MATHEMATICAL MODEL OF TRANSPORT AND TRANSFORM OF METALS FOR RIVER SYSTEMS

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河流中重金属迁移转化数学模型

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内容简介

本书是对作者近年来有关河流重金属污染的理论研究、数学模型和实验研究成果的系统论述。

本书主要内容包括：河流泥沙随机吸附理论和随机吸附模型、河流泥沙吸附重金属的实验研究、重金属释放动力学、影响重金属释放因素的实验研究、河流紊动条件下重金属释放动力学模型、河流中重金属迁移转化的一维和二维确定性数学模型及解析解等。

本书的研究内容得到了国家自然科学基金和陕西省自然科学基金的资助。

本书可供从事水资源保护、环境工程、市政工程、环境影响评价、环境化学、水处理等方面的科技工作者及大专院校师生参考。

前　言

随着工业的发展，排入到河流中的大量污染物质、特别是重金属污染物，严重地污染了河流水体，使河流水质恶化，给人类造成了一系列不利的后果。为了对河流环境污染进行控制和治理，需要探明河流中重金属迁移转化规律，建立河流重金属水质模型，来预测河流中重金属污染物浓度随时间和空间的变化情况，并为确定河流中重金属水环境容量提供基本依据。

建立数学模型是水污染控制研究工作的重要内容之一，水质模型的研究已有 60 多年的历史。早在 1942 年，美国两位工程师 Streeter 和 Phelps 在关于美国俄亥俄河天然净化过程的研究中，建立了世界上第一个水质模型。半个世纪以来，许多研究者在这个模型基础上，不断地改进、发展和完善。现在已发展成各式各样的、应用于不同情况的（河流、海湾、河口、水库、湖泊和地下水等）较为完善的水质数学模型。不过这些模型主要是针对 BOD、DO 等水质指标而言的。对于重金属污染物在河流的迁移转化模型，文献报导不多。虽然在重金属对河流的污染方面，人们已经作了不少研究工作，但是关于重金属污染物的河流水质模型的研究还不多，这主要是因为大多数重金属污染物具有生物可给性，在水环境中不易为微生物所降解，而且能被水生生物累积富集等。另一方面，因为重金属在水体中的吸附、解吸、络合、沉降、絮凝等化学过程及物理化学过程非常复杂，因此，对重金属水质模型的研究大多停留在定性研究阶段，虽然也有一些定量研究成果，但不够系统化。要建立一个完整的河流重金属水质模型，是一个涉及多学科的复杂问题，它与河流中重金属的迁移转化过

程、河流流动规律、河流泥沙运动规律以及河流中生态因素都有密切的关系。

河流中重金属迁移转化过程包括如下几个方面：水体中重金属污染物通过水面向空气中的扩散过程；吸附于悬浮物和沉积物后向固相迁移过程；底部沉积物中已吸附的重金属向间隙水中释放而又重新进入水体的过程；重金属污染物在水体层流状态下的分子扩散迁移过程；在紊流状态下的对流扩散迁移过程；水体中悬浮物吸附重金属污染物后向底层沉降和流动中的絮凝过程。对这样的环境体系，把化学反应、扩散和传质过程等综合起来构成数学模型，确定有关的平衡常数、动力学常数、传质速度常数，经数学运算求得重金属污染物的溶解态、吸附态的浓度分布解析解或数值解，这就是河流重金属水质模型的基本内容。所以，一个较为完善的河流重金属水质模型，必须要充分考虑河流重金属迁移转化过程的各个方面，必须研究重金属在河流中的紊动扩散规律，研究重金属的吸附和解吸规律，研究河流悬浮物的运动规律，研究河流泥沙絮凝规律，只有把这些问题搞清楚了，才能建立较为合理的重金属水质模型。

全书由 8 章组成。

第 1 章对河流重金属水质模型、固体颗粒表面吸附模型、固体颗粒表面吸附实验研究、环境化学条件对底泥中重金属释放的影响、水流紊动条件下河流底泥中重金属释放等方面的研究成果进行了详尽评述。

第 2 章介绍了作者提出的河流泥沙随机吸附理论。即从随机过程的观点出发，建立了河流泥沙随机吸附模型，对随机模型的特性进行了详细的分析。随机吸附模型可以用来描述河流泥沙对重金属污染的吸附过程。讨论了吸附系数 k_1、平衡液重金属离子浓度 C 和均方差 D 对吸附量 W 的概率密度函数 $P(W)$ 的影响情况。提出了综合参数 Z 的概念。Z 能反映参数 k_1、C、D 的综合影

响效果。我们还收集了大量河流泥沙吸附重金属污染物的试验资料，对本文提出的河流泥沙随机吸附模型进行了验证，计算值和实测值吻合较好。提出的该随机吸附模型不仅可以描述河流泥沙吸附重金属污染物的吸附过程，还可以用来描述土壤对化肥、农药的吸附过程，并且经适当修正，可以用来描述固体颗粒对气体的吸附过程。

