

图 27-12 加拿大安大略湖中鱼类的平均物种数与 pH 之间的关系  
(Matuszek 和 Beggs, 1988)

▲ 食鱼水鸟,如潜鸟(*Gavia immer*)和秋沙鸭(*Mergus merganser*),它们的繁殖成功率和丰度在较高 pH 和低浓度铝的条件下会更高,但是仍然可以在 pH 低至 4.5 的湖泊中成功地繁殖。影响鸟类的主要原因似乎与 pH 关系不大,而只是间接影响,这是由于在低 pH 湖区可捕食的鱼类种群的减少或消失造成的(Doka 等,1997;Jeffries,1997)。然而,低 pH 的北温带北部森林地区的湖泊也是高度贫营养的,捕食被污染鱼类的鸟类受酸度、营养状况(Kerekes 等,1994)、水色(影响水下视觉)和高汞含量的影响(见第 28 章),这意味着很难辨别导致鸟类繁殖成功率变低的真正原因。

所记录的鱼类生存最低 pH 高估了其忍受限度,因为成年鱼为了成功繁殖甚至可以突破这样的忍受极限。由产卵或卵发育失败或刚孵化的幼体死亡导致的繁殖失败是鱼类种群丧失的最常见原因。不幸的是,对于那些渔民或研究寿命较长的猎用成体鱼的生物学家来说,是很难发现这些鱼类繁殖失败的现象的。因此,基于一些特殊的猎用成体鱼存在的测定方法,是不能准确衡量水体或特定物种是否已受酸化影响。物种的年龄分布清晰地表明,当 pH 和环境条件超出了鱼类成功繁殖界限的情况下,一些成鱼个体或物种(如鲈鱼)变得更能抵抗低 pH 所带来的影响。虽然繁殖已经受损,但是一些成鱼的生长率甚至加强了,这可能是食物竞争压力减弱而导致的现象(Ryan 和 Harvey,1980)。

对物种损失的解释还会受到夏天高 pH 的困惑,高 pH 表明除了酸化外还有其他因素导致这种可观测现象的发生。然而,当高酸度的积雪在春天融化所引起的短暂酸化,或夏天周期性的大雨导致的 pH 降低的现象却被忽略了(图 27-7)。每一次在积雪融化期间,短期暴露在 pH 锐减的条件下会使卵和幼虫置身在 H<sup>+</sup> 或金属的急性毒性浓度下,而这种条件下的取样却很少或没有。

低 pH 水域往往都有高浓度的铝(图 27-6),其活性单体的毒性尤其高。大部分的铝来自于流域,另外的铝则来自沉积物的释放。因此,对溪流进行酸化的实验是用 H<sub>2</sub>SO<sub>4</sub> 将 pH 调到 4 左右,这样大量的铝释放到水中(Henriksen 等,1988)。但是在实验室观察到铝

的毒性效应(Parkhursts 等,1990),实质上与其他因素引起的影响相混淆,这些因素包括与  $H^+$  的相关性、钙的供给和吸收以及一些关于程度信息的缺失,即所测的溶解性铝含量能上升的范围,而溶解性铝是以变化的有毒单体形式存在的,并不吸附到 DOC 上或呈稳定状态。

### ▲ 27.10 酸化过程的建模

从简单的经验模型到复杂的动态模型,多种模拟酸化过程模型已被开发出来,这些模型考虑了流域风化过程和接收水域决定 ANC 的化学平衡。比较好的过程模型非常适合于研究得比较透彻的流域和水生系统,因为许多信息可以获得(Reuss 等,1986)。

#### 机制和经验模型

目前,最有影响力的基于过程的分析模型是流域地下水酸化模型(MAGIC)。这个简单的模拟模型应用少数关键的物理和化学过程,这些过程控制着土壤和水中主要的溶解态和吸附态离子的平衡。

与复杂的模型相比,对数据量要求适中的 MAGIC 模型使用更容易,但它会忽略某些重要的过程。模拟模型可以用来预测表层水质随大气降水改变的响应时间。值得一提的是 Cosby 等(1985)的预测模型,这个模型考虑了酸化所需时间和在较好特征流域的不同土壤类型的恢复所需时间,模拟结果与 20 年后所观测的结果接近。

