

天然湖水表面微层砷形态分析

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摘要 采用玻璃板表面微层水采样器采集表面微层湖水, 利用高效液相色谱-氢化物发生-原子吸收联用技术测定水样中亚砷酸盐、砷酸盐、一甲基胂酸盐(MMA)和二甲基胂酸盐(DMA)含量, 并和相应表层湖水(水面下 0.5 m)中相同 4 种砷形态含量对比。结果表明, 4 种砷形态在湖水表面微层和表层中的含量分布有较大差异, 表面微层水中的含量通常高于表层水。它们在湖水表面微层中具有一定的富集现象, 富集倍数分别为 $As(III)$ 1.66, $As(V)$ 1.35, MMA 1.58, DMA 1.09; 湖水表面微层和表层中占优势的砷形态均为 $As(V)$, 在表面微层和表层湖水中共存的有机砷形态主要为 DMA; 砷存在形态及含量随采样站位不同而有所不同。

关键词 湖水表面微层, 采样器, 砷, 形态分析。

海洋和淡水表面微层是具有独特物理、化学和生物特性的界面环境。空气、水的物质交换过程通过水表面微层进行, 这一交换过程在物质的地球化学循环中起着非常重要的作用。疏水性物质、重金属及其它环境污染物、颗粒物、微生物等在水表面微层的积累, 已有很多报道^[1-4]。了解水表面无机和有机污染物及微生物的富集状况, 对于污染物预测和控制是非常重要的。砷是水环境中普遍存在的有害污染物, 有关水表面微层砷形态分析, 还鲜见报道。本文旨在初步探讨砷的不同存在形态在湖水表面微层及表层中的分布特征和差异。

1 实验部分

1.1 水样的采集

水样采自天津某湖水, 表面微层水用玻璃板表面微层采样器采集 30—60 μm 的表层湖水, 采样方法参见文献^[5]。表层湖水(0.5 m)按常规采样方法采集。采样站位布设如图 1 所示。

1.2 样品分析

水样中 4 种砷形态: 亚砷酸盐 $[As(III)]$ 、砷酸盐 $[As(V)]$ 、一甲基胂酸盐(MMA)、二甲基胂酸盐(DMA)的测定采用高效液相色谱-氢化物发生-原子吸收法测定。高效液相色谱仪由 YSB-2 型国产平流泵(中科院上海分院科学仪器厂)、六通阀进样器和定量管组成, 分离色谱柱

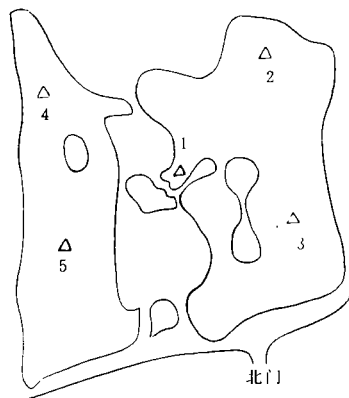


图 1 采样站位

为北京化工冶金研究院研制的 YSA-III 型阴离子交换柱(粒径为 10 μm)。4 种砷形态分离采用分阶淋洗法, 即进样后经 5 s 去离子水后, 用 0.015 mol/L $K_2HPO_4-KH_2PO_4$ (pH=6.2—6.3) 缓冲液淋洗 3.0 min, 用 0.02 mol/L MH_4HCO_3 、1.0 mol/L $NH_3 \cdot H_2O$ 溶液淋洗 1.0 min, 然后用去离子水淋洗 20 min。色谱柱后淋出物用 1.0% (W/V) KBH_4 和 0.375 mol/L HCl 将砷化合物还原为相应氢化物, 生成的氢化物由氮气载入具石英管原子化器的原子吸收分光光度进行测定。

2 结果与讨论

收稿日期: 1994-12-17

表 1 和表 2 分别为砷的 4 种不同形态和溶解态总砷含量在各采样站位通常高于表层湖水，特别是无机砷酸盐含量在微层湖水中远高于表层湖水。湖水中砷的主要存在形态中，无机砷酸盐占绝对优势，其含量占溶解态总砷的 42%—74%。而二甲基砷酸盐是微层湖水和表

表 1 湖水表面微层和表层水中各形态砷含量(μg/L)

