

**STUDIES ON DISTRIBUTION AND
FRACTIONATION OF HEAVY METALS IN
YAMUNA RIVER SEDIMENTS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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FRACTIONATION OF HEAVY METALS IN
YAMUNA RIVER SEDIMENTS**

by

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Submitted

**in fulfillment of the requirements for the degree of Doctor of Philosophy
to the**



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CERTIFICATE

This is to certify that the thesis entitled “**Studies on Distribution and Fractionation of Heavy Metals in Yamuna River Sediments**”, being submitted by **Mr. Maneesh Jaiswal** to the Indian Institute of Technology, Delhi (India) for the award of the degree of **Doctor of Philosophy** in Civil Engineering, is a bonafide research work carried out by him under our joint supervision. The thesis work, in our opinion has reached the standard, fulfilling the requirements for the said degree. Further, we certify that this submission is Maneesh’s own work and that, to the best of our knowledge and belief, it contains no material previously published or written by another person which to a substantial extent has been accepted for the award of any other degree or diploma of any University or Institute, except where due acknowledgement has been made in the text.

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ABSTRACT

The data on the concentration, distribution and fractionation of heavy metals in sediments, as well as in the aqueous phase for Yamuna riverine system are a requisite for the development of a comprehensive understanding of the impact of trace metals on water quality of Yamuna. Through the use of such additional data, it may be possible to begin to identify sources and sinks and the fate and potential effects of toxic or environmentally necessary metals. Similarly, sediment-chemical data are a requisite for transport modelling, for estimating geochemical cycles, and for inferring the availability of various trace metals in an ecological system.

Sediment is an important and dynamic part of the river catchments and basins. Heavy metals make way in to the aquatic environment are ultimately incorporated into the aquatic sediments. In the natural water systems, toxic metals are typically of high orders of magnitude in the sediments as compared to those in overlying river waters. The total heavy metal load is more than 90 % in aquatic system is bound to the particulate matter and sediments. Many factors like geology, agricultural activity, industrialization, changes in land use pattern and biological productivity regulate the metal load in the river sediments. Recently, the heavy in sediments has received much attention due to the toxic and persistent characters.

Trace metals making way to natural water become part of the water-sediment system. Their distribution processes are controlled by a dynamic set of physical–chemical interactions and equilibria. The distribution of metals between the solid and liquid phase of the riverine system may be due to variety of processes including solubilization, competitive chelation, ion exchange, precipitation, sedimentation, adsorption and complexation phenomena. They are not permanently fixed by sediment. The metal solubility is principally controlled by pH,

concentration and type of ligands and chelating agents, oxidation-state of the mineral components and the redox environment of the system.

Most of earlier studies have been carried out mostly on total metal concentrations in water and sediments which generally does not provide significant indication of toxic potential of heavy metals. Very limited analysis has been performed on speciation/fractionation of heavy metals in the sediments of Indian rivers and therefore the need for intensive work/research in these areas being felt. In Indian context, the majority of studies are centred around the stretch of Yamuna river in Delhi and a few cities on other Indian rivers. This gives a bigger scope of studies for all Indian rivers at great length. Therefore, the scope of present study also includes fractionation analysis of heavy metals in sediments of Yamuna river throughout its stretch beginning from near Yamunotri, Uttarkashi district of Uttarakhand till near Sangam in Prayagraj district of Uttar Pradesh.

This study investigated different types of heavy metals namely, arsenic, cadmium, chromium, copper, lead, nickel, zinc and manganese found in water and sediments of Yamuna River along with their speciation studies. This Fractionation study helps in assessing bioavailability and potential toxicity due to heavy metal in the river water. The seasonal variation of the water quality and heavy metals concentration in Yamuna River water have also been covered under this study.

The study reveals that there is a considerable variation in the concentration of heavy metals in water and sediments of Yamuna River. This variation may be due to the change in the volume of industrial and sewage waste being added to river at different sampling stations. Both natural processes, such as precipitation inputs, erosion, weathering of rocks, and anthropogenic sources, viz. municipal wastewater, industrial effluents and agricultural runoff are identified to be the contributors of heavy metals to the Yamuna River system. Important among the natural sources is the weathering of rocks whereas agricultural runoff, municipal wastewater and

industrial effluents contribute heavy metal content to different degrees depending upon the quantum of load. Mining activities are not common in this stretch of the river. Municipal and industrial wastewater discharge constitutes a constant source of pollution, whereas surface run-off is a seasonal phenomenon, largely affected by climate in the basin. Seasonal variations in precipitation, surface run-off, interflow, and ground water flow have a strong effect on river discharge and subsequently on the concentration of pollutants in river water. Discharges of industrial, agricultural wastes and of municipal sewage water appear as the major sources for water quality deterioration in this study area. The elevated levels of these heavy metals could ultimately contaminate the cultivated crops, fish and thus making them toxic for human consumption.

