湘江水系和京津地区河流中锌背景值的研究

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锌属于生命元素，其含量是重要的水质指标之一．过多或缺乏锌均能引起不良的生物效应，损害人体健康．寻求锌的水环境背景值及其在天然水体中的正常含量能提供衡量水污染的程度，判断水质状况．本工作研究湘江水系和京津地区河流中锌的水环境背景值，为水质评价、研究其地球化学过程和合理利用水资源提供科学依据．

一、工 作 方 法

湘江水系采样点设在河源段及主支流上游，共布点27个，见图1．京津区设在供水区并兼顾各河流具有代表性，共布点21个，见图2．

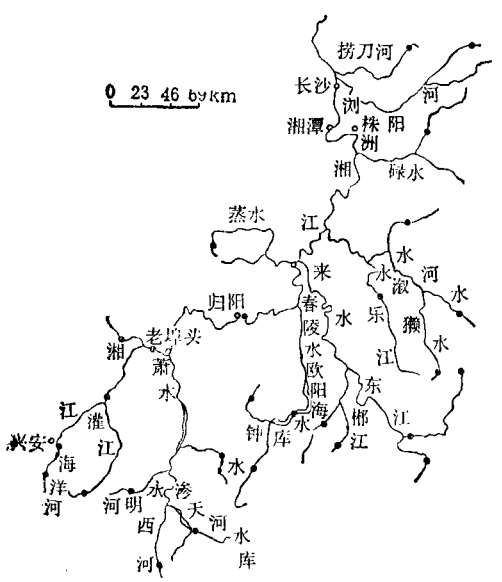

图1 湘江水系采样点示意图

1983 年 10—11 月和 1984 年 11 月对湘江水系采样．1984 年 10 月对京津各河段采样．

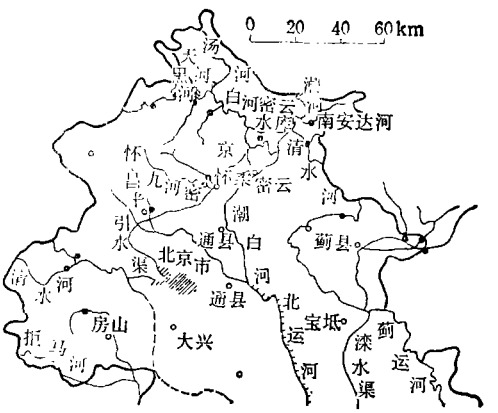

图2 京津地区采样点示意图

水样中锌用悬汞电极 DPASV 法测定．沉积物中锌用 Y-2 型火焰原子吸收法测定．

为将锌的背景值表达得更合理，对河水和沉积物中锌浓度的频数分布类型均作了数理统计检验．结果为正态分布，用算术平均值及其标准差表示．对数正态分布，则用几何均数及其标准差表示．偏态分布，用百分位数法，求第 10 和第 90 百分位数分别作背景值的下限和上限，第 50 百分位数表示背景值．

二、结 果 与 讨 论

1. 锌背景浓度的特征

锌背景浓度的各特征数值列于表 1．

从表 1 元素的全距和变异系数看，湘江水系锌总量与溶解态含量各自的变差不大，最大值与最小值之比分别为2.5 和2.9．总量

表 1　湘江水系和京津地区河水中锌的背景值

环境单元		形　态	样品数（个）	全　距	置信域 95%	背景值	标准差 S	变异系数 %	分布类型
湘江水系	河水（ppb）	总　量	27×2	2.5—6.4	2.3—5.9	4.1	0.92	22	正态
		溶解态	27×2	2.0—5.8	1.9—5.1	3.5	0.81	23	正态
		颗粒态	27×2	0—2.5	0—1.8	0.59	0.63	107	正态
	沉积物（ppm）	原　样	53	12.5—114.3	18.9—112.9	70.9	26.0	36.7	正态
京津河水（ppb）		总　量	21	0.7—3.0	0.54—3.4	1.4	1.59	113	对数正态
		溶解态	21	0.6—2.6	0.54—2.9	1.3	1.52	117	对数正态
		颗粒态	21	0—1.5	下限 上限 →0—0.44	0.06	—	—	偏态