第 3 章介绍了渭河和汉江泥沙的吸附特性，提出了吸附容量的概念。着重分析了含沙量、温度、矿化度、pH 值、泥沙种类对渭河、汉江泥沙吸附量的影响情况。

第 4 章根据一级反应动力学，考虑到重金属释放过程中的再凝聚、吸附、络合及其沉淀等的影响作用，建立了底泥中重金属释放的动力学方程。按最小二乘原则，编写了模型参数估计程序，以静态悬浮条件下 Cd、Cu、Zn、Pb 的释放实验结果对动力学模型进行了验证，得到了满意的结果。

第 5 章依据所建立的重金属释放动力学模型，以渭河底泥中重金属的释放为研究对象，系统研究了 pH 值、碱度、底泥粒度、污染浓度、悬浮底泥浓度、底泥厚度、重金属结合形态等对重金属释放动力学过程的影响。通过对底泥理化指标如粒度分布、不同粒级底泥重金属背景值浓度、矿物组成、总有机碳（TOC）、溶出碱度等的分析，探明了该底泥中重金属释放的特点。形态分析的结果表明，重金属的离子可交换态和碳酸盐结合态是构成重金属释放的主要结合形态。另外还强调指出了沉积物粒度、溶出碱度在重金属吸附和释放过程中的作用。

第 6 章介绍了模拟河流底泥中污染物（如重金属）释放的动态试验研究成果，建立了水流紊动条件下河流底泥中重金属释放的动力学方程。在不同水流紊动条件下，对底泥中重金属的释放进行了试验研究。试验过程中，对 pH 值、溶出碱度、重金属结合形态、含沙量等指标也进行了测定分析，得出了与静态悬浮实验

条件下基本一致的结论。所不同的是，悬浮底泥中重金属浓度由于其粒度组成的沿程细化而有所增加，重金属释放的动力学过程也略有变化。利用回归分析的方法求得了水流挟沙力计算公式。根据因次分析的方法，得出了相同条件下，同一时刻重金属释放浓度与水流紊动指标 Re 数的相关关系，并结合泥沙运动力学和重金属释放动力学，建立了水流紊动条件下河流底泥中重金属释放的动力学方程。验证结果表明，该模型可有效的描述不同水流紊动条件下的重金属释放动力学过程。

第 7 章介绍了重金属污染物迁移转化的一维确定性模型，研究了一般性定解条件下的重金属污染物在河流中迁移转化的一维确定性数学模型的求解问题。该数学模型包括了河流悬移质泥沙吸附作用、推移质泥沙吸附作用、底泥吸附作用以及河流的对流作用、扩散作用、重金属释放特点等对重金属质量变化的影响。在一般性的定解条件（初始值为任意函数、边界值为任意函数）下，运用拉氏变换方法，求解河流中重金属迁移转化数学模型，给出了溶解态重金属浓度和吸附态重金属浓度的积分表达式。最后用该模型对黄河兰州段上游 Hg 分布情况进行了计算，计算值和实测值基本吻合。

第 8 章介绍了重金属污染物迁移转化的二维确定性模型，研究了河流中重金属迁移转化纵竖向二维数学模型。该模型考虑了河流中悬移质吸附作用和重金属释放的动力学过程，在恒定流情况下，求解重金属迁移转化的二维数学模型，给出了吸附和释放情况下溶解态重金属和吸附态重金属浓度的分析解。

作　者

1995 年 6 月　于西安

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Preface

Since the industrial revolution, the increase amount of waste materials discharged into aquatic environment caused many serious environmental problems and social problems. A growing population further aggravates the situation. This often resulted in transforming lakes, rivers, and coastal waters into sewage deposits where the natural ecological balance is severely disturbed and in some cases totally disrupted. In order to control and treat aquatic pollution, we need to develope mathematical model of heavy metal transport which predicts heavy metal concentration distribution in sediment-laden river water. To set up a complete mathematical model of heavy metal transport in sediment-laden river is a complex problem with a multi-disciplinary approach. Knowledge such as adsorption of heavy metal ions onto sediment, suspended particl transport in river water, turbulence flow and ecology condition are all required inputs.

For water quality model about normal pollutants in river without sediment, there are many research works. Only a few research works about water quality model of heavy metal ions, Cd^{2+}, Cr^{2+}, Pb^{2+} and Hg^{2+} transport in sediment-laden river water can be found. We know that river sediment can adsorb heavy metals, and the amount of heavy metal adsorbed is the main component of total heavy metal in river water. So the water quality model for heavy metal should include adsorptions of suspended sediment and bed load, and advection/diffusion by water flow. One problem in attempting to model heavy metal transport in sediment-laden river is the development of an adsorption-desorption function that accurately describes the rate of heavy metal transfer between the solution and solid phase. The choice of an appropriate function is often difficult due to lack of the knowledge of adsorption-desorption processes for specific chemicals in river sediments. So, follow problems are mainly concerned in this book:

(1) A stochastical adsorption mathematical model of heavy metal onto river sediments and suspended particles has been established by using stochastical process theory. According to this adsorptive model we can find that relative adsorption value of heavy metal adsorbed by sediments and probability density function are influenced mainly by C, the concentration of dissolving heavy metals; K_1, the adsorption coefficient; D, dispersion coefficient. Based on the experimental results, we have tested and verified the stochastical adsorption model of heavy metals on sediment. The stochastical adsorption mathematical model can be also applied to describe the adsorption of chemical materials on soil particles and the sorption of gas on solid surface.

