重金属在胶州湾表层沉积物中的分布与富集*

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提要 用原子吸收法测定了胶州湾表层沉积物中重金属的含量并运用平均富集因子(*AEF*)对其污染与富集状况进行了分析与评价,发现重金属在胶州湾表层沉积物中的分布极不均衡,高浓度值主要分布在河口区,与历史资料相比,平均含量都有所升高,Cu、Zn、Pb、Cd、Hg、Cr、As已有不同程度的污染富集。污染源主要来自工业和居民生活排污,沉积物中有机质的存在也对重金属的分布与富集起着重要的作用。

关键词 胶州湾,沉积物,重金属,分布,富集
中图分类号 P931

作为污染物的"存储器",海洋沉积物在污染物的输运和存储过程中都起着重要的作用,因此被许多研究者用来确定有毒污染物的来源、扩散途径及归宿(Mann *et al*, 1983; Rule, 1986; Sarmani *et al*, 1992; Murray, 1996; 贾成霞等, 2004; 田 蕴等, 2004; 宋金明等, 2004)。由此沉积物正在被越来越多地用于评价人类活动对水环境造成的冲击(Bryan *et al*, 1992; Bubb *et al*, 1994; Daskalakis *et al*, 1995; 郑丽波等, 2003)。沉积物中不断积累的有毒物质和不断增加的有机质会对底栖生物或依靠沉积物生存的生物产生毒害作用,并通过食物链富集和传递,最终对人类健康造成影响(Lawrence *et al*, 2001)。众多污染物当中,重金属由于其毒性和持久性而成为影响沉积物质量较严重的一类(Srinivasa *et al*, 2004)。因此,具有源和汇双重作用的沉积物在重金属污染评价中至关重要(Chapman *et al*, 1999)。

胶州湾是一个典型的半封闭型浅水海湾,位于山东半岛南岸西部,为青岛市所包围,面积为390 km^2,平均水深7m。湾口仅宽2.5km,以此与黄海相通。胶州湾最重要的淡水输入源来自大沽河,年平均流量为$6.61\times10^8 m^3$,其它多条入湾河流海泊河、李村河、娄山河等常年无自然径流,上游常年干涸,中、下游已成为市区工业废水和生活污水的排污沟渠。近年来,尽管在几条河流的入海处都建成了大型的污水处理厂,但每年仍有数千万吨废水污水排放入海,同时海上运输、观光旅游、养殖与捕捞等人类活动都给予胶州湾生态系统以强烈的影响。国家海洋局第一海洋研究所和北海分局监测监视中心分别于1980年和1989年对胶州湾沉积物样品进行了重金属的分析研究(海湾志编辑委员会, 1992),陈先芬(1991)和殷效彩等(2001)也曾先后报道了其表层沉积物中重金属的含量与分布,但未见有关沉积物中重金属富集状况的分析报道。针对该不足,作者于2003年11月在胶州湾采集表层沉积物样品33个,测定了

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其中有机质和金属元素(Zn, Pb、Cd、Cu、Hg、As、Cr、Al、Fe、Mn)的含量,并与历史资料相比较总结了其分布规律;计算了各元素的富集因子,对胶州湾沉积物中重金属的污染状况进行了评价。

1　采样及样品处理

本次调查在胶州湾布设的表层沉积物有效监测站见文献(李　玉等, 2005)。用抓斗式采泥器在33个站点采集底泥,用塑料勺取其中央未受干扰的表层0—2cm泥样于聚乙烯袋中,0—4℃下保存,回实验室待测。将解冻至室温的样品在80°C烘箱内烘干24h,用玛瑙研钵将其研碎并全部通过160目筛,充分混匀后取样以供测定(为避免样品被玷污,取样及碎样等工具及器皿均先净化处理)。铅、镉用石墨炉原子吸收分光光度仪测定(Bay *et al*, 2003);铜、铬、锌、铁、锰以火焰原子吸收分光光度法测定,汞用冷原子吸收法测定(黄华瑞, 1988);铝用等离子体发射光谱仪测定(Leivuori, 1998),砷以原子荧光光谱法测定(乔永民等, 2004)。沉积物消解方法见《海洋监测规范》(国家海洋局, 1998)。为检测分析方法的精确性,本文中作者测定了标准沉积物样品(代号GSBZ50012-88,国家海洋局北海分局提供)中各元素的含量,并与其参考值对比。沉积物中总有机质的含量以灼烧法来测定,用烧失量(loss of ignition, LOI)表征。作者以550℃、灼烧2h的条件(Borg *et al*, 1996),测定了沉积物中的总有机质的含量。用统计软件Statistica 5.1进行数据处理。