表 2　湘江、二松河源段水中锌的各种形态含量比例（%）

河流	形　态		$M+MA_1+ML_1$	MA_2	ML_2	MA_3	ML_3	MA_4	ML_4
湘江	颗粒态	21	—	—	—	—	—	—	—
	溶解态	79	26.6	62.5	0	4.7	0	4.6	1.7
二松	颗粒态	17.6	—	—	—	—	—	—	—
	溶解态	82.4	17.2	15.6	5.8	4.5	6.6	30.2	2.5

注：M——自由金属离子，MA_1——不稳定无机络合态，ML_1——不稳定有机络合态，
MA_2——不稳定无机吸附态为主＋不被 Chelex-100 树脂截留的不稳定无机络合态，
ML_2——不稳定有机吸附态为主＋不被 Chelex-100 树脂截留的不稳定有机络合态，
MA_3——稳定无机络合态，ML_3——稳定有机络合态，
MA_4——稳定无机吸附态为主＋不被 Chelex-100 树脂截留的稳定无机络合态，
ML_4——稳定有机吸附态为主＋不被 Chelex-100 树脂截留的稳定有机络合态.

在 3.5 至 5.0ppb 范围的样点占 67%，溶解态含量在 3.4 至 4.0ppb 范围的亦占 67%，二者都较集中。与此相比，京津地区河水中，锌两种含量的离散度均较高，各自的最大值与最小值之比都为 4.3。这与不同河流经的岩层等环境条件的差异有关。

湘江与京津区河流中，锌的溶解态含量占极大比例，颗粒态含量都很低，有的河段接近零。这与表 2 所列湘江与第二松花江（以下简称二松）河源段水中锌的形态含量类同。说明天然清洁的河水中，锌的溶解态是影响其行为的主要部分。

湘江与京津河水中锌背景值在世界淡水正常背景浓度范围内。但与国内其他河湖水相比，湘江水中锌含量略偏低，京津河水中锌含量显著偏低。

湘江沉积物中锌的背景值反映了该流域的岩石、土壤与生物等的地球化学特征。从流域有关物质中锌的天然含量比较，该背景值略低于其他河、湖沉积物，但又高于本流域大部分岩石中锌的含量，说明本区河流沉积物锌背景值是亚热带湿热气候条件下，区域表生地球化学过程的综合反映。

2. 湘江水体中锌的形态

环境中元素存在的化学形态与它们的生态效应、迁移转化及其和沉积物之间的相互作用密切相关。所以研究重金属的背景值，不仅要掌握其总量，还要进一步探讨它的存在状态。这样，才能阐明背景值的成因和对水质评价提供全面的科学依据。

表 2 列出湘江河源水中锌的颗粒态和溶解态占总量的比例及溶解态所包含的七种形

态的百分比．锌的溶解态中以不稳定态 MA_2 和 $M + MA_1 + ML_1$ 为最多，二者之和占溶解态总量的 89%．说明湘江清洁水体中，锌的溶解态特别是其中的不稳定态是影响该元素水化学行为的主要成分．这种形态分配比可能与该河源水清沏，颗粒物很少，元素含量低有关．从无机态和有机态总量比看，无机态含量远高于有机态$\left(\frac{\Sigma MA}{\Sigma ML} \gg 1\right)$．这是因湘江上游河床沉积物质地粗、基本上是砂子和卵石，水中有机物含量低，并且流域气候湿热、河水富氧、使有机物分解快．

