

(HUANJING KEXUE)

ENVIRONMENTAL SCIENCE

第35卷 第1期

Vol.35 No.1

2014

中国科学院生态环境研究中心 主办

斜 学 出 版 社 出版



ENVIRONMENTAL SCIENCE

第35卷 第1期 2014年1月15日

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滇池沉积物中主要污染物含量时间分异特征研究

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摘要:基于滇池10个监测点(1991~2010年)表层沉积物中主要污染物(Cd、Cr、Cu、Hg、Pb、Sn、Zn、TP以及KN)含量数据,利用SOM自组织映射神经网络对污染物时间演变特征进行识别.将1991~2010年分为4个阶段,1991~1995年低含量阶段;1996~2001年高含量阶段;2002~2006年含量波动阶段;2007~2010年含量回落阶段.各沉积物中污染物的变化模式不尽相同,但各类重金属含量峰值多集中出现在1996~1999年、2005~2007年2个时间段内.在污染物含量变化的时序分析基础上,参考人湖污染负荷、污染源普查数据等相关资料,分析人类活动对滇池沉积物中主要污染物的影响,发现人类活动对沉积物中污染物含量变化的影响很大,在污染物排放量大的时期,沉积物中污染物含量也会随之出现明显升高,在采取污染控制及治理措施后,沉积物中污染物含量会随之下降.

关键词:沉积物; SOM; 时间分异特征; 滇池; 人类活动

中图分类号: X131.2; X524 文献标识码: A 文章编号: 0250-3301(2014)01-0194-08

Study on the Stages of Major Sediments in Dianchi Lake

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Abstract: The statistical technique self-organizing maps (SOM) was applied for stages analysis of Lake Dianchi sediments, southwestern China. The dataset of nine pollutants, including Cd, Cr, Cu, Hg, Pb, Sn, Zn, TP and KN, was observed and collected for 10 monitoring sites from 1991 to 2010. The results show that the 20 years' study could be divided into 4 stages. In stage one (1991 to 1995), concentrations of sediments are relativity low. In the second stage (1996 to 2001), concentrations of most sediments are higher than the stage before and show increasing trends. In the following stage (2002 to 2006), majority of the observed sediments exhibit fluctuation characteristics. Nevertheless, different concentration patterns exist among different pollutants, the concentration climaxes of most pollutants have been observed during the year 1996 to 1999 and 2005 to 2007. According to the relevant information gathering from yearly lake pollution load, the national survey of pollution sources etc., the reason for the above stages and concentration patterns of observed sediments are analyzed. The result shows that sediment concentration is sensitive to human activities in the basin, such as pollution emission as well as controlling.

Key words: sediments; SOM; time stages; Lake Dianchi; human activities

滇池是我国著名的高原湖泊. 近 20 年来,由于受到流域经济发展、人口增长的影响,滇池水质恶化程度不断加剧,在人为环境干扰的作用下,滇池沉积物中污染物含量已远超出土壤本底值,且整体污染情况逐年加重^[1]. 沉积物会再悬浮造成内源污染,如营养盐、重金属的释放^[2],从而进一步影响到湖泊水质、水环境安全与健康. 针对滇池沉积物的研究开展较多. 李宝等^[3]研究了滇池沉积物内源营养盐的释放通量,李仁英等^[4]揭示了滇池沉积物中污染物的形态分布,邵晓华等^[5]探讨了滇池沉积物中污染物的时空分布情况,陈云增等^[6]对滇池沉积物中污染物的时空分布情况,陈云增等^[6]对滇池沉积物中污染物含量的时间演变模式,尤其是结合人类活动对沉积物变化的成因进行分析,却鲜见报道.

沉积物污染的历史,可以反映湖泊污染的发展 过程,同时记录了流域内人类活动与自然环境的相 互作用^[7]. 通过研究过去 20 a 滇池沉积物主要污染物的时间分异性,结合入湖污染负荷、污染源普查数据、滇池治理等相关资料进行讨论,可以更好地剖析滇池沉积物污染物的整体变化过程,评判人类活动对沉积物中污染物的影响方式与程度.