The fractionation profile of heavy metals in sediments indicates bioavailability of associated metal in different fractions and hence different potential of toxicity. It seems the fractionation profile obtained for some metals in the study matches with some earlier reports, however for some metals like lead different results have been obtained.

Delhi is the major contributor of pollution in the Yamuna river, followed by Agra and Mathura. There is considerable enrichment of metals at Delhi and Agra due to massive population, haphazard urbanization and presence of huge number of small scale industrial units which discharge its untreated and partially treated wastewater into the Yamuna river. As a result, the Delhi segment of the river is considered as one of the intensely polluted rivers stretches of the world.

Finally, it may be recommended that regulatory steps should be taken by the government to check the heavy metal pollution of the Yamuna river system which is continuously being used for drinking, agriculture, religious and other industrial purposes.

सारांश

तलछट में भारी धातुओं की सांद्रता, वितरण और अंशांकन/ भिन्नकरण के साथ-साथ यमुना नदी प्रणाली के जलीय चरण पर डेटा, यमुना के पानी की गुणवत्ता पर ट्रेस धातुओं के प्रभाव की व्यापक समझ के विकास के लिए आवश्यक है। इस तरह के अतिरिक्त डेटा के उपयोग के माध्यम से, स्रोतों और सिंक और विषाक्त या पर्यावरणीय रूप से आवश्यक धातुओं के भाग्य और संभावित प्रभावों की पहचान करना शुरू करना संभव हो सकता है। इसी प्रकार, तलछट-रासायनिक डेटा परिवहन मॉडलिंग के लिए, भू-रासायनिक चक्रों का अनुमान लगाने के लिए, और पारिस्थितिक तंत्र में विभिन्न ट्रेस धातुओं की उपलब्धता का अनुमान लगाने के लिए आवश्यक है।

तलछट नदी जलग्रहण क्षेत्रों और घाटियों का एक महत्वपूर्ण और गतिशील हिस्सा है। भारी धातुएँ जलीय वातावरण में प्रवेश करती हैं और अंततः जलीय तलछट में शामिल हो जाती हैं। प्राकृतिक जल प्रणालियों में, ऊपरी नदी जल की तुलना में तलछट में विषैली धातुएँ आमतौर पर उच्च स्तर की होती हैं। जलीय प्रणाली में कुल भारी धातु भार 90% से अधिक है जो कण पदार्थ और तलछट से जुड़ा है। भूविज्ञान, कृषि गतिविधि, औद्योगीकरण, भूमि उपयोग पैटर्न में परिवर्तन और जैविक उत्पादकता जैसे कई कारक नदी तलछट में धातु भार को नियंत्रित करते हैं। हाल ही में, विषाक्त और लगातार बने रहने वाले लक्षणों के कारण तलछट की भारी मात्रा पर बहुत अधिक ध्यान दिया गया है।

प्राकृतिक जल में प्रवेश करने वाली ट्रेस धातुएँ जल-तलछट प्रणाली का हिस्सा बन जाती हैं। उनकी वितरण प्रक्रियाएं भौतिक-रासायनिक अंतःक्रियाओं और संतुलन के एक गतिशील सेट द्वारा नियंत्रित होती हैं। नदी प्रणाली के ठोस और तरल चरण के बीच धातुओं का वितरण घुलनशीलता, प्रतिस्पर्धी कीलेटीकरण, आयन विनिमय, वर्षा, अवसादन, सोखना और संयोजन क्रिया सहित विभिन्न प्रक्रियाओं के कारण हो सकता है। वे तलछट द्वारा स्थायी रूप से स्थिर नहीं होते हैं। धातु की घुलनशीलता मुख्य रूप से पीएच, संघटन और लिगेंड और चैलेटिंग एजेंटों के प्रकार, खनिज घटकों के ऑक्सीकरण-अवस्था और सिस्टम के रेडॉक्स वातावरण द्वारा नियंत्रित होती है।

पहले के अधिकांश अध्ययन पानी और तलछट में कुल धातु सांद्रता पर किए गए हैं जो आम तौर पर भारी धातुओं की विषाक्त क्षमता का महत्वपूर्ण संकेत नहीं देते हैं। भारतीय नदी के तलछट में भारी धातुओं के भिन्नकरण-अंशांकन अध्ययन पर बहुत सीमित विश्लेषण किया गया है और इसलिए इन क्षेत्रों में गहन कार्य-अनुसंधान की आवश्यकता महसूस की जा रही है। भारतीय संदर्भ में, अधिकांश अध्ययन दिल्ली में यमुना नदी के विस्तार और अन्य भारतीय नदियों पर स्थित

