黄渤海沿岸经济贝类体内的石油烃的测定*

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摘要 在 1990-07—1991-12 期间，监测了黄渤海沿岸经济贝类体内的污染物残留量；计算了沿岸软体动物体内石油烃含量的本底值为 3.47—19.7 mg/kg(湿重)，用本底值的上限作为评价标准，对沿岸贝类的石油污染状况，按污染程度做了海区划分，结果是大连湾、长江口、锦州湾的经济贝类是石油烃污染严重的区域；从鸭绿江口至大窑湾的北黄海沿岸是未受石油烃污染的最好环境区域.

关键词 经济贝类，石油烃，本底值，黄渤海沿岸.

我国做过一些关于生物石油污染调查研究方面的工作[1,2]，但范围小，只限于某个海域. 本次调查选用《海洋监测规范》中的测定方法，使用统一的油标准物质，数据的可比性强，为全海域近岸生物石油污染评价提供了可靠的基础资料.

1 采样与分析

1.1 布设站位

采用不等距方式布站，以当地有经济价值的优势品种为样品，依分布特征布站采样(站位见表 1 和表 2).

1.2 采样和运输

在各站位上采集到双壳类软体动物样品后，依据国际贻贝监测[3]方案中确定样品大小范围规定，各站位间尽量采集大小一致的样品；在现场采集到生物样品后，用清洁海水洗净样品，控干后，用不锈钢刀剥壳，取出软组织，将其放入预先处理好的聚乙烯塑料袋里，冰箱冷冻后，用广口保温瓶迅速带回实验室，解冻后，用高速生物组织捣碎机匀浆，把匀浆液放入广口玻璃瓶中，于－20℃冰柜内冷藏、备用.

1.3 样品的分析

准确称取贝类软组织匀浆液 2.00 g，按《海洋监测规范》中生物体石油烃测定要求，进行皂化、萃取，收集萃取液氟里昂(F113)，用旋转蒸发器蒸发掉氟里昂，残余部分用氮气吹干，再用环己烷定容至 10.0 ml 试管中，在日立 650-60 型荧光分光光度计上测定；仪器条件为：EX 310 nm，EM 360 nm，狭缝均为 10 nm，PM 增益为正常. 每个样品都做了双平行测试，用相同条件下的工作曲线计算样品的石油烃含量，油标准物质选用全国海洋环境监测互校油 20-2#油. 在分析样品前，首先在实验室间进行互校，其相对偏差小于 10%. 为避免高浓度试样所产生的荧光猝灭现象影响，高浓度试样均稀释到工作曲线所控制的范围进行测定.

2 结果与讨论

2.1 沿岸贝类石油烃含量

黄渤海沿岸共设 29 个采样区域，45 个采样点，采集贝类品种 13 个，见表 1 和表 2. 共获得 83 个分析数据.

调查区内，贝类石油烃含量是 2.50—483mg/kg，平均含量是 16.6 mg/kg. 最高值出现在大连湾海茂村外，是采自海带筏子上的紫贻贝；其原因是受近岸几家石油化工企业废水

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表1 调查站位、贝类品种和石油烃含量(湿重结果)/mg·kg^{-1}

