

松花江主要汞污染源治理对渔民发汞值影响的研究

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摘要 在松花江主要污染源根治汞 8 年后渔民发汞较 70 年代下降 78.30%—82.57%, 较 80 年代初下降 71.48%, 取得了明显的健康效益与环境效益。但至今该地区渔民的发汞值仍超过国家诊断标准。这些渔民发汞仍显著地高于非汞污染区渔民, 并有 1.92% 渔民的发汞值仍超过国家诊断标准。这些渔民主要分布在三岔河口以下的第一松花江段, 而在二松渔民中发汞超过标准者极少, 并对其原因作了讨论。

关键词 水污染, 松花江, 汞中毒, 生物监测。

发汞由于样品采集容易、运输和保存方便和测定方法准确度高, 因而在评价环境中得到了广泛的应用^[1,2]。我国标准 GB6989-86 也把发汞值作为水体污染慢性甲基汞中毒诊断的重要根据^[3]。70 年代初发现松花江受汞和甲基汞的严重污染^[4], 而沿江少数渔民发汞已超过日本水俣病的最低发病值。受到了政府和社会的普遍关注, 投入了大量资金进行了治理, 主要污染源自 1978 年开始治理, 并于 1982 年末得到根治, 停止了向松花江排放含汞和甲基汞废水。为了评价环境汞污染治理对渔民健康的效应, 确定对江底沉积汞的处理, 于 1990 年前后对二松下游和一松三岔河口以下近 100km 江段采集、测定了 1302 名渔民的发样。

1 对象和方法

1.1 对象

选择年吃鱼量较高的第二松花江下游渔民 499 人, 第一松花江扶余市三岔河口以下江段渔民 803 人为调查组, 以基本无汞和甲基汞污染的新立城和海龙水库渔民 173 人为对照组。在 4—9 月于现场采集不少于 0.5g 的后发际发样, 装入纸袋送检。

1.2 发样处理

经中性洗涤剂浸泡后, 用去离子水冲净, 以乙醚脱脂阴干, 剪碎。加氧燃烧-冷原子吸收光度法测定^[5]。在测定中用标准发样进行质控。

2 结果与分析

2.1 发汞值及其分布

影响人发汞量的因素很多, 除与食鱼量, 鱼汞含量有关外, 还与生活习惯、职业状况、发样的采集部位和季节有关。我国标准规定发汞超过 10μg/g 者有诊断意义^[3], 未受到汞污染的发汞值一般不超过 5μg/g。表 1 为 2 组渔民发汞值的分布, 调查组最高发汞值为 18.08μg/g, 有 1.92% 的人发汞超过 10μg/g, 而对照组发汞值为 4.01 μg/g(最高值), 只有 2.31% 的人发汞超过 3μg/g。

表 1 污染区与对照区渔民发汞值的分布

发汞值 (μg/g)	污染区		对照区	
	人数	%	人数	%
<3	1018	78.19	169	97.69
3	171	13.13	4	2.31
5	88	6.76		
>10	25	1.92		
合计	1302	100	173	100

监测江段与对照区发汞的中位数与平均值列于表 2, 发汞值数据分布呈正偏态分布、而不呈正态分布, 不拟以算术均值表示, 但是考虑到国外的一些资料和以往的研究报告, 多应用了算术均值, 为了进行比较, 这里也将算术均值列出。一松渔民发汞值明显地高于二松, 而二松发汞值

又明显高于对照组,经中位数检验 χ^2 值分别为 8.63 与 7.24, P 值均 <0.01 ,有显著差异。

表 2 监测江段与对照区渔民的发汞值($\mu\text{g/g}$)

监测江段	人数	平均值	中位数
第一松花江	803	2.530	1.771
第二松花江	499	1.811	1.461
对照区	173	1.209	1.149

2.2 渔民发汞与年龄的关系

表 3 为不同年龄组渔民的发汞中位数。一松和二松的渔民发汞中位数与渔民的年龄关系不大,不同年龄组之间亦未看到发汞有显著差异。这是与发汞主要与近期内汞的摄入有关,而当摄入汞量减少或停止摄入后,人体经过一段时间随着汞的不断排出、体内汞蓄积可以减少,而使发汞也随之而下降。