(2) Experimental study on heavy metal ions onto sediment of Wei River, a main branch of Yellow River, and Han River in China has been made. By introducing the concept of adsorptive capacity, it can be used to well describe the adsorption characteristics of heavy metal onto river sediment with high concentration. Environmental factors such as temperature, total ion number, sediment type, heavy

metal ions species, pH value, coexisting of different heavy metal ions will affect the adsorption value of heavy metal ions onto Han River sedimant and Wei River Sediment.

(3) A kinetic model of heavy metal release is developed. Based on the kinetics of the first-order reactions and in consideration of the effects of coagulation, adsorption, complexation, coprecipitation etc., during the heavy metal release from sediments, a kinetic model is developed. Under the laboratory static conditions, by making use of the experimental results of Cd, Cu, Zn, Pb releasd from the suspended sediments to testify the kinetic model, it is proved that the kinetic model can satisfactorily describe the kinetic process of heavy metal release. Under the experimental condition, the effect of water turbulent intensity on heavy metal release is also discussed.

(4) A systematic experimental study on heavy metal release is completed. According to the kinetic model, and by taking the sediments of Wei River, a main branch of Yellow River, as the studied object, systematic experiments and analysises are carried out, which mainly concern the effects of various factors on the processs of heavy metal release. These factors include pH value, dissolved alkalinity, sediment's size fraction, concentration of particulate metal, sediment depth and chemical bounds of heavy metals in the sediment. Through analysing the physical and chemical indexes of the sediment such as particle size distribution and the distributions of the metal geochemical concentrations, mineral compositions, total organic carbon as well as the dissolved alkalinity in different size fraction of the sediments, the characteristics and the regularity of heavy metal release are ascertained. Analysises on the chemical bounds of metals indicated that the exchangeable and the carbonate bounds of

particulate metals are the main fraction affecting the metal release. In addition, it is emphasized that the size fraction and dissolved alkalinity of the sediment play important roles in the process of metal adsorption and desorption.

(5) A kinetic model of heavy metal release fiom river sediments reflceting the effect of water flow turbulence is developed. A formula to calculate the capacity of water flow carrying sediment is obtained by regression analysis. Based on the principle of dimensional analysis, it is derived that the concentration of heavy metal release is corelated with Reynold's number, Re, which reflects the turbulent flow intensity. In view of the dynamics of sediment transport and the kinetics of heavy metal release, a kinetic model of heavy metal release from river sediments reflceting the effect of water flow turbulence is developed. Verifications indicate that this model can efficiently describe the kinetic process of heavy metal release in different flow turbulent conditions. Under different turbulent flow conditions, a series of experiments on the process of heavy metal release are carried out. Some indexes, such as pH value, dissolved alkalinity, metal's chemical bounds, as well as suspended sediment concentration, are also measured and analysed during the experiment, their effects on heavy metal release are basically the same as those gained under the laboratory static conditions. Heavy metal concentration in the suspended sediment increases along the flowing coures and the kinetic process of heavy metal release correspondingly changes a littile because of the increase of fine fraction of the suspended sediment along the flowing course.

(6) 1-D and 2-D equations have been derived and their solutions are also obtained to describe heavy metal transform in rivers,

based on heavy metal adsorption on river sediments. The one-dimensional equation of heavy metal transport in sediment-laden river is obtained. An analytical solution has been derived for heavy metal transport in sediment-laden river under general boundary and initial condition. Equilibrium isotherm for bottom sediment adsorption and kinetic adsorption model for suspended particles adsorption have been incorporated. Using this analytical solution, we have predicted the mercury ions concentration along a section of Yellow River in Lan Zhou China. The analytical solution of heavy metal transport two-dimensional equation has also been derived.

(7) 1-D and 2-D equations have been derived and their solutions are also obtained to describe heavy metal transform in rivers and release from river sediments. Heavy metal release from river sediments is in close relationship with the motion state of the river sediments. According to the characteristics of sediment's movement in rivers, it is considered that the increase of the sediments concentration along the river course during the sediment undersaturation transport is of greater significance for studying heavy metal release. A one-dimensional diffusion equation to simulate the process of heavy metal release in rivers is derived by combining the regularity of the river's sediment transport with the kinetic model of heavy metal release and by taking into account the flow turbulent diffusion in the river. The great differences of the characteristics between the sediment transport and the heavy metal release determine that there is little deviation to treat the undersaturation transport as saturation transport of the river sediments in studying heavy metal release. Then, under the general initial and boundary conditions, analytical solution of the diffusion equation is derived with Laplace Transform

method. With the same method to develop the one-dimensional equation, a two-dimensional diffusion equation is built. By reasonably simplifying the model's initial and boundary conditions, the analytical solution of the two-dimensional equation is also obtained by means of Laplace Transform.

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in Xi'an, P. R. China

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