1 材料与方法

1.1 样品的采集与测定

1991~2010年每年3月,对滇池草海、外海共10个监测点(图1)进行采样,采用北京新地标土壤

收稿日期:2013-04-01;修订日期:2013-06-06

基金项目:国家自然科学基金项目(41222002); 国家水体污染控制 与治理科技重大专项(2013ZX07102-006)

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设备有限公司生产的活塞式柱状沉积物采样器,进行表层沉积物取样、样品保存、运输、风干、初粉碎、缩分,细粉碎,过100目样筛.按文献[8]分别对沉积物中的Cd、Cr、Cu、Hg、Pb、Sn、Zn、TP、KN进行含量分析测定.考虑到底泥相对于水质较稳定的特征,每年1次采样可基本代表当年的污染变化情况.

1.2 分析方法

为获得滇池沉积物主要污染物在 1990~2010年间的时间演变模式,在散点图分析的基础上,联合使用因子分析法 (FA)和自组织映射神经网络 (SOM).因子分析旨在对沉积物指标进行降维,剔除冗余信息,确保分析的准确性.在此基础上,采用基于不分层最近邻居法分类的(K Nearest Neighbors)自组织映射神经网络实现不同年份数据的特异性分析^[9,10].

本研究数据预处理和多元统计过程采用 Microsoft Excel 2010、STATISTICA 8 以及基于 MATLAB® 2012 计算平台的 SOM Toolbox (Ver. 2.0)工具箱[11].

2 滇池沉积物主要污染物的时序分析

1991~2010年间,滇池沉积物中主要污染物含量呈现出波动变化,且有明显尖峰的特征.从空间分布情况看,监测点间的空间分异性不强,主要表现为草海与外海沉积物含量的差异(表1),但变化趋



图 1 滇池沉积物监测点位示意

Fig. 1 Monitor stations for Lake Dianchi sediment survey

势无显著差别. 从沉积物主要污染物时间变化趋势看,污染物的变化模式可以分为3类:①先上升后下降再回升模式;②先上升后下降模式;③波动变化模式.

表 1 滇池沉积物空间分类情景1)

Table 1 Spatial classification of sediments in Lake Dianchi

		Tuble 1	patiai ciassification (or seamments in Buite	Bidiiciii	
序号	11左301 上 />			景		
175	监测点位	2	3	4	5	6
1	草海中心(草海)					
2	白鱼口					
3	观音山东					
4	观音山中					
5	灰湾中					
6	滇池南				0	0
7	观音山西				0	0
8	海口西			Δ	Δ	Δ
9	罗家营			Δ	Δ	\Diamond
10	断桥(草海)	☆	☆	☆	☆	☆
正确率	线性判别	0. 970	0. 945	0. 625	0. 555	0. 505
11. 州平	贝叶斯判别	0. 975	0. 950	0. 765	0.650	0.610

1)不同符号代表不同的空间分类类别.

2.1 滇池沉积物重金属的时序分析

沉积物 Sn、Cr 含量呈先升后降再回升的趋势 [图 2(a)、2(b)]. 对于大多数监测点,Sn 含量在 1996~1999 年间达峰值(文中所指峰值均在含量分

布的 10% 之外),随后下降,2003~2005 年起开始小幅回升. Cr 含量在 2005~2006 年间达到峰值,后快速下降,2008 年起开始小幅回升.

沉积物 Cd 含量呈先上升,后下降的变化趋势

[图 2(c)]. 在 1991~1995年间 Cd 含量逐渐上升, 1999~2010年间波动回落,含量在 1996~1998年间达到(除罗家营监测点)最高.

沉积物 H_g 、 P_b 、 C_u 、 Z_n 含量呈现无规律波动变化[图 $2(d) \sim 2(g)$]. H_g 含量峰值集中在 1996 ~ 1998 、 $2005 \sim 2006$ 年 2 个时间段内. P_b 含量峰值较为分散,集中在 1996 ~ 1998 、 $\sim 2002 \sim 2007$ 年

间. Cu 含量峰值非常分散,不同监测点峰值在1993、1996~1999、2007~2009年间均有出现. Zn 含量峰值主要集中在1996~1998年、2005~2007年内.

综上所述,滇池沉积物重金属污染物的变化模式虽不尽相同,但各类重金属含量峰值多集中出现在为1996~1999、2005~2007年2个时间段内.