2　结果与讨论

2.1　胶州湾表层沉积物中有机质的含量及其分布特征

图1为胶州湾表层沉积物中有机质的含量及分布图。从该图上可以看出,有机质在全湾的分布极不均衡,最高值为27.72%,出现在海泊河口B0站,最低值则出现在湾外站,为0.89%,在内湾有机质的含量范围在4.91%—10.23%之间。有机质与重金属Cu、Zn、Pb、Cd、Hg、Cr之间的Pearson相关分析(表1)表明了沉积物中有机质的存在对重金属分布的影响。那么有机质与重金属之间有着怎样的线性关系呢? 经计算认为,胶州湾表层沉积物中有机质的含量与重金属的浓度之间为$y = 59.29 + 2.29Zn$; $y = -25.08 + 6.71Cu$; $y = 24.33 + 1.01Pb$; $y = 0.052 + 0.028Cd$; $y = -0.11 + 0.027Hg$; $y = 36.76 - 0.76As$; $y = 14.08 + 12.49Cr$。从上面的方程可以看出,在有机质与金属之间除了As外,其它重金属都有正相关关系。作为一个良好的重金属的结合底物(Soares *et al*, 1999),有机质含量与成分的变化是决定表层沉积物中重金属分布的主要因子之一(Borg *et al*, 1996)。

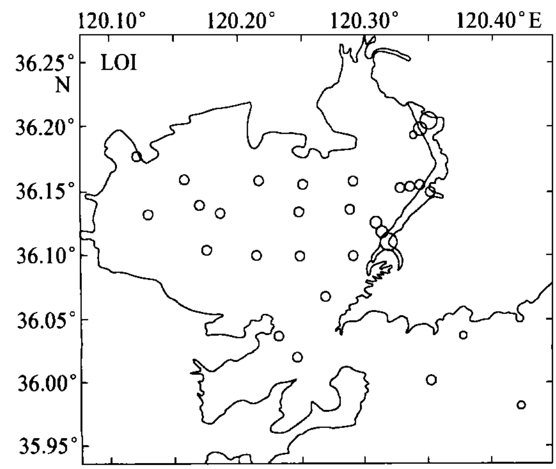

图1　胶州湾表层沉积物中有机质(LOI)的含量(%)分布

Fig. 1　The distribution of LOI contents(%) in surface sediments in Jiaozhou Bay

◦ 0.89—1.46; ○ 1.46—4.91; ○ 4.91—10.23; ○ 10.23—16.21; ○ 16.21—27.72

2.2　胶州湾表层沉积物中重金属的浓度及分布特征

通过测定标准沉积物样品得出各元素的分析误差(表2),结果发现,所有元素的分析误差皆在5%以内。胶州湾表层沉积物中Cu的含量为9.74—499mg/kg,平均值为53.04mg/kg,高于1980年和1989年调查结果的平均值,见表3。与国内及国外海湾相比,胶州湾表层沉积物中Cu的浓度高于渤海湾、G ll k 湾、Saros 湾、İzmir 湾、C diz 湾表层沉积物中Cu的含量,但低于美国Boston港口表层沉积物中Cu的含量。从图2上来看,含量在各监测站间差异较大,最高值出现在娄山河口,最低值出现在胶州湾西部,这种分布趋势与1980年及1989年的调查结果基本一致。从表1可知,Cu、Zn、Cd、Cr之间具有显著的正相关,表明胶州湾表层沉积物中这几种重金属可能有着共同的来源:城市污水和海事活动。本次调查结果中Zn的平均浓度为95.88mg/kg,是1980年调查结果(70.355mg/kg)的1.36倍。与其它海湾相比较,