从表 2 湘江与温带二松源头水中[1]锌的各种形态含量的比较看出，它们具有共性和个性．相同点是溶解态含量都高于颗粒态，溶解态中无机态占有比例均大于有机态．再是湘江水中无机态比例数值高于二松，这与湘江河源水中有机物含量比二松源头水中少有关(前者总有机碳含量为 0.5ppm，后者腐殖质含量为 0.9ppm)．不同点是湘江水中锌以不稳定态为主，其中 MA_2 最多，而二松则以稳定态为主，其中 MA_4 占比例最高．

表 3 湘江河源沉积物中锌的各种形态含量比例(%)

形 态	可交换态	碳酸盐态	铁锰氧化物态	有机硫化物态	残渣态
含量比例	0	6	21	5	68

表 3 列出湘江河源沉积物中锌的五种结合态含量比．除去残渣态外，铁、锰氧化物态占比例最高，其次是碳酸盐态，有机硫化物态很少．湘江流域地表物质富铁、锰，水又偏碱且富氧，使铁、锰易生成水合氧化物胶状沉淀，对重金属有较强的亲合力．另外，据报道在湘江沉积物样品的重金属吸附量中，粘土矿物的吸附占主要地位．由这些结果，可认为在湘江河源，锌从河水进入沉积物的主要途径是通过与粘土矿物及铁锰水合氧化物结合，在这过程中，锌大部分可能先形成 MA_2 形态．其次，锌通过与水中丰富的 HCo_3^- 和 Co_3^{2-} 作用或与其他碳酸盐共沉淀形成各式碳酸盐络合物，即可能形成 MA_1 和 MA_3 形态．水相和沉积物中，锌有机态含量都少，所以锌通过与有机物结合进入沉积物的可能性小．

三、小 结

1. 湘江和京津地区河水中，锌的背景值在世界内陆淡水的背景值范围内．但与国内其他河湖水中锌的天然含量比，湘江水中略偏低，京津河水中明显偏低．湘江河流沉积物中锌的背景值也在世界河湖沉积物中锌的天然浓度范围内，稍偏低．产生这些背景值差异的原因，主要是流域的地质条件及其元素组成、河水的物理化学性质和表生地球化学作用的影响．

2. 湘江河源水中，锌的溶解态含量远大于颗粒态，溶解态中不稳定 MA_2 形态比例最高，这是影响锌环境化学行为的主要因素．根据河水和沉积物中锌存在的形态及报道的有关微量元素吸附试验的结果，认为锌从河水进入沉积物的主要途径是锌和粘土矿物、铁、锰等水合氧化物结合，其中首先可能形成 MA_2 形态．

参 考 文 献

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Abstracts

Studies on the Bio-treatmen Possibility of LAS and the Toxicity of LAS toward *Dephnia magna*

Fan Fengshen and Zhang Zhongxiang (Beijing Municipal Research Institute of Environmental Protection); *Sun Xiaoran* (Tianjin Municipal Research Institute of Environmental Protection, Tianjin)

The results of this work indicate that the removal of LAS (linear alkyl benzene sulfonate) in the municipal sewage plant is due to absorption of activated sludge and biodegradation. LAS in the wastewater will not have great effect on respiration of activated sludge and TOC as well as total nitrogen removal when its below 20 to 40 mg/L. The toxicity of wastewater containing LAS toward *Dephnia magna* will decrease greatly after the biological treatment. The 96h-LC_{50} of LAS to *D. magna* is 6.2mg/L. Thus, when LAS concentration in fishery water is below 1.0mg/L, it may be considered safety. (See pp. 2—8)

Uptake and Depuration of Carbofuran by the Fish and Clam in Water

Chen Jian, Chen Hexin and Fan Defang (Department of Plant Protection, Zhejiang Agricultural University, *Hanzhou*)

There was no significant accumulation of carbofuran in the fish *Tilapia nilotica*, but a slight accumulation occurred in the clam *Anodonta woodiana*. Depuration of carbofuran in the fish and clam after being transfered to carbofuran-free water was rapid. Depuration of carbofuran from dead clam was much slower than living ones. This indicated that physiological and biochemical processes had a significant effect on the depuration of carbofuran from the clams. It was shown that clams could reduce the pH value in water. Because of biodegradation by the clams, the degradation of carbofuran in water was enhanced. In a simulation experiment, it was shown that absorption of carbofuran by bottom mud was not significant. (See pp. 8—12)