表 3 各不同年龄组渔民发汞的中位数($\mu\text{g/g}$)

年龄(岁)	<20	20—30	30—40	40—50	50—60	60—	合
第一松花江	1.46	2.08	2.54	2.63	2.32	2.04	2.36
第二松花江	1.86	1.70	1.84	1.54	1.63	1.38	1.64

2.3 渔民食鱼与发汞值的关系

渔民食鱼调查和发汞的测定是双盲法条件下进行的。渔民食鱼量是回顾性调查,逐个询问登记。第一松花江沿岸渔民的年均食鱼量为 124.41kg,二松因鱼产量较低,渔民年均食鱼量为 89.38kg,低于一松。渔民的平均食鱼与发汞中位数列于表 4。可以看出渔民的发汞随着吃鱼量的增加而增高。这与我们以前报告的结果相一致^[5]。年均食鱼量与发汞中位数的相关系数为 0.971,呈高度相关(图 1)。

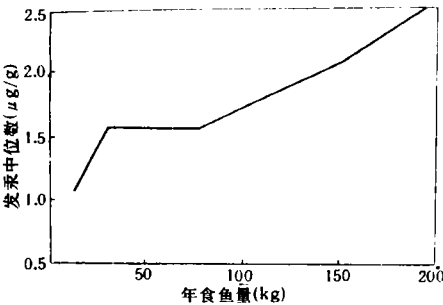


图 1 松花江渔民年均食鱼量与发汞值的关系

表 4 各不同食鱼量(kg/a)渔民发汞的中位数($\mu\text{g/g}$)

年食鱼量	<25	25—50	50—100	100—200	>200	合计
调查人数	72	201	376	427	187	1263
发汞中位数	1.168	1.623	1.586	2.125	2.536	1.853

3 讨论

自日本发生水俣病以来,流行病学调查中都把发汞值作为评价人体受环境汞污染水平的重要指标。日本把 50 $\mu\text{g/g}$ 发汞值定为水俣病的发病界限。之后也曾将发汞 10—20 $\mu\text{g/g}$ 者定为病者,这是由于在发病一段时间后发汞分析测得的结果^[2]。当人体减少和停止从环境中摄取汞和甲基汞以后,由于不断地代谢和排泄,体内的汞和甲基汞蓄积量可以逐渐减少,而发汞值亦可随之而降低。在 70 年代松花江汞污染高峰时期,曾发现发汞值有 29 人超过 50 $\mu\text{g/g}$,最高的发汞值达 118.8 $\mu\text{g/g}$ ^[6]。图 2 为 1974 年以来测得的发汞值与本次测得的结果比较,可以看出渔民的发汞值以 70 年代为最高,在 70 年代末由于开始进行了治理,渔民的发汞值已经有了下降,而在完全停止排汞 8 年以后本次调查结果渔民的平均发汞值较 70 年代下降了 80.27%—92.40%,较 1982 年下降了 74.07%,证明松花江环境汞污染治理对于降低渔民体内汞蓄积已取得了明显的效果。

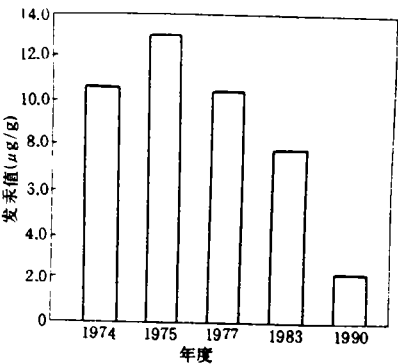


图 2 松花江渔民各主要年度的发汞值($\mu\text{g/g}$)

我国标准规定发汞值为 10 $\mu\text{g/g}$,调查中发现超过此值的有 25 人,其中一松 22 人,占 88%,二松 3 人,占 12%。其超标率分别为 2.74%和 0.60%,二者有显著差异(下转第 61 页)