表 **1** 各污染物间 **Pearson** 相关系数($P< 0.05$)

Tab. 1 Pearson correlation coefficients($P < 0.05$) among pollutants

元素	Cu	Zn	Pb	Cd	Hg	As	Al	Cr	Mn	Fe
Zn	0.903									
Pb	0.736	0.705								
Cd	0.745	0.749	0.530							
Hg	0.934	0.912	0.780	0.763						
As	-0.393	-0.336	-0.231	-0.187	-0.371					
Al	-0.433	-0.363	-0.125	-0.349	-0.446	0.697				
Cr	0.943	0.934	0.714	0.653	0.881	-0.354	-0.301			
Mn	-0.020	-0.072	0.134	-0.332	-0.147	0.648	0.600	0.073		
Fe	0.622	0.499	0.842	0.521	0.582	0.077	0.178	0.596	0.385	
LOI	0.745	0.732	0.459	0.714	0.675	-0.354	-0.481	0.701	-0.240	0.398

表 **2** 本研究中测定的标准沉积物样品中各元素的含量与其参考值的对比

Tab. 2 Comparison of values of elements of reference sediments obtained in the present study with certified values

元素	本研究中测定值	参考值	分析误差(%)
Cu(mg/kg)	28.2	28.1	0.36
Zn(mg/kg)	60.1	61.5	2.28
Pb(mg/kg)	23.6	24.0	1.67
Cd(mg/kg)	0.034	0.035	2.86
Hg(mg/kg)	0.0169	0.0173	2.31
As(mg/kg)	9.21	9.56	3.66
Al(%)	14.49	14.9	2.75
Cr(mg/kg)	78.48	79.9	1.78
Mn(mg/kg)	1111	1063	4.48
Fe(%)	3.06	3.07	0.33

胶州湾表层沉积物中 Zn 的含量远高于红海湾, 远低于西班牙的 C diz 湾, 略低于美国 Boston 港口。从图 2 上来看, Zn 的高值主要出现在胶州湾东部海泊河口、李村河口、娄山河口及青岛港邻近海域。与 1989 年的调查结果相比, 本次调查所监测到的胶州湾表层沉积物中重金属 Pb 的含量并不高, 且分布也较均匀, 绝大部分海域的含量值都在 21.64—51.87mg/kg 之间, 但较之 1980 年, 平均值则增加了接近 5 倍。与文献所报道的国外各重要海湾相比, 发现胶州湾沉积物中 Pb 的含量高于土耳其的 G ll k 湾、Saros 湾和 İzmir 湾, 但远低于美国的 Boston 港口。从图 2 可见, 最大值出现在青岛港。由此可知, 港口内部及周围海域的海上运输活动对沉积物造成了重金属 Pb 的局部污染。胶州湾表层沉积物中重金属 Cd 的分布趋势与 Pb 相似, 但在湾内 B3 站出现一个高值 (0.805mg/kg), 平均浓度(0.496mg/kg) 与 1989 年的调查结果(0.46mg/kg) 及 G ll k 湾的含量(0.56mg/kg) 接近。胶州湾表层沉积物中 Hg 的分布特征与 Zn 极为相似, 含量在各测站间差异较大, 高值主要出现在胶州湾东部海泊河口、李村河口、娄山河口及青岛港邻近海域, 平均值为 0.212mg/kg, 分别是 1989 年和 1980 年平均含量的 1.39 和 1.66 倍, 但最高含量则分别是 1989 年和 1980 年的 3.3 和 3.7 倍。表层沉积物中重金属 Cr 的分布趋势与其它金属相似, 高值出现在胶州湾东部河口区及邻近海域, 但与历史资料相比, 无论是含量还是空间分布特点都有了极大的不同, 平均值是 1989 年的 3 倍, 最高值则是 1989 年最高含量的 10 倍, 在分布上胶州湾东部站位与西部站位差异较大, 并不似 1989 年报道的均衡分布(海湾志编辑委员会, 1992)。与其它海湾相比, 胶州湾表层沉积物中 Cr 的平均含量高于渤海湾, 但远远低于 C diz 湾