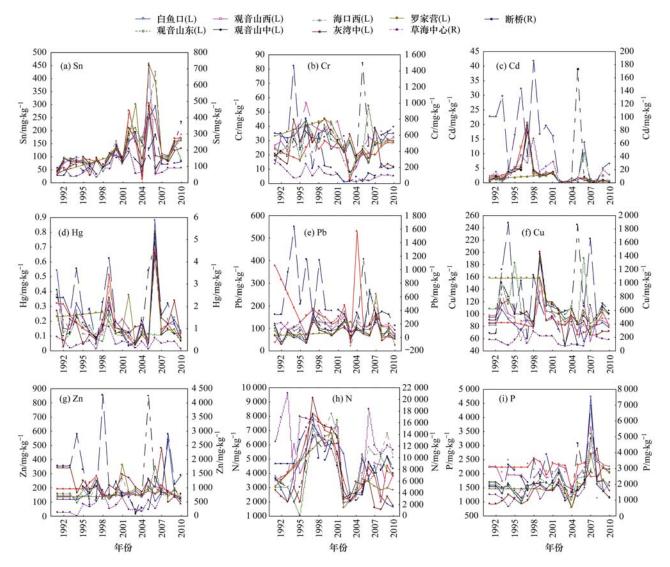


图 2 1991~2010 年滇池沉积物主要污染物含量变化

Fig. 2 Concentrations of major sediments in Dianchi during year 1991 to 2010

2.2 . 滇池沉积物营养盐的时序分析

滇池底泥 KN含量呈先升后降再小幅上升的变化趋势. 除罗家营外,其他点位的 N含量在1996~1999年维持较高水平. 从图 2(h)可看出,KN含量自2000年起有明显回落过程,2002~2004年间各监测点含量普遍维持在相对较低水平,2005年后再度回升.

滇池底泥 P 含量呈波动变化趋势见图 2(i),除

海口西和滇池南监测点外,其余监测点峰值出现在 2007、2008年,海口西、滇池南监测点分别在 2004、 2007以及 2007、2008年内出现谷值(<10%).

3 滇池沉积物主要污染物的时间演变模式分析

3.1 滇池沉积物主要污染物的因子分析

考虑到沉积物污染物指标较多,且污染物通常 具有协同排放特点,不同监测指标会包含重复信 息^[12],导致分析准确性的降低,故采用因子分析对原始数据进行降维.

KMO 检验(KMO = 0.87)、Bartlett's 球形检验(P < 0.05)表明本文数据适合进行因子分析. 当总累计

方差 > 80% 时, 共提取 4 个因子, 解释总体方差的 85.13%, 较好地反映了原始变量. 经最大方差旋转后, 得到因子1 代表 Sn、Hg、Pb、Cd、Cu 和 Zn, 因子 2 代表 KN, 因子 3 代表 P, 因子 4 代表 Cr(表 2).

表 2 因子载荷矩阵1)

Table 2 Rotated component matrix (varmix)	Table 2	Rotated	component	matrix ((varmix)
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指标	因子1	因子2	因子3	因子4	指标	因子1	因子2	因子3	因子4
N	0. 230	0. 101	0. 045	0. 953	Pb	0.898	0. 027	0. 176	0. 146
P	0. 168	-0.023	0. 976	0.034	Cd	0.747	-0.012	-0.017	0. 421
Sn	0.880	0.079	0.034	0. 218	Cu	0.843	0.032	0. 353	0. 128
Hg	0.824	-0.074	0.119	0. 143	Zn	0.857	-0.029	0. 122	0. 159
Cr	-0.009	-0.993	0.020	-0.084					

¹⁾粗体代表各因子所包含指标的因子载荷

3.2 滇池沉积物时间演变模式的 SOM 分类

对经因子分析处理过的数据进行 SOM 分类,根据 David-Boulding 指数可以确定最优分类数,滇池沉积物中重金属时间变化的 SOM 分类结果如图 3 所示,当分类数为 4 时, David-Boulding 指数最小,实现最优分类(图 3).