站位名称	海区	经济贝类品种1)	含量
东沟	鸭绿江口	2, 4, 5, 9	3.70—12.5
庄河		2, 4, 5, 8	5.10—6.30
皮口		2, 5, 8	5.30—5.40
凉水湾		1, 4	6.30—8.10
小窑湾		1	7.50
大窑湾		1, 6	5.00—7.60
大孤山	大连湾	1	8.00
红娘子礁	大连湾	1	64.1
甜水套	大连湾	1, 2	25.2—27.2
海茂	大连湾	1	483
老虎滩	大连市	1, 2	8.10—21.5
黑石礁	大连市	1	12.7
河口	大连市	1, 2	7.80—8.70
龙王塘	旅顺	1	5.80
老虎尾	旅顺	2	23.2
柏岚子	旅顺	1, 2	11.1—11.8
北海	旅顺	1, 2	7.30—7.90
金州湾		1, 2	9.50—12.9
复州湾		1, 2	9.50
熊岳		2	8.80
鲅鱼圈		1, 2, 3	2.50—13.1
辽河口		3, 4	9.30—11.3
小笔架山	锦州湾	2, 3	25.3—40.3
老河口	锦州湾	2	34.5
葫芦岛	锦州湾	2, 3	16.8—46.1
山海关		2, 3	14.1—17.1
秦皇岛		1, 2, 3, 8	12.4—53.0
汉沽	渤海湾	3, 5	12.6—16.8
南排河口	渤海湾	3	30.2
马颊河口	渤海湾	6	14.4
黄河口		4, 5	7.80—14.0
莱州湾		3	16.6
蓬莱市		1, 2	12.3—13.5
烟台市		1, 2	10.0—19.0
威海市		1, 2	22.2—23.4
沧口	胶州湾	1	8.20
大港	胶州湾	2	32.6
团岛	胶州湾	1, 3	11.3—18.3
赣榆县	海州湾	4, 5	5.40—7.90
连云港	海州湾	3	16.5
射阳县		5	15.4
吕泗		3, 4, 5, 8	11.1—48.7
大丰县		5, 7, 11	5.00—8.00
老港	长江口	12	4.60
白龙港	长江口	13	179

1) 表中经济贝类品同表2中种类编号

影响，多年水质监测，水中油含量都在二类海水水平上下[4]. 栖息于该水中的贝类，必受其害，它的干重分析结果计算出的富集系数高达1.97×10^5，这与国外报道贝类对石油的富集系数最高可达2.0×10^5[5]相当. 其次，是长江口白龙港的河蚬，含油量为179 mg/kg；再次则是锦州湾的菲律宾蛤仔，含量是46.1 mg/kg. 锦州湾也是我国石油污染最严重的海湾之一，通过五里河，平均每天接纳葫芦岛市石油化工企业的含油废水2万t之多，这对锦州湾的生物资源造成了影响.

从表1结果可见，除大连湾外，北黄海沿岸的贝类石油烃含量是很低的，是整个调查区内环境最好的岸段.

2.2 沿岸贝类石油烃含量环境背景值的计算

选取远离污染源站位上所采集的样品分析数据为样本，同时考虑了品种的分布特征. 计算本底值之前，对数据进行数学统计[6]，首先，用Grubbs法进行检验，剔除那些由于污染或样品的沾污以及其它原因造成的异常值. 通过检验与分析得出，黄渤海沿岸的软体动物石油烃含量的背景值总体呈对数正态分布. 故采用几何均值乘除几何标准差的平方(M/D^2—$M\cdot D^2$)表示其背景值的总体范围，结果是3.47—19.7 mg/kg.

2.3 沿岸主要海区贝类石油烃污染评价

采用计算出的环境背景值上限为“评价标准”，用指数法评价黄渤海沿岸经济贝类的石油烃污染现状.

指数法公式：$I = c_i/c_{si}$, (1)

式中，c_i为软体动物体内石油烃实测均值(某海区内平均)；c_{si}为环境背景值上限(评价标准)；I为污染指数.

按公式(1)计算各海区软体动物污染指数，按污染程度的高低，可将沿岸经济贝类石油烃的污染状况划分为3个区域：低背景水平区，海区内实测均值低于环境背景值的几何均值($M=8.26$)；高背景水平区，其海区内的实测均值大于背景的几何均值(M)，并且还低于背景值的上限值($M\cdot D^2=19.7$ mg/kg)，指数范围在$1/D^2<I<1$，即$0.420<I<1$；异常区(污染区)，海区内贝类油含量大于背景值的上限($M\cdot D^2=19.7$). 超过背景值上限的海区，软体动物体内石油烃的自然富集要低于人为活动累加的影响，可视超过了生物环境评价标准，是生物体