表 3 胶州湾和其它海湾表层沉积物中金属元素的浓度(范围和平均值:mg/kg)

Tab.3 Concentrations (range and mean: mg/kg) of trace metals in surface sediments in Jiaozhou Bay and other bays

海 区	Pb	Cu	Cd	Hg	Cr	Zn	As	Mn	Fe	Al
胶州湾[1)]	14.19—91.21 35.17	9.74—499 53.04	0.072—1.94 0.496	0.018—2.11 0.212	42.7—430 99.2	47.64—170 95.88	21.02—37.84 30.27	243—883 474	1.11—2.09 1.73	21.0—37.8 13.2
胶州湾[2)]	3.7—70.9 26.6	8.8—133.6 36.18	0.02—2.31 0.46	< 0.1—0.639 0.152	29.54—44.61 38.09					
胶州湾[2)]	< 12.0 5.953	1.5—62.3 11.327	0.45—3.75 1.39	0.008—0.571 0.128		19.5—256.4 70.355				
渤海湾[3)]	11.4—41.2 22.4	7.8—36.2 26	0.04—0.54 0.15	0.005—0.560 0.065	26.7—66.7 49	35.3—151.2 73.6	8.88—18.1 13.8	248—1007 626	3.54	
红海湾[4)]	18.9—59.1 34.7					17.6—89.7 48.7				
红海湾[4)]	22—62.4 38.9					17.5—90.3 45.1				
Güllük 湾[5)]	20	25	0.56			81				
Saros 湾[6)]	22	19				73				
İzmir 湾[7)]	23—52	13—49				45—114				
Cádiz[8)]	28				224	186				
Boston 港[9)]	86	67			131	118				

1)本研究; 2)海湾志编辑委员会,1992; 3)黄华瑞,1988; 4)甘居利等,2000; 5)Dalmanö, Demirak A, Balci A, 2005. Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the Southeastern Aegean Sea (Turkey) by atomic absorption spectrometry. Food Chemistry; 6)San *et al*, 2002; 7)Balci A *et al*, 1993; 8)Carrasco *et al*, 2003; 9)Bothner *et al*, 1998

(224mg/kg)和美国 Boston 港口(131mg/kg)。As 的空间分布与其它金属不同(图 2),含量为 21.02—37.85mg/kg,平均值为 30.27mg/kg,在大沽河口(A11 站),C3 站(青岛港附近)及湾外 D8 站出现较高值,而在胶州湾东部海泊河口、李村河口、娄山河口则出现较低值。

