

水生生态系统对稀土元素富集作用的模拟研究*

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摘要 模拟研究了混合稀土进入水生生态系统后, 在浮萍、鲤鱼、水及底泥中的富集和分布。结果表明, 外源稀土进入水生生态系统后, 在底泥和水中的含量随时间波动不大, 而在浮萍和鲤鱼中的含量随时间却有很大的变化。外源稀土在该水生生态系统各组分中的质量以底泥中居多, 约占添加稀土总量的96%以上; 进入浮萍中的稀土在添加稀土总量的0.26%—1.61%之间, 水中则在0.54%—0.91%之间; 鲤鱼中的稀土分量虽均在添加稀土总量的0.035%以下, 但其随时间延长却几乎呈线性增加。文中还分析了鲤鱼对稀土的生物浓缩因子。

关键词 水生生态系统, 富集, 稀土元素, 生物浓缩因子。

稀土微肥可使作物增产和品质得到改善, 因此近年来在我国得到了广泛地推广应用。但交换态^[1]稀土很易进入并污染水环境。有人报道了稀土进入水体后对水生动物的影响^[2-4], 但所涉及的仅是水体和水生动物2种组分。而实际水生生态系统是复杂的, 它应包括多种组分, 因此研究稀土进入水生生态系统后的行为更具现实意义, 目前这方面尚无文献报道。本文研究了稀土进入模拟水生生态系统后, 在浮萍、鲤鱼、底泥及水中的分布、累积情况, 并着重探讨了外源稀土在鲤鱼体中的变化情况。

1 实验部分

1.1 模拟水生生态系统

实验用水生生态系统模拟Y湖(湖面面积约10万m²)主要组成, 所用样品均取自Y湖。将水样500 ml置于1000 ml烧杯中, 并放置鲤鱼(*Cyprinus carpio*)2条(2.0 g/条)、浮萍20.0 g(湿重)、底泥30.0 g(湿重), 加入浓度为1.0 mg·ml⁻¹的混合稀土溶液(以99.9%的La₂O₃、Gd₂O₃和Y₂O₃配制, 其中La:Gd:Y=2:1:1)2.5 ml计2.5 mg(所加稀土量参照大田施用稀土微肥之实际用量^[5]和外源稀土进入土壤后部分呈交换态^[1]而可能进入水体)。

共培养处理10份, 分成平行2组, 每组5份。每10 d取平行2份分析鱼、浮萍、水及底泥中的稀土含量。

实验期间保持水量在50 ml, pH6.5。

1.2 稀土测定

水样经过滤, 鱼样经HNO₃消化、HClO₄冒烟处理^[6], 底泥样品经Na₂CO₃熔融处理, 浮萍经混三酸(HNO₃:H₂SO₄:HClO₄=8:1:1)消化^[7]。所有处理之样品均经阳离子交换分离富集^[6]后以三溴偶氮氯膦光度法测稀土含量。测定的精密度在±13%以内, 回收率在87%—107%之间。

2 结果与讨论

2.1 外源稀土在系统各组分中的富集

图1表示模拟水生生态系统各组分中稀土含量(为平行培养2份之平均值。鱼、浮萍、底泥均为干重测量含量)的变化情况。由图1可见, 外源稀土进入模拟水生生态系统后, 在浮萍中的含量仅低于底泥中且随时间而急剧变化, 实验前半段(3 d之前)浮萍对外源稀土具有

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强富集作用，而后却具有快速释放作用。

鱼体中的稀土含量高于水中却低于浮萍和底泥中，且在整个实验过程中一直处于上升趋势，这预示着经过较长时间有可能达到较高的水平。

表 1 为实验期间鲤鱼可食部分(鱼肉)及非可食部分中(骨、鳃、内脏等)稀土含量的变化情况。从表 1 中可看出，在整个实验期间，鱼肉

入人体，因此其稀土含量的这一变化趋势应引起人们的警惕，对此应做进一步的深入研究。

外源稀土在水体中的浓度在 $0.029-0.046\text{ }\mu\text{g}\cdot\text{ml}^{-1}$ 之间波动，说明水体对外源稀土仅有弱的富集和释放作用。底泥中稀土含量最高但变化不大且有一“谷底”，此点正好出现在其余组分曲线的最高处。这一结果说明底泥在此时向外释放稀土，而释放的稀土则转移到了该系统其它组分之中，也就是说底泥富集的稀土在一定时段可产生二次污染。