表2 采样种类和石油烃含量(湿重)/mg·kg⁻¹

种类编号	生物名称	学 名	采集率/%	平均值	含量范围
1	紫贻贝	*Mytilus edulis*(Linne′)	25.3	36.1	5.80—483
2	菲律宾蛤仔	*Venerupis philipinarum*	26.5	17.3	2.50—40.3
3	毛蚶	*Arca subcrenata*(Lischke)	13.3	16.4	5.10—30.2
4	文蛤	*Meretrix meretyix* Linne′	8.43	9.48	3.70—26.6
5	四角蛤蜊	*Mactra guadrangularis*	12.0	9.85	5.40—15.4
6	长牡蛎	*Ostrea gigas* Thumberg	2.41	9.70	5.00—14.4
7	缢蛏	*Sinonovacula constricta*(Lamarck)	1.20	8.60	
8	日本镜蛤	*Dosinia japonica* Reeve	4.82	28.1	5.00—53.0
9	中国蛤蜊	*Mactra Chinensis*	1.20	6.20	
10	栉孔扇贝	*Chlamys farreri*	1.20	16.2	
11	青蛤	*Cyclina simens*(Gmelin)	1.20	5.00	
12	泥螺	*Bullacta erarata*	1.20	4.60	
13	河蚬	*Corbicula fluminer* Miiller	1.20	179	

表3 黄渤海沿岸主要海区软体动物体内石油烃含量/mg·kg⁻¹背景分区

低背景值区			高背景值区			异常区(或污染区)		
海 区	平均含量	*I*	海 区	平均含量	*I*	海 区	平均含量	*I*
鸭绿江口	7.21	0.366	大连市	11.8	0.597	大连湾	109	5.52
庄河市	5.45	0.277	旅 顺	11.2	0.568	锦州湾	32.6	1.65
皮 口	5.40	0274	金州湾	11.2	0.568	秦皇岛	23.3	1.18
凉水湾	7.20	0.365	熊 岳	8.80	0.447	威海市	22.8	1.16
小窑湾	7.50	0.381	辽河口	10.3	0.523	吕 泗	24.6	1.25
大窑湾	6.30	0.320	山海关	15.6	0.792	长江口	91.8	4.66
复州湾	6.55	0.332	渤海湾	18.5	0.939			
鲅鱼圈	6.90	0.350	黄河口	10.9	0.553			
大丰县	6.93	0.352	莱州湾	16.6	0.843			
			蓬莱市	12.9	0.655			
			烟台市	15.1	0.765			
			胶州湾	17.6	0.893			
			海州湾	9.93	0.504			
			射阳县	15.4	0.782			

石油污染海域，那里的贝类食用价值降低．各海区环境背景状况分区列于表3.

3 结论

(1) 我国部分港湾中的贝类已经受到了石油烃的严重污染，最严重的海区是位于北黄海的大连湾，湾内紫贻贝石油烃含量高达483 mg/kg，是“评价标准”的24.5倍.

(2) 利用分析结果，计算出了黄渤海沿岸经济贝类石油烃污染的环境背景值，其总体范围是3.74—19.7 mg/kg.

(3) 北黄海沿岸的贝类未受石油烃污染(除大连湾外)，高背景值区主要分布在渤海和南黄海沿岸，污染严重区域有大连湾、长江口、锦州湾等海区.

(4) 为保障人民食用安全，要制定贝类石油含量的卫生标准，并要制定软体动物石油污染的环境评价标准．为保护海洋水产资源，应限制石油入海的排放量.

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Longsheng et al. (Institute of Marine Environmental Protection, SOA, Dalian 116023): *Chin. J. Eviron. Sci.*, **17**(5), 1996, pp. 56—58

In this paper, the residue of pollutants in economical shellfish along the coast of Huanghai and Bohai Seas during July 1990 and December 1991 was investigated. The background value of concentration of the petroleum hydrocarbons in mollusc along the coast has been calculated. Its overall range is 3.47—19.7 mg/kg (wet), and upper limit of the background value was utilized as assessment standard for the pollution level of oil in shellfish along the coast, the sea area division on pollution degrees of oil in mollusc was done. The results showed that content of oil in shellfish of Dalian bay and Changjiang River estuary and west Jinzhou bay is higher, and the coast of north Huanghai Sea from Yalujiang River mouth to Dayao bay is lower.

Key words: economical shellfish, petroleum hydrocarbons, background value, the coast of Huanghai and Bohai Seas.