日 期	站 位	微 层						表 层					
		DMA	As(Ⅲ)	MMA	As(V)	$\frac{As(Ⅲ)}{As(V)}$	TDA _s	DMA	As(Ⅲ)	MMA	As(V)	$\frac{As(Ⅲ)}{As(V)}$	TDA _s
1993-03-19	1	1.01	1.50		5.44	0.275	7.95	1.35	0.75		2.75	0.272	4.85
	2	1.35	1.81		3.33	0.543	6.44	1.26	0.32		3.34	0.094	4.97
	3	2.03	1.76	0.27	6.37	0.276	10.43	1.94	0.77	0.18	3.65	0.211	6.54
	4	2.34	2.60	0.50	7.13	0.364	12.57	1.63	1.58	0.37	3.76	0.420	7.30
	5	1.37	1.76	0.38	3.38	0.520	6.89	1.27	1.34	0.20	1.53	0.875	4.34
	平均值	1.62	1.80	0.38	5.13	0.396	8.86	1.49	0.95	0.25	3.01	0.374	5.60
1993-04-12	1	0.99	1.34		1.57	0.850	3.90	0.93	1.28		1.50	0.853	3.71
	2	1.29	1.15		1.98	0.581	4.42	1.05	1.21		1.73	0.699	3.99
	3	0.93	1.28		2.07	0.618	4.28	0.88	1.06		1.73	0.163	3.67
	4	1.17	1.60		1.91	0.837	4.68	0.82	1.38		1.38	1.00	3.58
	5	1.05	1.37		1.85	0.740	4.27	1.29	1.06		1.73	0.613	4.08
	平均值	1.08	1.35		1.88	0.726	4.31	0.99	1.20		1.61	0.755	3.81
1993-05-06	1	0.45	1.12		3.40	0.329	4.97	0.45	0.62		4.88	0.127	5.95
	2	0.44	0.65		4.10	0.158	5.19	0.45	0.55		2.93	0.187	3.93
	3	0.56	0.65		3.85	0.169	5.06	0.56	0.55		3.33	0.165	4.44
	4	0.59	0.60		3.52	0.170	4.71	0.48	0.56		2.69	0.208	3.73
	5	0.45	0.59		2.44	0.242	3.48	0.42	0.55		2.26	0.243	3.23
	平均值	0.50	0.72		3.46	0.213	4.68	0.47	0.57		3.21	0.186	4.25

层湖水中主要的有机砷形态。

表 3 为 4 种砷形态及溶解态总砷在湖水表面微层的富集情况。可见，各种砷形态及溶解态总砷在湖水表面微层中有不同程度的富集现象，富集的原因除了与大气迁移过程有关外，还与生物的代谢转化有关。亚砷酸盐 MMA 和 DMA 的含量微层高于表层的原因与以下因素有关：① 表面微层湖水可以富集藻类等浮游植物及浮游动物的幼体^[6]，大型藻类的分解及生物碎屑的产生等对溶解的有机砷有贡献作用^[6]；② 生物对吸收到体内的无机砷酸盐具有还原和甲基化作用，无机砷的生物利用导致溶解态亚砷酸盐和甲基砷酸盐在表面微层水中释放，导致微层水砷形态富集^[7-9]。砷酸盐含量微层高于表层的原因可能与下列因素有关：① 微层水

中浮游植物的光合作用可受到一定程度抑制^[10, 11]，造成浮游植物对砷酸盐吸收减少；② 大气中砷沉降导致大气-水界面砷酸盐含量高；③ 水体底部气泡上浮将部分砷酸盐带到水面。

3 结束语

砷的不同化学形态在湖水表面微层和表层中的含量分布有明显差异，在湖水表面微层中具有一定的富集现象。砷存在形态在湖水表面微层的分布受大气环境和水环境中物理、化学和生物因素的制约。

天然水表面微层是一种重要的环境界面，它在污染物的生物地球化学循环中起着极其重要的作用。鉴于国内学者对表面微层的研究甚少，有关此方面的研究值得进一步深入开展。

表 2 湖水表面微层和表层水中各形态砷占溶解态总砷百分率(%)

日 期	站 位	微 层				表 层			
		DMA	As(Ⅲ)	MMA	As(V)	DMA	As(Ⅲ)	MMA	As(V)
1993-03-19	1	12.70	18.86		68.43	27.83	45.46		56.7
	2	20.80	27.89		51.31	25.35	6.44		68.21
	3	19.46	16.87	2.59	60.11	29.66	11.77	2.75	55.81
	4	18.61	20.68	3.98	56.72	22.32	21.64	5.07	51.51
	5	19.88	25.54	5.51	49.06	29.26	30.87	4.61	35.25
	平 均 值	18.20	21.97	2.21	57.13	26.88	17.23	4.41	51.75
1993-04-12	1	25.38	34.36		40.26	25.06	34.50		40.44
	2	29.18	26.02		44.80	26.31	30.32		43.37
	3	21.72	29.90		48.36	23.98	28.88		47.14
	4	25.00	34.14		40.81	22.90	38.54		38.56
	5	24.59	32.08		43.32	31.61	25.98		42.41
	平 均 值	25.17	31.17		43.76	25.97	31.51		42.52
1993-05-06	1	9.05	22.53		68.41	7.56	10.42		82.01
	2	8.47	12.52		78.99	11.45	13.99		74.55
	3	11.06	12.84		76.09	12.61	12.39		75.00
	4	12.52	12.74		74.73	12.87	15.01		72.12
	5	12.93	16.95		70.11	13.00	17.03		64.94
	平均值	10.80	15.51		73.67	11.50	13.77		74.72