根据原始分类结果并经校正后,可将 1991 ~ 2010 年划分为 4 个阶段(表 3),第一阶段 1991 ~ 1995 年;第二阶段 1996 ~ 2001 年;第三阶段 2002 ~ 2006 年;第四阶段 2007 ~ 2010 年.第一阶段,各类污染物含量较低;第二阶段,污染物含量开始上升,且含量较高;第三阶段,各类污染物含量变化趋

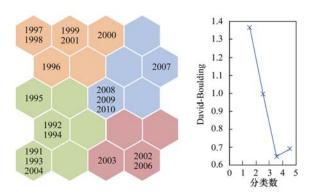


图 3 滇池沉积物时间变化的 SOM 分类结果及最优分类数确定

Fig. 3 Stages of major sediments in Dianchi using SOM method and the optimal number of categories

表 3 滇池沉积物主要污染物时间演变阶段表

Table 3 Stages of major sediments in Lake Dianchi

类别	阶段(年)	特征	第一类沉积物 (Sn、Hg、Pb、Cd、Cu、Zn)	第二类沉积物 (Cr)	第三类沉积物 (P)	第四类沉积物 (N)
1	1991 ~ 1995	低值	含量相对较低,除 Hg,其 余沉积物含量略上升	含量相对较低、略有 上升趋势	含量相对较低、略有 上升趋势	含量相对较低、波动上升趋势
2	1996 ~ 2001	高值	含量陆续达到峰值,主要 集中在1996~1999年	含量上升	含量上升	含量维持在较高水平
3	2002 ~ 2006	波动	含量波动, Sn、Hg、Pb、 Cd、Zn 出现第二峰值	含量上升,2005、2006 年达到峰值	含量波动上升	2002~2003年含量回落, 2004~2006年含量上升
4	2007 ~ 2010	回落	含量回落,并维持相对较 低水平	含量大幅降低	2007年达峰值,随后 含量下降	含量呈下降趋势

势不统一,多为波动变化;第四阶段,各类污染物含量总体呈下降趋势.

3.3 滇池沉积物主要污染物时间演变成因分析

3.3.1 沉积物主要污染物直接来源分析

湖泊是流域上各物质搬运的最后归宿^[13].污染物进入湖泊底层的途径主要有两种:①在重力的作用下,水相中的污染物通过沉积作用沉入湖泊底层;②在水力冲刷的作用下,入湖河道中的沉积物冲刷进入湖泊,并在湖流作用下,在湖泊底泥中进行

分布. 目前,滇池入湖河流年均输沙量在 36.94 万 $m^{3[14]}$,占湖体沉积物总量的 0.4%.

相关分析表明,滇池沉积相污染物含量和水相污染物浓度相关性较低. 比较草海中心、断桥、灰湾中3个监测点入湖口沉积物污染物含量,与同点位湖泊水体、入湖河流水体以及入湖河流沉积物污染物含量的相关性,发现湖泊沉积物与入湖河流沉积物中污染物的含量呈显著相关(表4). 散点图分析可以看出,上述两者在变化趋势上亦具有较高一

致性(以断桥监测点为例,图4),入湖河流沉积物含量峰值较湖体沉积物提前0~2a出现.

湖泊沉积物含量仅表现为与人湖河流沉积物含量相关性高的原因可能是:①重金属污染物在排入水体后会迅速沉降在河道内[15],沉降后的重金属污染物可随河道底泥在水力冲刷作用下再迁移[16],最

终进入湖泊. ②滇池入湖河流 pH 值均值为 7.94. 通常,在碱性条件下沉积物中重金属不易再释放进入水相^[17],因而水相中重金属污染物含量很低. ③对于 N、P 营养盐,在水相和沉积相间发生着复杂、密切的转换过程,但沉积相含量远高于水相浓度,因此这两者难以呈现出简单的线性相关关系(表 4).