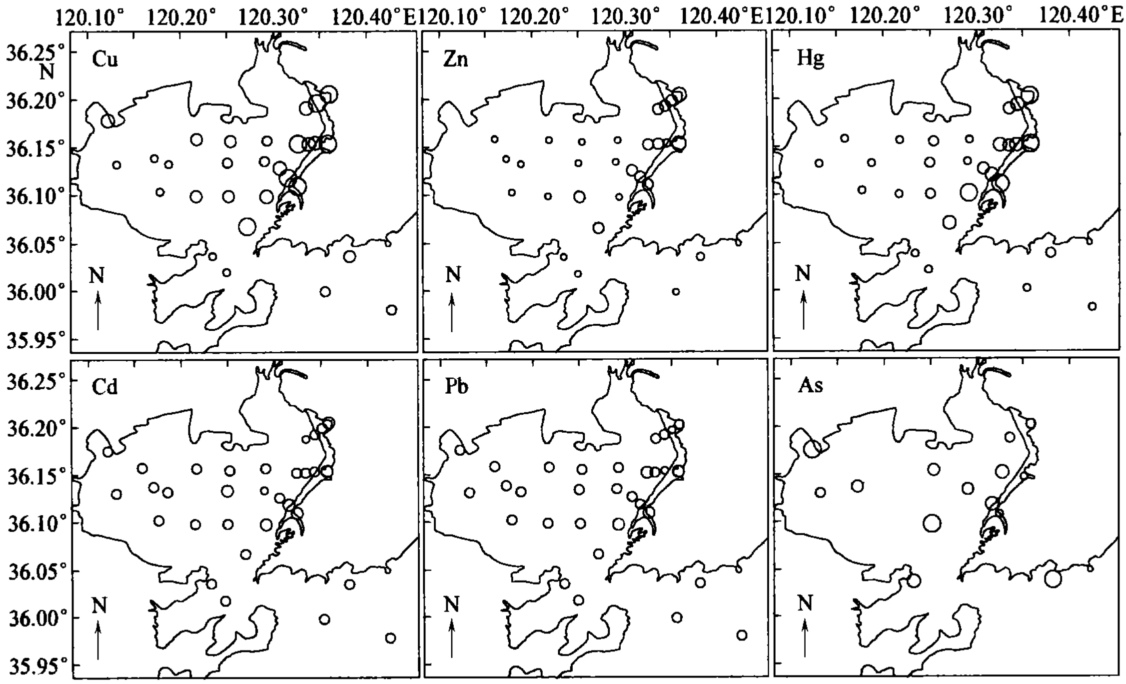

图 2 胶州湾表层沉积物中重金属的空间分布

Fig. 2 The spatial distribution of heavy metals in Jiaozhou Bay surface sediments

Cu: ◦ 9.74—19.32; ○ 19.32—24.51; ○ 24.51—32.91; ○ 32.91—46.59; ○ 46.59—498.9

Zn: ◦ 47.64—94.45; ○ 94.45—102.4; ○ 102.4—151.2; ○ 151.2—170.5

Hg: ◦ 18.39—41.11; ○ 41.11—84.8; ○ 84.8—158.7; ○ 158.7—409.9; ○ 409.9—2111

Cd: ◦ 0.072—0.103; ○ 0.103—0.799; ○ 0.799—1.94

Pb: ◦ 14.19—21.64; ○ 21.64—51.87; ○ 51.87—91.27

As: ◦ 21.02—23.16; ○ 23.16—31.06; ○ 31.06—32.77; ○ 32.77—35.55; ○ 35.55—37.85

2.3 胶州湾表层沉积物中重金属的富集状况

为了表征胶州湾表层沉积物中重金属的富集及污染状况,作者计算了各重金属的平均富集因子 *AEF*。数学表达式如下(Cobelo-Garcıa *et al*, 2004): $AEF_{Me}=AC_{Me}/BV_{Me}$,AC_{Me}指的是被测金属的平均浓度,BV_{Me}指的是被考察海区此金属的背景值(吴景阳等, 1982)。根据 H¼kanson(1980)给出的定义,胶州湾表层沉积物金属污染可分为三类:轻度污染($AEFs<2$),其中有 Zn、Pb、Cr、Mn 和 Fe、*AEF* 分别为 1.06、1.04、1.52、0.80、0.45;中度污染($AEFs=2$—3),包括 Cu($AEF=2.06$)和 Cd($AEF=2.07$);严重污染($AEFs>3$),包括 As 和 Hg,其 *AEF* 分别为 3.03、5.03。从图 3 中可知,Cu、Zn、Pb、Cd、Hg、Cr 的 EF 高值都出现在胶州湾东部娄山河口、李村河口、海泊河口、青岛港及邻近海域,As 则是在大沽河口出现 EF 高值。因此可以说,胶州湾东部的入湾河流及青岛港是 Cu、Zn、Pb、Cd、Hg、Cr 等的主要点污染源,并对沉积物造成了局部污染,而导致 As 污染的则主要是来自大沽河的农业污水。