(1)第 I 组数据是在 $c_r/c_s < 1$ 的情形下计算的。此时河流存在稀释能力,形成允许排污量的机制包括稀释和净化 2 部分。从表 3 中可以看出,因是稀释为主,所以小流量为不利条件,当流量为 $26.17\text{m}^3/\text{s}$ 时,允许排污量为最小。

(2)第 II 组数据是在 $c_r/c_s > 1$ 的情形下计算的。也就是上面所谈的 $c_s - c_r \leq 0$ 的情形,组成允许排污量的机制主要是借靠净化功能,所以流量愈大愈不利。表 3 的计算实况正是流量为 $111.31\text{m}^3/\text{s}$ 时,允许排污量为最小。

(3)第 III 组数据也是在 $c_r/c_s > 1$ 的情形下计算的。其计算结果与第 II 组正相反,最小允许排放量是发生在小流量($26.17\text{m}^3/\text{s}$)之时。可见在 $c_r/c_s > 1$ 的情形下有 2 种可能。

(4)由上述实例讨论可见,当 $c_r/c_s < 1$ 时,无疑小流量为不利,设计流量仍然可用现行办法。当 $c_r/c_s > 1$ 时,情况较复杂,必须通过试算决定

设计流量。如 $c_r/c_s \gg 1$,可以肯定,大流量是不利条件。

但应指出,用大流量作为设计流量并不意味着洪水流量,因为一旦流量加大背景浓度(c_r)也将随之改变。所以在表 2 的计算中,流量还是枯水流量,只是保证率不一样,这样其背景浓度还是不利于枯水期。

上面仅是针对淮南段实例展开讨论,是否有一般性还有待深入探索,本文只起抛砖引玉作用。

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(上接第 40 页)($x^2=7.47, P<0.01$)。从表 2 也可见渔民发汞的均值也是一松显著地高于二松。这是与二松与嫩江汇合以后形成第一松花江,嫩江的汇入不但极大地稀释了松花江的污染物,使有害污染物的浓度下降,而且带来了大量的饵料,为鱼类的生存和繁殖带来了良好的条件,因而鱼产量明显地高于二松,渔民的食鱼也相应地较二松要多,前者渔民年均食鱼量为 124.4kg ,后者年均食鱼量为 89.4kg ,而渔民的食鱼量与发汞含量是紧密相关的。从松花江、尤其是第一松花江少数渔民发汞值仍然超过标准这一事实

说明,为了预防人体内过量的汞蓄积,食松花江的鱼量仍应作适当限制。

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美国和墨西哥试图建立第一个国际大气污染控制区

美国和墨西哥正在建立第一个国际大气污染控制区,它有权控制边境两边的工业发展。这项努力要想获得成功,它最初就应包括一个环得克萨斯州埃尔帕索和墨西哥华雷斯城的地区。但未来,该项目的支持者想让该控制区拥有这种权力:制定和实施排放标准,以及确定何时、何地 and 如何建造工厂。该控制区的建立不需要得到国

会批准,因为可以将它作为美-墨现有一项涉及环境问题的条约的附属物。虽然它的建立与北美自由贸易区协议(NAFTA)无关,但它可以减少基于环境原因的、对 NAFTA 的批评。环境保护基金会是该控制区的主要鼓动者。

淮海译自 ES&T,1993,27(11):2260

River. Yu Changrong et al. (Jilin Provincial Institute of Environmental Protection, Changchun 130012); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 35—38

Since the main industrial sources of mercury discharged into the Songhua Jiang River were eliminated eight years ago, the total mercury and methylmercury contaminations in fish from the reaches of the river from Jilin City to Sanchahekou and from Sanchahekou to Tongjiang have been reduced to a light level of contamination and a medium level of contamination, respectively. The average levels of total mercury and methylmercury contaminations in fish from both reaches of the river exhibited; the highest in carnivorous fish, lower in omnivorous fish, and the lowest in herbivorous fish; higher in the underlayer fish than in the medium and upper layer fish; and higher in the scaleless fish than in the scaled fish. In the muscle of each species of fish from both reaches of the river, the level of methylmercury was in a significantly positive correlation with the level of total mercury while being in a significantly negative correlation with the activities of urease and lactate dehydrogenase (LDH). The level of total mercury in the muscle of fish was in a significantly multiple linear, multiple logarithmic or multiple exponential correlation with the level of total mercury in river water. The level of methylmercury in the muscle of fish was in a significantly multiple logarithmic correlation with the level of methylmercury in river water.