Heavy Metals in the Beijing Atmosphere

Wang Anpu, Huang Yanchu and Yan Shulan (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing)

Variations in concentrations of some heavy metals have been observed in different seasons for four years in Beijing area. The results showed that in general the concetrations of heavy metals in particulates were higher in winter than in summer and autumn. The heavy metals Pb, Zn and Cr in fine particles ($<2.3\mu m$) were found to be high at all sampling sites. The enrichment factor (EF) of some heavy metals were calculated. The EF values of metal Fe and Mn at the district of steel industry were higher than those of other sites, but metals Cu, Pb, Zn, Cd, Cr, Co and Mo had high EF values in all sites. This might be due to pollution of anthropogenic sources. The increasing coal combustion in winter and automobile exhaust would be one of important anthropogenic sources of air pollution in Beijing. (See pp. 12—17).

Hazardous Characteristics and Leaching Behaviour of Waste Lead and Zinc Slags

Yang Jingtian, Su Xinjie, Wu Tsingfen and Yun Guichun (Institute of Nuclear Energy Technology, Tsinghua University, Beijing)

Basic emphasis of this work is to analyse and to measure the main physical, chemical and mechanical properties of waste slags from lead and zinc refining processes. Their hazardous characterics are searched according to "The Pollution Control Standard of Solid Waste in Non-ferrous Metals Industry". The results show that both waste slags are harmless.

The factors affecting water-leachable bahaviour of both slags are temperature, pH and precipitation strength. Leaching concentration and amount of most toxic pollutants in the waste slags are increasing as temperature is getting high. So temperature is a significant factor. Leaching of the heavy metals in the waste slags is negatively relative to pH of leach liquor, but positively relative to the anions of fluorine and arsenic. In addition, leaching amount of all pollutants in the waste slags is decreased as rainfall strength increased. In each case arsenic is one of the most hazardous element that pollutes the environment, the next is flourine. The maximal leaching concentrations of arsenic and flourine are 1075 μg/L and 8.48 mg/L respectively in the experiment. (See pp. 17—22)

A Method for Establishing Urban Ecosystem Information Data Base

Wu Shishan, Li Da and Yu Renyuan (Beijing Municipal Research Institute of Environmental Protection, Beijing)

In this paper, how to setablish and use environmental information data base has been discussed. There has been a large number of precious data which were accumulated in the research of environmental problems in Beijing for past years. It is necessary for us to manage them scientifically with advanced techniques. We have established environmental information data base in microcomputer by applying DBASE-II data arrangement system for research of Beijing urban ecosystem and of Beijing district planning evaluation (DONGCHENG). The effect is satisfactory. The method is appropriate to DBASE-III too. (See pp. 27—29)

Background Values of Zinc in the Waters of Xiangjiang River and of the Rivers in Beijing-Tianjin Area

Chen Xibao and Zhang Shen (Institute of Geography,

Academia Sinica, Beijing)

Zinc is an important element for life. Studying its background values in aquatic environment is significant for evaluation of water quality. This work describes that zinc contents in water samples taken from Xiangjiang River in Hunan Province and from from the rivers in Beijing-Tianjin area have been analysed by flame AAS. The distribution types of background values of zinc were handled by mathematical statistic method. The results show that the background values of zinc in the waters above mentioned are in normal ranges compared with world levels. The chemical speciation of zinc in water and sediments of Xiangjing River were studied as well. ASV-labile zinc in dissolved zinc were found as predominant forms in water. The bound to Fe-Mn oxides are major speciations of Zn in the sediments except residual. The background values of zinc and its different species in water are mainly affected by its geochemical charater and environmental factors. (See pp. 30—33)