对胶州湾表层沉积物中各种污染物进行因子分析可以证明以上所得结果,由统计分析得知前三个因子可以解释总变量的 86.48%。因子 1 的贡献率为 52.61%(图 4),其特点表现为因子变量在 Cr、Cu、Zn、Cd 的浓度上有较高的正载荷,因此表征了工业排污和生活污水对沉积物的污染;因子 2 的贡献率是 17.37%,在有机质(LOI)上的载荷为 0.809,除 As 外,所有重金属与 LOI 都呈显著

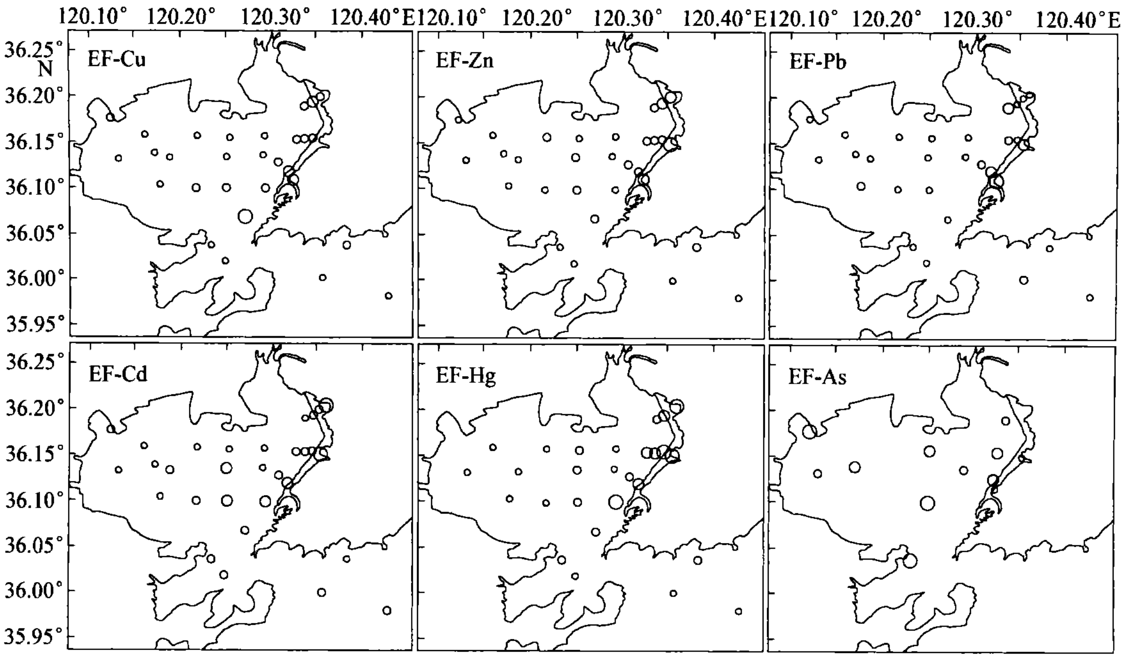

图3 胶州湾表层沉积物中重金属富集因子的分布

Fig.3 Distribution of enrichment factors (EF) in heavy metals in Jiaozhou Bay surface sediments