Key words: the Songhua Jiang River, total mercury, methylmercury, contamination, fish.

Study on the Level of Mercury in Fishmen's Hair Since the Elimination of Major Sources of Mercury Pollution in the Songhua Jiang River. Wu Shi'an et al. (Jilin Provincial Station of Sanitation and Antiepidemics, Changchun 130021); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 39—40

Since the major sources of mercury pollution in the Songhua Jiang River were eliminated 8 years ago, the level of mercury in the hairs of fishmen living along the river has reduced by 78.30%—82.5% as compared with that in the 1970s, and by 71.48% as compared with that in the early 1980s, showing that obvious health benefit and environmental benefit have been obtained. However, it was found that so far the fishmen living along the river still have a significantly higher level of hair mercury than those living in a non-mercury polluted area, and 1.92% of them have a level of hair mercury exceeding the national diagnostic standards. They were found to be mainly distributed along the first Songhua Jiang reaches of the river downstream Sanchahekou. Extremely less number of cases for the fishmen living along the second Songhua Jiang reaches of the river were found to have a level of hair mercury exceeding the national diagnostic standards, and the causes for this were discussed also.

Key words: mercury poisoning, water pollution,

biological monitoring, Songhua Jiang River.

Determination of Phthalic Esters in Aqueous Extracts from Solid Wastes. Dai Tianyou, Wang Shufang (China National Environmental Monitoring Center, Beijing 100012); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 41—43

The HPLC determination of phthalic esters in aqueous extracts from solid wastes were reported. In this study, a HPLC system equipped with a Zorbax-CN column and a 224 nm UV detector and using a n-hexane mixed with 0.1% isopropanol as eluting agent was established and used to determine the phthalic esters in aqueous extracts from municipal refuses in Beijing. The system was effective to separate phthalic esters from non-polar organics in the extracts and to eliminate the interference likely resulted from some organic compounds which had a polarity similar to phthalic esters. Having been extracted with n-hexane and then concentrated, the extracts in organic phase could be directly analysed with the HPLC system without a further purification (e.g., column chromatography). Water samples fortified with phthalic esters at a level in the range of 1—500 ppb were analysed, with a linear response in the range of 0.1—450 ppb, a recovery for phthalic esters of 70%—110%, and the detectable limits of 1.0 ng for dimethyl phthalate (DMP), 0.4 ng for diethyl phthalate (DEP), and 0.2 ng for each of di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP) and di(2-ethylhexyl) phthalate (DEHP), at 224 nm. The phthalic esters in aqueous extracts from several solid waste samples were found by using this system to be at a level of 5 ppb. The variation coefficient for 7 parallel tests on the extracts from solid wastes was within 10%.

Key words: phthalic esters, extracts, HPLC.

Study on the removal of Arsenic in Different States of Valence from Acidic Wastewater. He Shaoxian et al. (Dept. of Environmental Engineering and Chemical Engineering, Kunming Institute of Technology, Kunming 650093); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 44—46

Based on the process of iron salts neutralization to remove arsenic from wastewater, theoretical analysis and experiments indicated that, at a ratio of $\text{Fe/As} = 0.5—0.6$, $\text{As}(\text{III})$ was removed at a rate of about 60% lower than that of $\text{As}(\text{V})$, demonstrating that $\text{As}(\text{III})$ was more difficult to be removed from wastewater than $\text{As}(\text{V})$. In a further study, it was found that it was most suitable to oxidize $\text{As}(\text{III})$ in acidic wastewater containing a high level of arsenic by using a bleaching powder, $\text{Ca}(\text{ClO})_2$. For an acidic wastewater containing 782.5 mg/L of As at pH = 1, the oxidation/iron salts neutralization process used in a primary treatment produced an effluent containing less than 8 mg/L of As, with an arsenic removal of more than 99%. If followed by a further secondary treatment, the level of arsenic in the effluent produced would be lower