实际的模型存在很多问题,因为控制特殊流域的过程还不明确,使用广泛的预测模型是由 Henriksen(1980)开发的半经验模型,它侧重于测量水线以下的碱度变化,而不像 MAGIC 和其他过程模型,这些模型侧重于流域和沉积物中产生可测量碱的过程。Henriksen 模型已得到了改进(Wright,1983a;Henriksen 和 Brakke,1988),但是,因为在简单的原始版本中,此模型的基本观点和用途都很清楚,在此仅简单论述。

Henriksen(1980)设想了一个具有碱度水体酸化的过程,该过程是用位于表面的强酸( $H_2SO_4$ )进行滴定的方法测量的。他用 ANC 作为未调查流域过程的指示指标,这些过程可解释许多内陆水体的缓冲能力。用酸在整个水生系统进行滴定,其性质就像是在烧杯里用  $Ca(HCO_3)_2$  溶液滴定一样,其程序就是用来确定内陆水体的碱度(图 27-13;见 14.4 节)。

在特定程度上,Henriksen 模型中的酸化可通过碱度(ANC)的改变来表示:

$$\text{酸化程度} = \text{酸化前碱度}(ANC_0) - \text{目前的碱度}(ANC)$$

酸化前碱度的数据很少,并假定存在离子平衡,这样简化了阴、阳离子平衡中的大部分成分,有可能得出如下结论:

$$2[Ca^{2+}]^* + 2[Mg^{2+}]^* = [HCO_3^-] - [H^+] \quad \text{式 27-12}$$

式 27-12 中单位为  $\mu\text{eq/L}$ ,星号(\*)表示非海洋来源的浓度。因此:

$$ANC_0 = [Ca^{2+} + Mg^{2+}]^* \quad \text{式 27-13}$$

但是, $Ca^{2+}$  是迄今为止最重要的阳离子,并假定与  $Mg^{2+}$  和其他阳离子有固定的关系,故方程可以进一步简化:

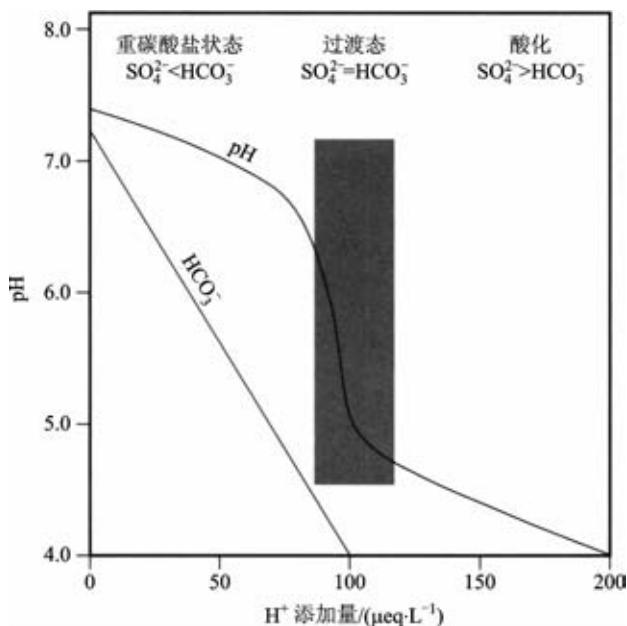


图 27-13 在烧杯中用逐渐增加的强酸来滴定特定含量 (100  $\mu\text{eq/L}$ ) 的碳酸氢钠溶液得到的滴定曲线 [此方法用来阐明酸化过程以及缓冲能力弱 (未酸化; pH 为 5 ~ 6) 的水域对酸化的极度敏感性。酸敏感的清水湖沿 pH 梯度的变化以曲线表现。随着酸化的增加, 能抵抗酸化的碳酸氢盐水域逐渐变成了过渡型水体, 在该水域只要增加少量  $\text{H}^+$  就能引起 pH 的巨大改变并常常导致鱼类的死亡, 过渡型水体最终变成了缺乏鱼类且 pH 稳定的酸性水域。] (Henriksen, 1980)

$$\text{ANC}_0 = [\text{Ca}^{2+}]^* \quad \text{式 27-14}$$

虽然酸化过程中 ANC 会下降, 但是钙却不受影响。如果假定式 27-12 至式 27-14 是正确的, 那么被酸化的水体在任何特定 pH 条件下应该比非酸化系统有更多的  $[\text{Ca}^{2+}]^*$ , 并且这个现象已经被观测到 (Overrein 等, 1980)。虽然  $\text{pH} : [\text{Ca}^{2+}]^*$  比或  $[\text{Ca}^{2+} + \text{Mg}^{2+}]^* : \text{HCO}_3^-$  比为确定酸敏感水域是否酸化提供了有用的指标, 但它们仍不能用来预测  $\text{H}^+$  或  $[\text{SO}_4^{2-}]^*$  变化所带来的影响。为了使这些预测成为可能, Hensiksen 描绘出了湖泊酸化的 3 个阶段(同样适用于流水和湿地系统):