2.2 外源稀土在系统各组分中的质量分布

外源稀土进入模拟水生生态系统后，在各组分中稀土质量与加入稀土总质量之比称之为分配比，以 D_i 表示， $D_i = \frac{m_i}{M} \times 100\%$ ，式中 m_i 为稀土在某组分中的质量，等于各组分不同时间的稀土含量(见图 1)乘以相应的质量(水、底泥质量不变，浮萍、鱼质量随时间略有变化见表 2)， M 为所施加的外源稀土总质量计 2.5 mg 。利用 D_i 对时间做图(图 2)，可以直观地比较 D_i 的大小来考察进入水生生态系统的稀土在组分中的质量分布情况。

表 2 浮萍、鲤鱼在不同时间时的质量(干重, g)¹⁾

组 分		时 间 (d)				
		10	20	30	40	50
鱼	a	1.3004	1.3104	1.3997	1.4242	1.5998
	b	1.3012	1.3889	1.4021	1.4401	1.5012
浮萍	a	2.3429	1.6105	1.4204	0.9224	0.5247
	b	2.0333	1.8096	1.2165	0.7857	0.8067

1) a、b 为平行 2 组，每一时间取平均值计算 m_i

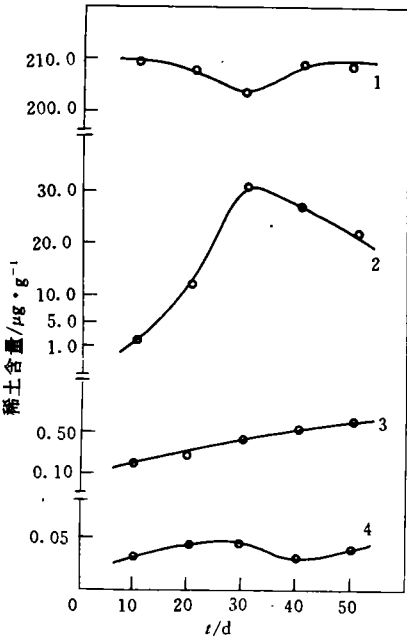


图 1 外源稀土在模拟水生生态系统各组分中的富集值

1. 底泥 2. 浮萍 3. 鱼 4. 水(稀土浓度单位为 $\mu\text{g}\cdot\text{ml}^{-1}$)

表 1 鲤鱼可食部分与非可食部分中稀土含量之比较

时间(d)	10	20	30	40	50
CRE可食($\mu\text{g}\cdot\text{g}^{-1}$)	0.005	0.017	0.036	0.064	0.091
CRE非食($\mu\text{g}\cdot\text{g}^{-1}$)	0.335	0.543	0.764	0.996	1.049

中稀土含量远远低于非可食部分中的稀土含量，即进入鱼体中的稀土主要富集在鱼的非可食部分中。但是实验结果亦显示出，实验结束时鱼肉中的稀土含量已达 10 d 时的 18.2 倍，而此时非可食部分中稀土含量却只有 10 d 时的 3.1 倍。可见随时间的延长，鱼肉中稀土含量的增加趋势远远大于鱼的非可食部分中稀土含量的增加。由于鱼肉中的稀土可通过食物链直接进

从图 2 中可以看出，在实验时间内，进入模拟水生生态系统的外源稀土有 96% 以上赋存于底泥中；水、浮萍中的稀土分量处于同一数量级，但浮萍中稀土分量的变化明显大于水中的稀土分量变化；鱼中稀土分量最小，但随时间的变化近似于直线上升。底泥中的“谷底”对应于其余组分的峰值。

综合图 1、图 2 及以上讨论，可以认为在此模拟水生生态系统中存在一个动态平衡，即在所加稀土总量不变的情况下，系统内一种组分释放稀土，必然伴随着其它组分吸收累积稀土，