表 3 不同形态砷化合物在湖水表面微层的富集情况

日 期	站 位	富集倍数(EF)				
		DMA	As(Ⅲ)	MMA	As(V)	TDAAs
1993-03-19	1	0.75	2.0		1.98	1.64
	2	1.07	5.72		0.98	1.31
	3	1.05	2.29	1.50	1.75	1.59
	4	1.43	1.65	1.35	1.90	1.72
	5	1.08	1.31	1.90	2.21	1.59
	平均值	1.08	2.59	1.58	1.76	1.57
1993-04-12	1	1.06	1.05		0.70	0.84
	2	1.23	0.95		1.40	1.32
	3	1.06	1.21		1.17	1.14
	4	1.43	1.16		1.31	1.27
	5	0.81	1.29		1.08	1.08
	平均值	1.12	1.13		1.13	1.13
1993-05-06	1	1.0	1.81		0.70	0.84
	2	0.98	1.18		0.40	1.32
	3	1.0	1.18		1.17	1.14
	4	1.23	1.07		1.31	1.27
	5	1.07	1.07		1.08	1.08
	平均值	1.06	1.26		1.13	1.13

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spectrophotometry.

Speciation of Arsenic in the Surface Microlayers of Natural Lakes. Yu Jianshuan (Xiamen Environmental Monitoring Station, Xiamen 361004); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 61—63

Water samples were collected both from the surface microlayers of natural lakes by using a glass plate surface microlayer water sampler and from the surface layers in a depth of 0.5 m under water surface by using a conventional water sampler, and analyzed for arsenite, arsenate, monomethylarsonate (MMA) and dimethylarsinate (DMA) by using a high performance liquid chromatography/hydride generation/atomic absorption spectrometry technique. The concentrations of arsenic species in surface microlayer water were compared to those in surface layer water. The results show that the arsenic species in surface microlayer water had a significantly different distribution from these in surface layer water and had their concentrations usually higher than these in surface layer water, indicating that they were richer in surface microlayer water with an enrichment factor of 1.66, 1.35, 1.58 and 1.09 for As(III), As(V), MMA and DMA, respectively. As(V) is a dominant arsenic species present in both surface microlayer and surface layer of lake water, and DMA is a major organic arsenic species present in both layers. The distribution of arsenic species was dependent on sampling sites.

Key words: lake, surface microlayer water, surface layer water, arsenic species, speciation, sampler.

Spectrophotometric Determination of Trace Chromium in Water Samples with Sym-Diphenylcarbazone. Li Huizhi et al. (Dept. of Chemistry, Shandong Institute of Building Material, Jinan 250022); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 64—66

Chromium(VI) was reacted with sym-diphenylcarbazone to form a red complex in the presence of sodium dodecylbenzenesulfonate and 0.15 mol/L of H_2SO_4 . The complex had a maximum absorbance at 560 nm with a molar absorptivity of 9.74×10^4 L/(mol · cm). Beer's law was obeyed in the range of 0—10 μ g of Cr(VI) in 25 ml solution. The common metal ions were able to be separated and concentrated by amberlite 717, giving a better selectivity. The method has been applied to determining chromium in water samples with satisfactory results.

Key words: chromium, spectrophotometric, sym-diphenylcarbazone.

Study on a General ICP-AES Method for Simultaneous Multielement Analysis of Water or Wastewater. Sha Weinan et al. (Dept. of Chemistry, Nankai Univ., Tianjin 300070); *Chin. J. Environ. Sci.*, **16**(3), 1995, pp. 67—71

A general ICP-AES method for simultaneous multielement analysis of water or wastewater was studied and samples pretreatment process, experimental condition optimizing, interference judging, correction and the aspects needed for paying attention during the analysis were discussed. The results showed that analytical data were accurate, reliable, and coincident with the standard values of certified reference samples with a recovery of 90%—110%. The overall relative standard deviation is within 5%. The detection limits were 0.1—100 μ g/L. The calibration curve has a wide linearity range of 4—6 orders of magnitude.

Key words: water, wastewater, ICP-AES.

Pretreatment for the Test of DEHP in Crops and Soil. Pang Jinmei et al. (Soil and Fertilizer Institute, Shanxi Academy of Agri. Sci., Taiyuan 030031); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 72—74

This paper deals with the pretreatment method for testing DEHP from farm soil and crops with $CHCl_3$ as a solvent and with the absorbent. Compared with those from Beijing, Denmark and United States of America, this method took a short extracting time of 0.5—0.7 h, 2—11 h shorter than others, and the solvent of 75—90 ml, 110—1200 ml less than others. This method is easy to use and has a high effective separation. There was a DEHP recovery rate of about 90%, except for cotton seeds. The coefficient of variability was less than $\pm 3\%$. It's very suitable to test phthalic acid esters.

Key words: DEHP, extraction, $CHCl_3$, absorbent.

Methodological Study of the Operating-Mode Sampling Method Applied to Collecting PAH Compounds in Exhausts from Diesel Engines. Sun Chen et al. (Beijing Municipal Environmental Monitoring Center, Beijing 100044); *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 75—77

A new method, operomode sampling method was presented for the first time for collecting polycyclic aromatic hydrocarbons (PAHs) in the exhaust from diesel engines. With benzo-a-pyrene (BaP) as a main index, the efficiency, precision