- 第 1 阶段: 此阶段在对酸敏感水体进行滴定的特点是碱度一定会下降, 但是 pH 略微下降, 为 5.5 ~ 6.0 (图 27-13),  $\text{HCO}_3^-$  缓冲系统基本上仍然完好无损。这种类型的系统被指定为碳酸氢盐系统。
- 第 2 阶段:  $\text{HCO}_3^-$  缓冲系统已基本被破坏, pH 季节波动明显。这种系统被称为过渡系统 (图 27-13), 它受周期性低 pH 的控制, 这种周期性表现在弱缓冲能力的积雪融化或夏秋季的暴风雨阻止水与土壤接触。酸化前的低  $\text{HCO}_3^- (< 50 \mu\text{eq}^{-1}$  或约  $50 \mu\text{S/cm}$ ) 及 pH 为 5.0 ~ 6.0 (图 27-13) 的水体很容易被酸化, 其中铝浓度也会周期性提高, 与此同时, 生物也会发生改变。一些碳酸氢盐类型的过渡型湖泊和溪流, 其碱度能缓解酸化的过程。其他位于未受影响区域的这类系统, 没有目前普遍存在的缓冲能力高, 一旦该地区开始获得强酸降水, 后者将是最容易酸化的一种水域。
- 第 3 阶段: 本阶段的水体为酸性系统, 系统内长期维持  $\text{pH} < 5$ 、高浓度的铝、鱼类物种丰度的减少 (图 27-13), 或无鱼。

为了完善预测平衡模型, Henriksen (1980) 首先建立系统中  $[\text{SO}_4^{2-}]^*$  和  $[\text{Ca}^{2+} +$

$Mg^{2+}]^*$  之间的经验关系,系统的 pH 分别为 5.2~5.4(平均 5.3)和 4.6~4.8(平均 4.7)。pH 范围在 4.7~5.3 可以将碳酸氢盐湖泊(第 1 阶段)和酸性湖泊(第 2 阶段)与过渡型湖泊区分开来(图 27-14)。当水域 pH=5.3 时,其 $[Ca^{2+} + Mg^{2+}]^*$  和 $[SO_4^{2-}]^*$  是基本平衡的。当 pH < 5.3 时, $HCO_3^-$  会缺失,pH 成为强酸和铝浓度的函数。最后两步需要预测在不同 ANCs 的内陆水域内酸性降水的平衡效应,包括确定降水中 $[SO_4^{2-}]^*$  和水体中 $[SO_4^{2-}]^*$  的相互关系,以及降水中平均 $[H^+]$  与 $[SO_4^{2-}]^*$  的关系,这两步完善了湖泊 pH 的预测(图 27-14)。