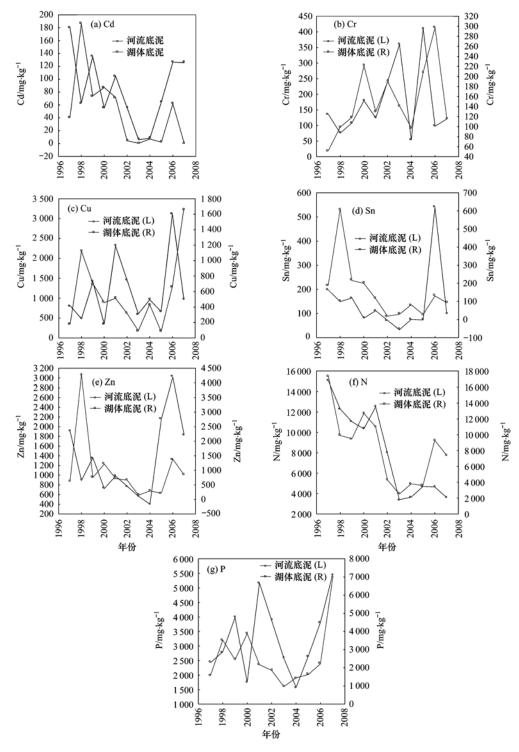


图 4 断桥监测点入湖河流底泥沉积物与湖体底泥沉积物含量变化

Fig. 4 Concentrations of major sediments in lake and river at Duanqiao station

Table 4	Correlation between	the concentrations of	major pollutant	ts in lake sediment	 lake water. 	river water and	river sediment

 沉积物	草海中心			断桥			灰湾中		
0117710	湖体	河流水体	河流沉积物	湖体	河流水体	河流沉积物	湖体	河流水体	河流沉积物
Cr	0. 151	0.003	0.850	0. 298	NaN	0. 781	0. 198	0.001	0. 872
Pb	0.460	0.066	0. 639	0. 198	0.047	0. 184	0.658	0.001	0. 467
Cd	0.409	0. 328	-0.112	0. 230	0.010	0.822	-0.184	0. 127	0. 798
Cu	0. 140	0.007	0.847	0.083	0.057	0. 162	-0.272	0.001	-0.061
Zn	-0.335	0.022	0. 330	0. 146	0. 689	-0.429	-0.055	0. 171	-0.057
KN	0. 152	0. 185	0. 506	-0.274	-0.319	0.814	-0.262	-0.198	0. 916
TP	0. 260	0.028	-0.304	0. 260	0.371	0. 140	0. 335	0.440	0.664

1)粗体为相关系数 > 0.5

3.3.2 人类活动对沉积物中污染物含量的影响分析 1991~2010 年间,滇池流域经历了区域快速繁荣的 20 a,在此期间,流域人口年均增长率为3.3%,GDP 年均增长率 18%,城市化率提高了17%^[18].但经济的飞速发展带给滇池流域巨大的环境压力^[19].滇池流域的工业自 1980 年代初开始大规模发展,初期主要以冶金、化肥等粗放式工业为主^[19],到 1990 年代初期,滇池周边厂矿遍布,产生的大量污染物未经任何处理便排入滇池,造成滇池水质迅速恶化. 1970 年代中后期滇池外海、草海水质为 II 类,但至 1990 年代,已全面恶化为劣 V类^[21],湖泊沉积物环境质量也呈现出污染加剧的趋势^[22].

随着对污染控制及滇池水体保护工作的不断开 展,尤其是"九五"期间,国家和地方开展了大量治 理工作. 2000 年前后,治理成效开始逐渐体现,湖泊 水质呈现出好转趋势, BOD、TN 浓度开始大幅降 低[23]. 潘珉等[24]研究了 1960~2006 年间滇池水质 与流域人口和 GDP 之间的相关关系,发现滇池水体 的 TN、TP 浓度与流域人口数和 GDP 密切相关,但 2000年后,相关性有所减弱. 众多相关资料表 明[25~27], 1999~2000年前后是滇池水质的一个转 折点[20],自1998年国务院对滇池"流域水污染防治 九五计划"及"2010年规划"做出正式批复后,多项 污染源治理措施在滇池流域展开. 1999 年流域开展 了"零点行动",清理关闭了云南印染厂、昆明造纸 厂、昆明冶炼厂等重点污染源,将昆明农药厂、福 保造纸厂制浆生产线等迁出滇池流域. 同时在昆明 市兴建4座污水处理厂,加大了对城市生活污水的 处理力度. 1998-03~1999-03, 滇池草海进行了底泥 疏浚工程,直接去除草海污染底泥量 424 万 $m^{3[25,26]}$.

上述多项治理措施的效果一定程度反映在沉积 物含量的变化上. 自 2001 年后滇池沉积物含量进 人了波动、下降的阶段,尤其以 KN、Sn、Cu 的下降 趋势最为明显. 虽然大部分污染物在 2002 ~ 2006 年间仍以波动变化为主,这是因为影响底泥污染物 的因素较多,外源污染物浓度削减效果往往需要一定时间才能反映在沉积物含量变化上^[27]. 随着"十五"、"十一五"治理项目的进一步开展,污染控制措施进一步严格,滇池湖体水质从 2004 年起逐步转向 IV类^[28],2007 年后,各类底泥污染物含量也相应 呈现出较明显的下降趋势.