कुछ ही शहरों पर केंद्रित थे। यह सभी भारतीय नदियों के लिए विस्तृत अध्ययन का एक बड़ा दायरा प्रदान करता है। इसलिए, वर्तमान अध्ययन के दायरे में उत्तराखंड के यमुनोत्री, उत्तरकाशी जिले से लेकर उत्तर प्रदेश के प्रयागराज जिले में संगम के पास तक पूरे हिस्से में यमुना नदी के किनारे भारी धातुओं पर अंशांकन अध्ययन भी शामिल है।

इस अध्ययन में यमुना नदी के पानी और तलछट में पाए जाने वाले विभिन्न प्रकार के भारी धातुओं जैसे आर्सेनिक, कैडमियम, क्रोमियम, तांबा, सीसा, निकल, जस्ता और मैंगनीज की जांच के साथ-साथ उनके भिन्नकरण अंशांकन अध्ययन की भी जांच की गई। यह फ्रैक्शनेशन अध्ययन नदी के पानी में भारी धातु के कारण जैव उपलब्धता और संभावित विषाक्तता का आकलन करने में मदद करता है। इस अध्ययन के अंतर्गत पानी की गुणवत्ता में मौसमी बदलाव और यमुना नदी के पानी में भारी धातुओं की सांद्रता को भी शामिल किया गया है।

अध्ययन से पता चलता है कि यमुना नदी के पानी और तलछट में भारी धातुओं की सांद्रता में काफी भिन्नता है। यह भिन्नता अलग-अलग सैंपलिंग स्टेशनों पर नदी में डाले जाने वाले औद्योगिक और सीवेज कचरे की मात्रा में बदलाव के कारण हो सकती है। दोनों प्राकृतिक प्रक्रियाएं, जैसे वर्षा, कटाव, चट्टानों का अपक्षय, और मानवजनित स्रोत, अर्थात् नगरपालिका अपशिष्ट जल, औद्योगिक अपशिष्ट जल और कृषि अपवाह को यमुना नदी प्रणाली में भारी धातुओं के योगदानकर्ता के रूप में पहचाना जाता है। प्राकृतिक स्रोतों में चट्टानों का अपक्षय महत्वपूर्ण है जबकि कृषि अपवाह, नगरपालिका अपशिष्ट जल और औद्योगिक अपशिष्ट भार की मात्रा के आधार पर अलग-अलग डिग्री तक भारी धातु सामग्री का योगदान करते हैं। नदी के इस हिस्से में खनन गतिविधियाँ आम नहीं हैं। नगर निगम और औद्योगिक अपशिष्ट जल का निर्वहन प्रदूषण का एक निरंतर स्रोत है, जबकि सतही अपवाह एक मौसमी घटना है, जो बड़े पैमाने पर बेसिन में जलवायु से प्रभावित होती है। वर्षा, सतही अपवाह, अंतर्प्रवाह और भूजल प्रवाह में मौसमी बदलावों का नदी के बहाव और उसके बाद नदी के पानी में प्रदूषकों की सांद्रता पर गहरा प्रभाव पड़ता है। इस अध्ययन क्षेत्र में पानी की गुणवत्ता में गिरावट के लिए औद्योगिक, कृषि अपशिष्ट और नगरपालिका सीवेज जल का निर्वहन प्रमुख स्रोत के रूप में दिखाई देता है। इन भारी धातुओं का ऊंचा स्तर अंततः खेती की गई फसलों, मछलियों को दूषित कर सकता है और इस प्रकार उन्हें मानव उपभोग के लिए विषाक्त बना सकता है।

तलछट में भारी धातुओं का अंशांकन प्रोफ़ाइल विभिन्न अंशों में संबंधित धातु की जैवउपलब्धता को इंगित करता है और इसलिए विषाक्तता की विभिन्न क्षमता को इंगित करता है। ऐसा लगता है कि अध्ययन में कुछ के लिए प्राप्त अंशांकन प्रोफ़ाइल कुछ पिछली रिपोर्ट से मेल खाती है, जबकि सीसा जैसी कुछ धातु के लिए अलग दृष्टिकोण भी उपलब्ध है।

यमुना नदी में प्रदूषण का प्रमुख योगदानकर्ता दिल्ली है, इसके बाद आगरा और मथुरा इत्यादि हैं। विशाल जनसंख्या, बेतरतीब शहरीकरण और छोटे पैमाने की औद्योगिक इकाइयों की उपस्थिति के कारण दिल्ली और आगरा में धातुओं का काफी संवर्धन हुआ है। परिणामस्वरूप, नदी के दिल्ली खंड को दुनिया की अत्यधिक प्रदूषित नदियों में से एक माना जाता है।

अंत में, यह सिफारिश की जा सकती है कि वर्तमान नदी प्रणाली में प्रदूषण स्तर की जांच के लिए सरकार द्वारा नियामक कदम उठाए जाने चाहिए, जिसका उपयोग लगातार पीने, कृषि, धार्मिक और अन्य औद्योगिक उद्देश्यों के लिए किया जा रहा है।

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