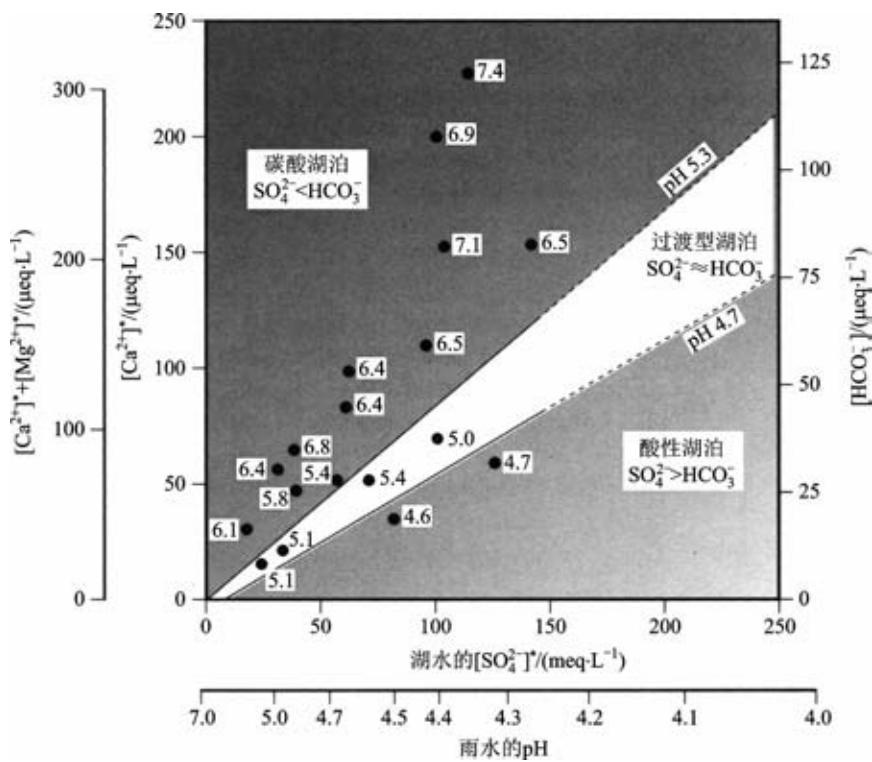


图 27-14 预测湖泊 pH 的诺模图,利用非海洋性 $[Ca^{2+}]^* + [Mg^{2+}]^*$ (或只有 $[Ca^{2+}]^*$ )和 $[HCO_3^-]^*$ ,以及湖水中非海洋性 $[SO_4^{2-}]^*$ 或降水的年加权平均 pH。所列的观测值为挪威南部大型湖泊的情况。](仿 Henriksen, 1980)

### 水的 pH 预测

基于小型湖泊的诺模图,也同样适用于较大的湖泊(图 27-14)。从诺模图中很容易看出,如果降水中 pH 进一步降低则会导致更多的内陆湖酸化。位于平均降水 pH=4.7 的区域中, $[Ca^{2+}]^*$  为 50  $\mu eq/L$  的湖泊仍将是碳酸氢盐湖泊,但降水中 pH 降至 4.5 时,它就会变为过渡型湖泊,当降水 pH 降至 4.3 时,最终会变为酸性湖泊。相反,该模型预测当 $HCO_3^-$  缓冲最终再次出现之前,pH < 4.3 的湖泊需要增加 pH 为 4.6~4.7 的降水。

其他的研究也证实,降水中 pH 年平均体积加权 4.7 的是一个临界值,低于这个值在

北美和欧洲的地质性高度敏感地区就会出现负效应(Wright, 1983b)。在敏感性略小的地区,降水的年加权平均 pH 为 4.0 ~ 4.5 时会出现酸化问题,但是,这些地方的降水中 pH 可能会偶尔达到 3.0。

### 临界负荷

Henriksen 模型预测的准确性已在欧洲和北美的其他地方得到了证实(Wright 等, 1980)。因为所有的模型都是简化的,其局限性不可避免;Henriksen 模型并未阐明在降水的酸性改变后,水体变酸或恢复所需的时间长度。最初的 Henriksen 模型并没有考虑铝和硝酸盐沉积物对缓冲能力和 pH 的影响,或高浓度的溶解有机物(DOC)对 pH 或阳离子的影响。

在斯堪的纳维亚半岛,利用降水中的 $[H^+]$ 和 $[SO_4^{2-}]^*$ 来预测湖泊对未来 SO<sub>2</sub>释放量变化的响应(图 27-14)。在北美洲,这个模型的构建经常会考虑到降水中 $[SO_4^{2-}]$ 的负荷对水中 pH 的影响。因此,美国 - 加拿大备忘录确定了一个负荷目标,即在 2010 年前北美东部 SO<sub>4</sub><sup>2-</sup> 的负荷目标为 40 keq SO<sub>4</sub><sup>2-</sup> · km<sup>-2</sup> · a<sup>-1</sup>(20 kg · ha<sup>-1</sup> · a<sup>-1</sup>)。但是,Gorham 等(1984)指出,这个目标所带来的降水中平均 pH 仅为 4.4。他们认为, $[SO_4^{2-}]$ 降低到大约 15 kg SO<sub>4</sub><sup>2-</sup> · ha<sup>-1</sup> · a<sup>-1</sup>,即降水中平均 pH 为 4.6 ~ 4.7 时,才能使最敏感的湖泊达到计划的负荷目标。近期关于阿迪朗达克(美国)最敏感湖泊的古湖沼学研究表明,在 1900 年左右,当估计的负荷在 5 ~ 10 kg · ha<sup>-1</sup> · a<sup>-1</sup> 时,这一地区的湖泊开始酸化(Cumming 等,1994),意味着在受威胁地区,需要大幅度降低 $[SO_4^{2-}]$ 才能保护当地的湖泊(降低 20 kg · ha<sup>-1</sup> · a<sup>-1</sup> 负荷的 50% 以上)。他们的结论支持了 $[SO_4^{2-}] < 8 \text{ kg} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ 作为临界负荷的观点,在瑞典最敏感湖区这个临界负荷已被采纳(Dickson, 1985)。