EF—Cu: ◦ 0.38—1; ○ 1—1.93; ○ 1.93—6.2; ○ 6.2—19.34

EF—Zn: ◦ 0.53—1.02; ○ 1.02—1.5; ○ 1.5—1.67; ○ 1.67—1.88

EF—Pb: ◦ 0.42—1.06; ○ 1.06—1.4; ○ 1.4—1.96; ○ 1.96—2.69

EF—Cd: ◦ 0.3—1.07; ○ 1.07—3.05; ○ 3.05—6.14; ○ 6.14—8.08

EF—Hg: ◦ 0.46—1.02; ○ 1.02—3.02; ○ 3.02—6.12; ○ 6.12—52.75

EF—As: ◦ 2.1—2.4; ○ 2.4—3.16; ○ 3.16—3.42; ○ 3.42—3.78

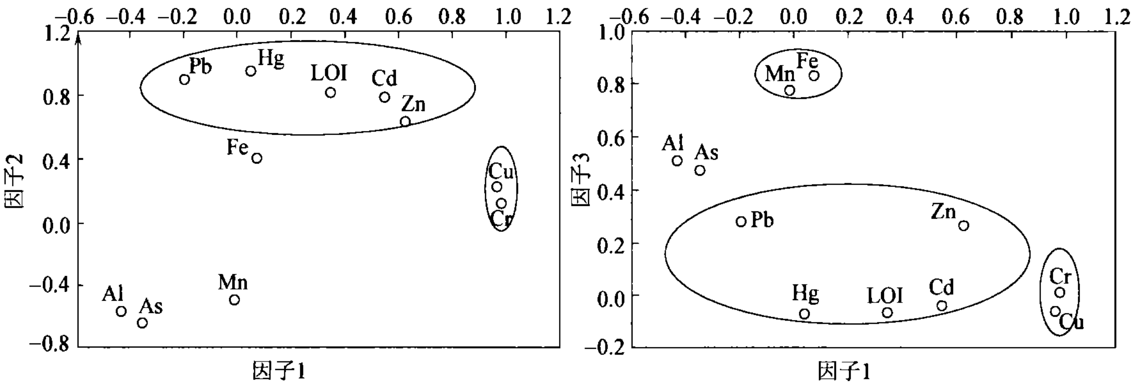

图4 各污染物的二维因子载荷

Fig.4 2-D-factor loading of each pollutant

正相关,说明了沉积物中有机质的存在对重金属的分布与富集起着重要的作用;因子3的贡献率是15.60%,其主要特征是在Mn和Fe的浓度上有较高的载荷。由于Mn和Fe是海洋沉积物中的主要化学成分,所以这个主成分主要表征了地球化学成分的变化对沉积物中污染物的影响(Krzysztof Loska *et al*, 2003; DelValls *et al*, 1998)。从图4中各种污染物所处的位置可以看出,Cu和Cr主要受第一主成分的支配;Hg、Pb主要受第二主成分的支配;As主要受第三主成分的支配;Zn、Cd总是位于Cu—Cr和LOI的中间,说明受第一主成分和第二主成分共同支配。

3 结论

胶州湾表层沉积物中重金属 Cu、Zn、Pb、Cd、Hg、Cr 主要分布在胶州湾东部海泊河口、李村河口、娄山河口、青岛港及邻近海域, As 的高浓度值出现在胶州湾西部的大沽河口。与历史资料相比, 除 Cr 外, 空间分布特征基本相似, 但平均含量都有所升高。根据平均富集因子对沉积物中重金属的富集状况进行分析, 发现 Cu 和 Cd 属于中度污染(*AEFs*= 2—3) , As 和 Hg 则在部分海区污染较为严重(*AEFs*> 3)。通过因子分析发现, 表层沉积物中重金属主要来源于工业排污和生活废水, 此外, 沉积物中有机质的存在对重金属的分布与富集也起着重要的作用。Owen 等 (2000) 指出, 判断半包围型海湾能否造成污染主要取决于工业废水与生活污水的排放和细沉积物扩散之间的平衡。胶州湾表层沉积物中重金属的空间分布特点与湾内潮流运动规律(刘瑞玉, 1992) 有着直接的关系。

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DISTRIBUTION AND ENRICHMENT OF HEAVY METALS IN SURFACE SEDIMENTS OF JIAOZHOU BAY

