10.8 | 207.8 | 94.3 | 80.4 | 60.7 | 31.6 | 33.7 |
| As | 0.2 | 0.1 | 5.1 | 3.3 | 1.6 | 14.7 | 0.6 | 8.26 | 8.25 |

Groundwater samples from Sikandra study area were characterized by pH values ranged from 7.6 to 8.8. The Cd ranges from 0.089 to 4.974 µg/L with an average value of 3.341 µg/L, which exceeded the limits of the Bureau of Indian Standards (BIS) guideline values for potable water. Other heavy metals slightly exceed the permissible limits. The groundwater chemistry is more influenced by industrialization activities and urbanization than by the aquifer rock type. Among the investigated toxic metals, Cd, Cu, and Zn are exceeding the BIS guideline values for potable water in respect of health hazard [6].

The hazards of soils in the vadoze zone as a secondary source of groundwater contamination at the Mar'ino site, we performed the predictive modeling of cadmium migration. Cadmium was selected as a pollutant because it is the heavy metal with the lowest maximum permissible concentration (MPC) in the groundwater used for potable water supply. The methodical approach included the following steps: (1) determination of cadmium distribution coefficient proceeding from the epignosis modeling; and (2) prediction of cadmium concentration coming from the vadoze zone at the groundwater table after the site building-up. According to the modeling results, the calculated dynamics of the vadoze zone condition shows that the outcome of elevated concentrations of dissolved cadmium will go on for centuries. The maximal concentration (0.34 mg/l or 340 MPC) was predicted for the year of 2400, which two orders exceeds MPC [7].

Cadmium migration with leakage from the factory in Sikandra study area was modelled for a period of 100 years with formation of cadmium concentration and adsorbed cadmium profiles in the beginning of a stage. The model with double porosity was adopted, with moisture mass transfer between these areas being proportional to the difference in moisture content [8]. The results showed that the cadmium concentration in water coming from the vadoze zone to the groundwater level is equal to 0.6 mg/l. Further, contamination will rise to reach the value of 1.2 mg. The contamination source was supposedly located in three points of water catchment basin differing in functional purpose and hypsometric elevations. The concentration that reaches the groundwater level according to the mass transfer modeling in the vadoze zone was taken as the initial concentration. The results showed that contamination front wherever it forms within the water catchment basin spreads mainly in the upper part of the aquifer. It appears to be attracted to the local drainage network with higher filtration and migration parameters; the further contamination front spreading is confined to this network. Somewhere the contamination front comes across surface water bodies, draining the groundwater flow. In this event, the contamination front advance slows down considerably, as the surface water captures the bulk of pollutants. The contamination front gradually penetrates also the deeper aquifers, which do not discharge to lakes or ponds. This deeper front moves through the Sikandra water catchment basin to the Yamuna River. However, its advance is very slow. It may reach the Yamuna River only in hundreds years.

## Conclusions

The results of joint studies at two key sites in Fatehpur sikri and Sikandra, area of Agra district of UP. (India) showed the multi element contamination of soils, mainly by heavy metals, in both cases. The contamination level and the composition of pollutants are controlled by the impact of industrial and municipal sources, which are similar in many respects for both megacities. The revealed differences are mainly related to the peculiarities in the territory use, different composition of deposits and specific features in element migration. The geological structural and hydrogeological differences between the key sites determined the use of different models for the investigation

of heavy metals migration in the vadoze zone and in the aquifers. The modeling results permitted assessing the hazard of contaminated soils at the Fatehpur sikri site as the secondary long-acting source of groundwater contamination. At the Sikandra key site, the modeling of ground- and surface water contamination proved that the area of polluted sewage influence on groundwater is limited and that there is no hazard of Yamuna river water contamination in the course of many years.

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