### 临界负荷的概念

20 世纪 90 年代,临界负荷的概念开始建立,即硫酸盐的湿沉降速率随相关水体的敏感性而改变,以及保护水生生物的 pH 至少大于 6.0。这个概念已经成为制定政策和指导管理的重要基础。临界负荷被定义为硫酸盐湿沉降的数量,确定这个标准量的目的是保护至少 95% 在历史上 pH > 6.0 的湖泊,使其不会因为酸化而造成 pH < 6.0。据估计,加拿大东部有 1.2 万 ~ 2.3 万个湖泊及相关溪流将会继续超过临界负荷,预计到 2010 年 SO<sub>4</sub><sup>2-</sup> 的减少量才能达到一定标准(Jeffries, 1997)。

临界负荷的概念并不能在 NO<sub>3</sub><sup>-</sup>沉积物中广泛应用,因为它在近 20 年来变化不大。在北部森林地区的典型营养缺乏流域,沉积的 NO<sub>3</sub><sup>-</sup>会很稳定地被保存在土壤里并被植物所吸收;但是,当 NO<sub>3</sub><sup>-</sup>的供给量超过了陆地和水系统的需求后,就会出现氮饱和现象。这个现象已经发生在欧洲中部受影响严重的区域以及加拿大东部的部分地区(Jeffries 等,1998)。过量的 NO<sub>3</sub>进入水体,促进了它们的酸化,这为一些在挪威湖泊记录的 NO<sub>3</sub>迅速增加的现象提供了可能的解释(见 18.1 节)。

### ▲ 27.11 湖泊管理:酸化水体的修复

通过石灰处理法暂时性修复酸化水体,该方法通常将细石灰石粉末撒到湖泊表面、河流边缘、湿地或流域的上游(图 27-15)。颗粒越小,石灰石溶解越快,以减少在水中沉淀而造成的损失。大约 5 g/L 的最可溶性颗粒和 10 g/L 颗粒较大、溶解性低的石灰石粉末会使 pH 从 4.5 升高到 6.5。当直接在湖泊或湿地中添加石灰石粉末时,它会中和酸,并使铝沉淀(图 27-6);这个平衡对来自大气或流入溪流的酸起缓冲作用。恢复的持续时间在很大程度上取决于石灰化合物被冲走的时间(式 9-3 和式 9-4)。

除了提供临时性的保护,石灰处理并非廉价的解决方法。1976—1982,瑞典有大约 6.5 万个湖泊和 6 万 km 的河流使用了石灰处理法。近几十年来每年约使用 20 万 t 石灰粉,每年的费用为 2 500 万美元。虽然花销巨大,但功效短暂,尤其在流速快或冲刷力强的地区,石灰处理法得不到广泛使用,即便如此,投放石灰后,水中的 pH 会迅速上升,铝、汞以及其他金属的含量会因为沉淀作用而下降(SMA,1982)。



图 27-15 在空中撒细石灰石粉末来中和酸化的加拿大湖泊(照片由 W. Keller 提供)