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Abstract Marine sediments, the sinks for pollutants, are widely recognized as a potential source of pollution, not only because they are always toxic above a certain level, but also they linger at sea bottom for long period. The sediments may therefore be indicative of long and medium-term metal loads. Heavy metals can be natural components of sediments. They come from rock outcrops and soils due to their geochemical mobility. They can be also anthropogenic, as artificial pollutants coming from industrial or urban discharges. Jiaozhou Bay is a semi-enclosed bay in eastern part of Shandong Peninsula, China, 390 km^2 and 7 m deep in average, surrounded by Qingdao City with 7 million population. A dozen of small rivers meet in the bay; the largest one is Dagu River, in annual average runoff of $6.61 \times 10^8 m^3$. Most of these rivers have become discharge passages for industrial and household wastes. In this study, concentrations of heavy metals (Zn, Pb, Cd, Cu, As, Hg, Cr, Al, Fe, and Mn) in surface sediments of Jiaozhou Bay were determined and the average enrichment factors *(AEFs)* were used to assess the metal contamination.

The contents of organic matter in samples in Jiaozhou Bay varied considerably, ranging between 27.72% and 0.89%. High concentration occurred in Haipo River mouth and Loushan River mouth, while low concentration in outer bay. In inner bay, the levels of organic matter were in median level between 4.91%—10.23%. The organic material in the sediment was positively related with Cu, Zn, Cd, and Hg. As a good binding substrate for these metals, organic matter can cause change of these metals in the sediments.

Cd, Cr, Cu, Pb, and Hg had a similar distribution pattern with the one in 1989; however, all the mean values were higher in this study. Compared to other bays in China, the contents of Cd, Cr, Cu, Pb, Zn, and Hg were higher than those in Bohai Bay; the mean value of Pb (35.17 mg/kg) was very close to the mean value of Pb (38.9 mg/kg) in Honghai Bay (near Shanwei of Guangdong), but the Zn content doubled for nearly 100 times in Jiaozhou Bay. As a whole, these metals distributed mainly in the eastern part of Jiaozhou Bay near river outfalls and the Qingdao Harbor. Moreover, a clear gradually declining in the concentration was shown from river mouths to outer sea. Anthropogenic inputs to inner bay were clearly indicated. But for As, there was an exception. High As values were observed at Dagu River mouth and near Qingdao Harbor, which may have resulted from run-off from agricultural areas using As-rich fertilizers or pesticides, or busy ocean shipping. In total metal concentration, Cu and Cr showed the closest positive correlation, indicating their similar origin and behavior.

To estimate the possible hazard of heavy metal contamination in the bay, the average enrichment factors, an indicator of average concentration of a given metal, and the background value were calculated. Using the classification of H¼kanson (1980), the metals in this bay can be divided into three groups: 1) negligible to low contamination, including Zn, Pb, Cr, Mn, and Fe; 2) moderate contamination including Cu and Cd; 3) severe contamination, including As and Hg.

These findings are supported by the results of principal component analysis (PCA). Three principal components were identified taking 86.48% of the total variance. Factor 1, the general loading of the bottom sediment with heavy metals, accounted for 52.61% and characterized by high levels of Cu, Cd and Cr. Therefore, Factor 1 is closely related to the point sources of metal contamination. Factor 2 accounted for 17.37% of the total variance. A high and positive loading occurred for LOI, corresponding closely to the concentration of organic matter in the bottom sediments, indicated the importance of the organic matter in banding metal ions in the sediments. The concentrations of elements examined were positively correlated with LOI. Thus, the degradation of organic matter and their concomitants would release metals and become secondary source of metal pollutant. Factor 3 was characterized by a high positive contribution of Fe and Mn. Fe and Mn are included in same geochemical matrix with other heavy metal elements; they could therefore be used as an indicator to heavy metal pollution.

A large amount of untreated land-sourced metal-bearing discharges entering the bay without getting sufficient dilution in the bay or fast transportation to outer sea, have caused the heavy metal accumulation in sediment. Besides, organic matters are important for the re-distribution and accumulation in the sediments.

Key words　Jiaozhou Bay, Sediments, Heavy metal, Distribution, Enrichment