重金属污染物在 1991 ~ 2010 年间含量出现了较大幅度波动. Wei 等^[29]研究了滇池流域重金属的本底值(mg·kg⁻¹), Sn: 3.50、Hg: 0.247、Cr: 115.18、Pb:65.76、Zn:153.95. 中国环境监测总站公布的云南土壤环境背景值(mg·kg⁻¹), Cu:33.6、Cr: 57.6、Cd: 0.104、Pb: 36.0、Hg: 0.045、Zn: 80.5^[30]. 从图 2 中可以看出,滇池沉积物重金属污染物含量大多超出了土壤本底值,峰值均呈尖峰形式. 朱广伟等^[31]对太湖沉积物重金属污染物的研究,认为超出本底值的尖峰多为人为因素造成的污染物含量激增. 高丽等^[32]的研究认为,引起滇池底泥重金属污染物变化的主要因素是外源重金属排放,其中以工业污染排放为主.

根据郭怀成等^[20]对滇池流域水环境与社会经济系统调查的结果,滇池流域内 Cr、Cd、Pb、Hg 这4类重金属污染物表现出显著的行业特征性,并集中在特定行业的重点工业中. Cr 是金属制品业的特征污染因子,主要的污染企业是昆明建芳工贸有限公司,其排放量占 Cr 排放总量的 84.66%. Pb、Cd、Hg 是有色金属冶炼及压延加工业的主要污染因子,其中仅云南铜业股份有限公司的排放量就分别占Pb、Cd、Hg 排 放 总量的 60.87%、98.76% 和93.70%.

滇池流域的重金属污染物具有显著的行业及重 点工业特征,工业活动中产生的重金属污染物是流 域重金属的主要来源,污染物随污水排放后会最终沉积到湖泊底泥中,造成湖泊沉积物含量变动.以Cr为例^[33],工业源Cr排放总量的88.7%来自昆明建芳工贸有限公司,该公司成立于2003年,其后1~2 a 中不同监测点底泥Cr含量出现同样的上升趋势,并于2005、2006年达到峰值.再以Sn为例,1988年滇池Sn超标率在33%~100%^[33],1990年代初期开始治理云南冶炼厂、昆明冶炼厂等高Sn排放量企业,1990年代后期,滇池底泥Sn含量呈现出较明显下降趋势.滇池流域的主要重金属来源于工业废水,由于重金属污染物排放后具有稳定、难降解的特征,因此流域工业生产中排出的重金属污染物在排放后0~2 a 内会进入湖泊沉积物,并在湖泊底泥中进行累积.

沉积物 KN 含量变化与人类活动也存在密切联 系. 不同于重金属污染物,滇池流域 TN 排放以农业 面源为主、生活面源为辅,工业企业污染源所占比 例较低[34]. 根据郭怀成等[20]对滇池流域水环境与 社会经济调查的结果,1988~2009年间,滇池流域 的污染物削减能力不断增强,在排放总量不断增加 的情况下,TN 入湖排放量从 2000 年起止升转降. 此外 1999 年,昆明市环保局开展了工业污染整治 "零点行动",清理关闭了如造纸厂、印染厂等一些 高氮污染物排放企业,大大降低了流域内的 TN 入 湖量. 滇池流域 TN 排放量在 2000 年前后的下降趋 势一定程度反映在沉积物含量的变动上,从图 2(h) 中可以看出,在1995~2000年间,各监测点 KN 含 量稳定维持在较高浓度水平,但从2000年起,沉积 物 KN 含量呈现出与 TN 入湖排放量一致的回落趋 势在 2002~2009年间,流域内的 TN 入湖排放量浓 度出现小幅度波动[19],相应滇池各监测点沉积物 KN 含量在 2002~2004 年间普遍在较低水平波动, 2005 年后开始小幅波动上升. 总体来说,沉积物 KN 含量变化存在明显、缓和的变化趋势,并与流域 TN 入湖排放量的变化趋势较为吻合.

滇池沉积物中总磷含量在 1991~2006 年间维持波动变化,部分监测点有小幅上升趋势,2007 年前后多监测点磷沉积物含量出现明显峰值. 然而滇池湖体 TP 浓度在 1991~2008 年间呈逐步上升趋势^[20],并未在 2007 年前后出现明显的浓度激增,尚未找到非常合理的依据来解释 2007 年前后底泥磷含量出现的峰值.