Study on the Spectrophotometric Determination of Lead with DBS-Chlorophosphonazo. Zhao Shulin et al. (Shenyang Institute of Chemical Technology, Shenyang, 110021): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 59—61

In acidic solution, lead forms a blue colour complex with DBS-chlorophosphonazo. This complex exhibits absorption maximum at 635 nm with apparent molar absorptivity of 4.7×10^4 $L\cdot mol^{-1}\cdot cm^{-1}$. The molar ratio of lead to DBS-Chlorophosphonazo has been found to be 1 : 2. Beer's law is obeyed in the concentration range of 0—20 μg per 25 ml. This colour reaction has been used directly for the spectrophotometric determination of lead in cosmetics and dust of smelting copper with satisfactory results.

Key words: DBS-chlorophosphonazo, lead, spectrophotometry.

Determination of RH-5992 in Aquatic Environment by Liquid Chromatography. Zhu Jiusheng. (Institute of Plant protection, Shanxi Academy. of Agri. Sci., Taiyuan 030031), K. M. S. Sundaram and R. Nott (Forestry Canada, Forest Pest Management Institute Ste., Marie P6A 5M7): *Chin. J. Environ. Sci.*, **17** (5), 1996, pp. 62—64

A method was developed to determine RH-5992 in some aquatic environment matrixes. The procedure included solvent extration, liquid-liquid partition, columm cleanup and liquid chromatographic determination. RH-5992 was analyzed on a liquid chromatograph equipped with a diode-array UV detector set at 236 nm, using a RP-8, 10 μm column with a mobile phase of acetonitrile-dioxane-water. Mean recoveries for analyte ranged from 85%to 98%, with coefficient of variation from 6% to 9%. Limits of detection were 0.050 mg/kg for natural waters and from 0.009 to 0.028 mg/kg for other matrixes.

Key words: RH-5992, aquatic environment, residual analysis, high performance liquid chromatography.

A Comparative Analysis for the Pollutants Derived from H Acid in Underground Water. Liu Meijun et al. (Dept. of Chem. Zhengzhou University, Zhengzhou 450052): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 65—67

The brown red pollutants in underground water derived from a dyestuff intermediate-H acid(4-amino-5-hydroxy-2,7-naphthalene disulfonic acid) were extracted by means of reduced pressure concentration, column chromatographic separation. The extracted pollutants were primarily tested by alkali fussion, and then undertaken the comparative analysis between the pollutants and some standard samples which were selected as possible pollutants in the light of the actual conditions. According to the thin layer chromatography and IR spectrometry of them. It can be established that the brown red pollutants were the derivatives of H acid oxidized by air for a period of time in underground water.

Key words: pollution in underground water, H acid, thin layer chromatography.

Fast Determination of Carbon Disulfide in Wastewater. Fang Haijun et al. (Shanghai Jiao Tong University, Shanghai 200240): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 68—71

This paper studied an improving method using spectrophotometry to determine CS_2 in wastewater. By using tube-strip system instead of washing gas bottle, the stripping efficiency was raised, and the stripping time was reduced greatly. Nearly no declining sensibility and accuracy of analysis, the time of analysis was shortened from 1—2 hours to several minutes. The carbon disulfide in wastewater can be determined quickly. Analytical precision is $<3\%$ of RSD, mass of detection limit<5 μg, recovery $>90\%$. If the wastewater sample is 10 ml, the lowest detection consistence is <0.5 mg/L.

Key words: wastewater, fast determination, spectrophotometry, CS_2.

The Studies and Assessment for Ecological Environment and Social Economic Conditions in the Upper Reaches of the Changjiang River. Zhong Xianghao et al. (Institute of Mountain Hazards and Eviroment, Chinese Academy of Sciences and Ministry of Water Conservance, Chengdu 610041): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 72—75

The area is distributed in the watersheds of the Wujiang River and the Changjiang River which includes the Jialingjiang River, the Qujiang River, the Fujiang River, the Tuojiang River and the upper reaches of Minjiang River in the upper reaches of the Changjiang River. Applied the integrated standpoint under guidance of the theory of systems science, the characteristics of natural and social economic environment and the assessment for their effects on the forests, ecological econoimc divisions and macroscopic overall arrangement of the ecology-economic protection forest system, and quantitative forecast for development prospects of the protection forests in each of the ecological economic divisions have been studied. A great quantity of technological data, and quantitative and qualitative assess-