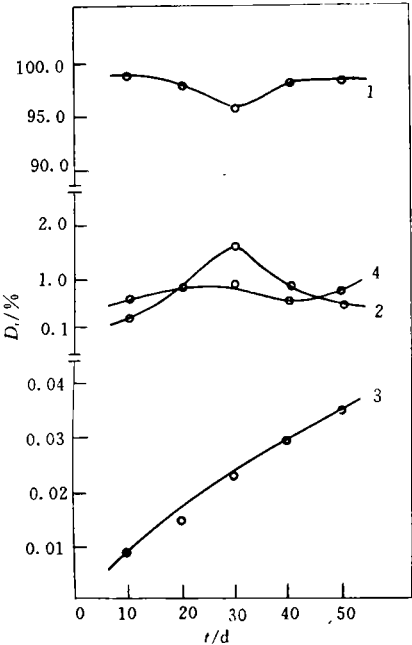


图2 外源稀土在模拟水生生态系统各组分中的质量分布
1. 底泥 2. 浮萍 3. 鱼 4. 水

反之亦然。而水体尽管与其余组分皆有直接接触，但其中稀土浓度与稀土分量仅微有波动，说明水体富集、释放稀土的能力均较弱，水体更重要的作用似乎是“传递”稀土，即水体将一组分释放的稀土“传递”给另一组分。

2.3 鲤鱼对外源稀土的生物浓缩因子

计算了不同实验时间鱼体对稀土的生物浓缩因子 BCF 值($BCF = \text{鱼体中稀土含量 } c_{RE\text{鱼}} / \text{水体中稀土浓度 } c_{RE\text{水}}$)如表 3 所示。从表 3 中可以

表 3 外源稀土在鲤鱼体中的生物浓缩因子(BCF)

时间(d)	10	20	30	40	50
$c_{RE\text{鱼}}(\mu\text{g} \cdot \text{g}^{-1})$	0.17	0.28	0.40	0.53	0.57
$c_{RE\text{水}}(\mu\text{g} \cdot \text{ml}^{-1})$	0.031	0.043	0.046	0.029	1.040
BCF	5.5	6.5	8.7	18.3	14.3

看出，在短时间(40 d)内，尽管水体中稀土浓度有波动，但随鲤鱼体中稀土含量增加，其 BCF 值也在增加。至 50 d 时，尽管此时鱼体中稀土含量是最高的，但由于这时水体中稀土浓度亦较高，故其 BCF 值却比 40 d 时还低。笔者认为，该水生生态系统中存在的多种组分皆会对水体中的稀土浓度产生影响，从而影响鲤鱼对稀土的生物浓缩作用。从表 3 中还可看出，20、50 d 时水中稀土浓度相差不大，而 BCF 值后者却是前者的 2 倍多，因此时间也是影响鲤鱼富集稀土的一个因素。

3 结语

(1) 外源稀土进入模拟水生生态系统后，其含量在底泥和水中变化不大，在浮萍中却急剧变化，在鲤鱼体中则始终处于上升趋势。

(2) 外源稀土在模拟水生生态系统各组分中的质量分布以底泥中居多，约占添加稀土的 96% 以上；浮萍、水中处于同一水平，约在 1% 上下；鲤鱼中最少，皆在 0.035% 以下。

(3) 模拟水生生态系统各组分皆影响外源稀土在鲤鱼体中的生物浓缩因子 BCF 值，时间也是影响 BCF 的一个因素。

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Study on the Catalytically Hydrogenated Conversion of CO₂ Using Ru/Al₂O₃ Catalyst. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 23–25

In this paper the catalytically hydrogenated conversion of CO₂ was studied using Ru/Al₂O₃ catalyst, the influence of different reaction conditions, such as reaction temperature (260–520 °C, 5000–10000 h⁻¹) and CO₂/H₂ ratio in inlet gas, on CO₂ conversion efficiency and CH₄ formation were reported. At reaction temperature higher than 350 °C the CO₂ conversion efficiency was over 95%, and CH₄ formation rate was about 45%–79%. There was no significant influence on CO₂ conversion efficiency and H₂O formation when the space velocity from 5000 h⁻¹ to 10000 h⁻¹. However, for the CH₄ formation efficiency there was a trough at the space velocity of 7000–9000 h⁻¹. The CO formation changed a little at space velocity of 5000–9000 h⁻¹, but it increased a lot at 10000 h⁻¹. The higher CH₄ formation efficiency was obtained when there existed excess of H₂. The highest CH₄ formation efficiency obtained was 98%.

Key words: carbon dioxide, catalyst, catalytically hydrogenated, methane.