此外,从沉积物含量的空间分布看,明显存在人 类活动对沉积物污染物浓度的影响. 草海区域接纳 了大量来自昆明市的生活污水和工业废水^[35]. 从图 2 中可以看出,滇池草海监测点沉积物各类污染物含量都远高于外海监测点沉积物含量,如 Sn、Cd、Hg 等污染物含量存在数量级上的差异.

4 讨论

本研究通过分析滇池 10 个监测点(1991~2010 年)表层沉积物中主要污染物含量数据,将1991~ 2010年分为低含量、高含量、含量波动以及含量回 落阶段. 其中大多数污染物浓度变化模式在 2000 年左右出现变化,结合滇池流域社会发展及污染调 查数据可以看出,1999年前后,流域内开展了多项 大规模的污染源治理,随之在2000年前后大多数沉 积物含量停止了增长或转为下降趋势,尤其以 KN 变化最为明显. 通过对现有资料的分析,重金属沉 积物如 Cr、Sn 含量都表现出与流域内相关污染源 排放量密切的关系,但限于资料有限,无法对各重金 属沉积物的变化原因——进行解释,也很难就短期 内沉积物污染物含量与人类活动建立定量关系. 然 而通过文中的分析,已经可以看出人类活动在很大 程度上影响了滇池沉积物污染物含量变化,不仅是 工业污染排放会造成沉积物含量的升高,污染控制 及治理也可以有效降低沉积物污染物含量.

但本研究需改进之处尚多,如:①提高采样频率,获得更为准确的沉积物污染物含量数据;②增加采样监测点,以更为全面反应滇池沉积物的情况;③在沉积物直接来源的分析中,考虑河道水体以及底泥中的污染物时,可以再结合流量信息,考虑入湖负荷更为准确;④本研究搜集到的滇池流域污染源排放数据、污染普查数据以及重点污染企业排污情况等数据有待补充,以更好地找到人类活动与沉积物含量变化的关系,尤其是对与沉积物 P 的变化过程,现有资料无法解释.

5 结论

- (1)1991~2010年间滇池沉积物主要污染物的时间演变模式总体分为4个阶段,1991~1995年低含量阶段、1996~2001年高含量阶段、2002~2006年含量波动阶段以及2007~2010年含量回落阶段.
- (2)重金属污染物含量峰值集中出现在 1996~1999 年、2005~2007 年, KN 含量高值区集中在 1996~1999 年间,P 含量峰值则出现在 2006、2007年前后.
 - (3)人类活动很大程度影响了滇池沉积物主要

污染物含量的变化过程,沉积物含量会在人类活动产生影响后的1~2 a 内出现相应的变化.

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(HUANJING KEXUE)

(月刊 1976年8月创刊) 2014年1月15日 35卷 第1期

ENVIRONMENTAL SCIENCE

(Monthly Started in 1976)
Vol. 35 No. 1 Jan. 15, 2014

		1 77 - 11 - 3 71 77			
主	管	中国科学院	Superintended	by	Chinese Academy of Sciences
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		18号,邮政编码:100085)			KEXUE)
		电话:010-62941102,010-62849343			P. O. Box 2871, Beijing 100085, China
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		E-mail; hjkx@ reees. ac. cn			E-mail; hjkx@ rcees. ac. cn
		http://www.hjkx.ac.cn			http://www.hjkx.ac.cn
出	版	4 学业版社	Published	by	Science Press
-	742	北京东黄城根北街 16 号			16 Donghuangchenggen North Street,
		邮政编码:100717			Beijing 100717, China
印刷装	订	北京北林印刷厂	Printed	by	Beijing Bei Lin Printing House
发	行	斜华出版社	Distributed	by	Science Press
		电话:010-64017032			Tel:010-64017032
		E-mail:journal@mail.sciencep.com			E-mail; journal@ mail. sciencep. com
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		(北京 399 信箱)			Shudian), P. O. Box 399, Beijing 100044, China

中国标准刊号: ISSN 0250-3301 CN 11-1895/X

国内邮发代号: 2-821

国内定价:90.00元

国外发行代号: M 205

国内外公开发行