Effects of Alkali and Alkaline Earth Groups of Population Growth of *Chlamydomonas Reinhardtii*

Shi Jinyuan et al. (Department of Tech. Physics, Peking University); Li Yunzhen (Department of Biology, Peking University)

The influence of alkali and alkaline earth group elementes of different concentrations on the population growth of green algae that is employed as a biological model. A certain regularity between biological effects of the elements and their position in the periodic table has been discussed. *Chlamydomonas reinhardtii* were cultured in the solution containing some inorganic salts. Based on relation rate of proliferation (R) on each element of IA and IIA Groups, the stimulating concentrations (when $R > 100\%$) and inhibitory concentrations (when $R < 100\%$) have been obtained. The results show that the toxicity of the elements on the algae will increase with the increase of their atomic number (Z) in the same group except Li and Mg. (See pp. 33—35)

Determination of the Quantity of Nonbiodegradable/Nonremoval Substances in Industrial Wastewater

Zhou Xiaojian (Environmental Protection Institute of the Ministry of Light Industry, Beijing)

According to the kinetics of biological process, this paper has proposed the determination of the quantity of nonbiodegradable substances in wastewater, which is then applied to the process of an anaerobic treatment and an aerobic treatment respectively. The results are as follows:

(1) In the anaerobic treatment of cotton pulp black liquor with an UASB reactor, when the COD concentration of the influent is 10—13g/L, the concentration of nonbiodegradable subsctances, through measuring and calculating, is 4.147g COD/L. Thus, the average value of the maximum COD removal is 63.3%. Meanwhile, in the batch experiment of the anaerobic treatment of cotton pulp black liquor, the result obtained in the same way is the maximum COD removal can be 63.9%, which further supports this result.

(2) As for the wine lees with the activated sludge process, the average value of the maximum COD removal can be expected to be 86.8%. (See pp. 36—39)

A Study on the Conditions for Treating Wastewater Containing Copper Complex by Reduction-Coagulation Method

Zhang Zhongyan, Yu Shouhui and Zhu Rongfen (Shanghai University of Industrial Technology, Shanghai)

The conditions for treating copper-containing complex wastewater by Fe^{2+} reduction coagulation have been studied. In the mean time, coprecipitation with other inorganic coagulants [$CaCl_2$, PAC, $Fe_2(SO_4)_3$] has been discussed. The results in lab and productive experiments show that when EDTA citric acid or tartaric acid exists in wastewater, the effect of single chemical precipitation on removing copper is very poor. As the unstability of complex copper in acidic solution, Cu^{2+} can be reduced to be Cu^{+} with Fe_2^{+} at $pH = 4.5—5$, and then by increasing pH to 8—9, coprecipitation will take place, In this way the residual copper in outflow is always less than Img/L. Thus, an economical and efficient technology will be presented for treating of cooper-containing complex wastewater. (See pp. 44—48)

Simutaneous Determination of Cobalt, Nickel, Copper, Zinc and Cadmium Using Kalman Filtering Spectrophotometry

Li Zhiliang (Hunan University, Changsha) and *Shi Leming* (China University of Sciences and Technology, Hefei)

A method for simultaneous determination of cobalt, nickel, copper, zinc and cadmium by Kalman Filtering Spectrophotometry has been proposed based on their chelate-forming reactions with 5-Br-PADN in the presence of Tween—80, Satisfactory results were obtained for the analysis of synthetic and river water samples by the method. (See pp. 56—57)

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in the Environment

Kang Junxing and Bao Zhicheng (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing)

Because of the extreme toxicity of some of the polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), the concerns for the health hazards of exposure to PCDD and PCDF led to growing Studies of PCDD and PCDF. The purpose of this review is to provide the information of toxicity, construction, major sources, pollution and human professional exposure of PCDD and PCDF. The current status of PCDD and PCDF in China was also discussed primarily in this article. (See pp. 59—67)