Monitoring on The Concentration of Atmospheric Methane of A Rice Cropping Region in Beijing Area. Cui Ping et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 26–28

Monitoring on methane concentration in the atmosphere in the rice cropping region was carried out between Oct. 1991 and Nov. 1993. Results indicated that the average concentration of methane of the two testing years in the local region were 1.16 and 1.17 µg/L respectively. The variation of methane concentrations showed a strong seasonal pattern. The concentration and concentration deviation were high in summer and low in winter. During rice vegetation period, the methane concentrations were closely related with the variation of methane emission rates from rice paddies indicating rice paddies is one of the most important methane sources of the region. Running analysis showed that the average increasing rate of atmospheric methane in the region was 0.2%, much lower than some previous reports.

Key words: methane, rice, monitoring, Beijing area.

A simulation Study on the Accumulation of Added Rare Earth Elements in Aquatic Ecosystem. Chen Zhaoxi et al. (Dept. of Chem. Eng., East China Institute of Metallurgy, Maanshan 243002); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 29–31

The accumulation and distribution coefficients of added rare earth elements (RE) in various parts of simulated aquatic ecosystem were investigated. The results showed that concentrations of added RE in bottom mud and water bodies varied smoothly and in *Lemna minor* and *Cyprinus carpio* varied extremely with the time in the period of experiment. Distribution coefficients of added RE in bottom mud were higher than 96%, in *Lemna minor*, were range of 0.26–1.61%, in water, were range of 0.54%

–0.91%; and in carp were less than 0.035%, but almost on linear increment in the period of experiment. Bio-concentration of added RE in carp was also discussed.

Key words: aquatic ecosystem, accumulation, rare earth elements, bioconcentration.

The Quantum Chemistry Studies of the biradical Mechanism of Destroying Ozone in the Atmosphere. Sun Huabin et al. (Institute of Military Medicine, Jinan Command, Jinan 250014); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 32–34

The reaction mechanisms of the singlet biradicals NH, CH₂, CCl₂ with ozone in the atmosphere have been studied using RHF method of quantum chemistry. The geometries of the reactants, intermediates and products of the above reactions are optimized with the gradient technique at the 3-21G level, their energies have been calculated at the 6-31G or 6-21G level. The structure data of all species have been obtained. The calculated results show that there are two stages in the above reactions, the reactions of the biradicals with ozone take place first to form the stable intermediates, then the intermediates are decomposed by illuminating to the stable molecules HNO, H₂CO and Cl₂CO etc., respectively. In terms of dynamics two reactions in two stages belong to the types [$\pi_{4s} + W_{2s}$] and [$\pi_{2s} + \pi_{2s}$], respectively, and they are permitted thermodynamically. In this study, a method to investigate complicated reaction based on the combining thermodynamics with Woodward-Hoffmann approach without calculation of transition state was attempted to provide by authors.

Key words: biradical, loss of ozone, reaction mechanism.

The Structure and Toxicity Relationship Study for Nitroaromatics to *Scenedesmus obliquus*. Lu Guanghua et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 35–36

ELUMO, EHOMO, $\Delta(\Delta H_f)$, μ and Q_{NO_2} of 18 nitroaromatic compounds were calculated using the quantum chemical method MNDO. The quantitative structure-activity relationships (QSAR) were developed using the five quantum chemical descriptors for the acute toxicity of nitroaromatics to *Scenedesmus obliquus*. Through step-wise regression analysis, one best equation contained three variables was obtained: $-\log EC_{50} = 2.92 - 0.077\Delta(\Delta H_f) + 0.08\mu + 0.28E_{HOMO}$, $n = 18$, $r = 0.961$, $S = 0.173$. The equation was used to estimate the toxicity of the studied compounds, and the toxic effect was discussed.

Key words: structure, toxicity, nitroaromatics, *Scenedesmus obliquus*.

Effects of Rare-Earth Elements on Growth and Reproduction of *Chlorella pyrenoides*. Hu Qin Hai et al. (Dept. of Environ. Sci., Zhejiang Agricultural University, Hangzhou 310029); *Chin. J. Environ. Sci.*, 17(2), 1996, pp. 37–38

It was studied that effects of rare-earth elements (La, Ce, Pr, Nd and their mixture) on growth and reproduction of *Chlorella pyrenoides*. The results showed that effects of rare-earth elements on growth and reproduction of *Chlorella pyrenoides* were not apparent under lower concentration (2 mg/L), but it was inhibited as the concen-