#### 石灰处理法和生物群落

投放石灰对生物群落的影响还不甚清楚,其原因是由于生物的世代时间不同。藻类一个世代仅几天时间,因此能对环境的变化作出快速反应;而大型浮游动物的世代时间长达几个星期甚至一年或者更多;高纬度地区的底栖昆虫,一年只有一个世代。事实上,在石灰的作用下藻类物种数量会相对快速地增加,并从耐酸的腰鞭毛虫变为金藻鞭毛虫群落,这与在非酸化的贫营养湖泊中发现的现象一致(图 21-10; Eriksson 等,1983)。然而藻类的变化率却没有预期的那么快,这也许是由于类似于未酸化的贫营养湖泊中所观察到的营养限制所决定的。此外,石灰提高了 pH 和 ANC,超出了其他未酸化的敏感湖泊,因此,投放石灰并不能使水体恢复到原始状态。

生物群落对投放石灰的快速反应之所以缺乏不仅是因为世代时间和营养条件造成

的,还因为投放石灰和酸雨减少后其他环境因素的变化。这些变化通常会降低水的透明度(见27.8节),从而导致混合深度减少(见11.7节),真光层厚度变小,底栖藻类生产量减少。另外,随着肉食性鱼类的增加,食物网结构会发生变化。这些鱼的后代直接或间接地影响到浮游动物和底栖生物(Gunn和Mills,1998)。

在石灰处理或酸雨减少以后,恢复的程度取决于种群的扩散能力和繁殖策略。以一个短的繁殖周期( $\leq 1$  a)作为标准,藻类的修复最快,其次是浮游动物和大部分底栖无脊椎动物。Yan等(1996)指出,在pH为5.7的石灰型湖泊中,完全恢复浮游动物需要10年,而在一些严重酸化( $pH \leq 4.5$ )和重金属污染的湖泊中则需要15年。对于大型水生物种(如软体动物和鱼类),即使修复后也不可能恢复,除非从流域其他地方迁移过来或重新投放。因此,生物完全修复远远落后于化学修复。影响生物群落修复的另一个因素是在酸化过程中消失的物种从其他湖泊或溪流进入修复湖泊需要的时间(Henrikson和Brodin,1995)。

一些实验研究探讨了以无机肥作为添加剂以取代施用石灰的方法,其结果由于光合作用的提高增加了 $CO_2$ 的去除,从而提高了pH(见14.2节)和ANC。Davison等(1995)建议应适当地使用肥料而不是靠施用石灰来提高碱度,这样对生物群落的影响程度最小,而且能适度增加高度贫营养湖泊的生产力。

## 27.12 展望

解决酸化的长期措施是大量减少 $SO_2$ 和 $NO_x$ 的排放, $SO_2$ 的大量减排可以用Henriksen模型来预测(图27-14)。

通过研究内陆水体及其流域对酸化的反应之后发现,酸前体的减排可以减少酸在流域的富集,基本与通过减少外部营养物质排放的延缓湖泊富营养化一样(见17.6节)。在加拿大的萨德伯里,已经通过监测得到了减排对湖泊影响的直接证据。位于那里的矿业冶炼工厂曾是世界上最大的 $SO_2$ 排放源,近10年来,它的排放量减少到 $5 \times 10^5$  t  $SO_2/a$ ,减少了约80%。当地湖泊随着排放量的减少逐步得到恢复(Keller和Gunn,1995)。例如,在10年之天鹅湖的pH从1997年的4.0上升到5.6,与此同时,湖水的透明度却降低了,湖水的颜色变深。根据以往沉积物岩心中的金藻可以推测(图27-16),湖水pH会逐步达到非酸化时的6.0。湖红点鲑(*Salvelinus namaycush*),一种长寿且中度抗酸性的物种( $pH > 5.1$ ),在pH上升到5.4~5.6时便可以成功繁殖(Gunn和Mills,1998)。

第2个全生态系统的“实验”发生在欧洲中部,1989年以后,随着一系列政治和经济政策变化,氮减少约30%,硫气体减排约40%。随之而来的 $SO_4^{2-}$ 、 $NO_3^-$ ,以及 $NH_4^+$ 沉降的减少使捷克高山湖泊的化学指标在不足10年内发生了明显的好转(Kopacek等,1998)。

恢复酸化区域的第3个证据是基于挪威的一个小型流域,根据实验判断,在 $H^+$ 负荷减少后流域得到恢复。这个流域被塑料顶棚遮盖,只接受自动洒水装置所喷洒出的非酸性水(Wright等,1998),与暴露在空气中的对照系统相比,该流域中强酸性阴离子 $SO_4^{2-}$ 和

$\text{NO}_3^-$  的输出量快速降低, pH 小幅上升。

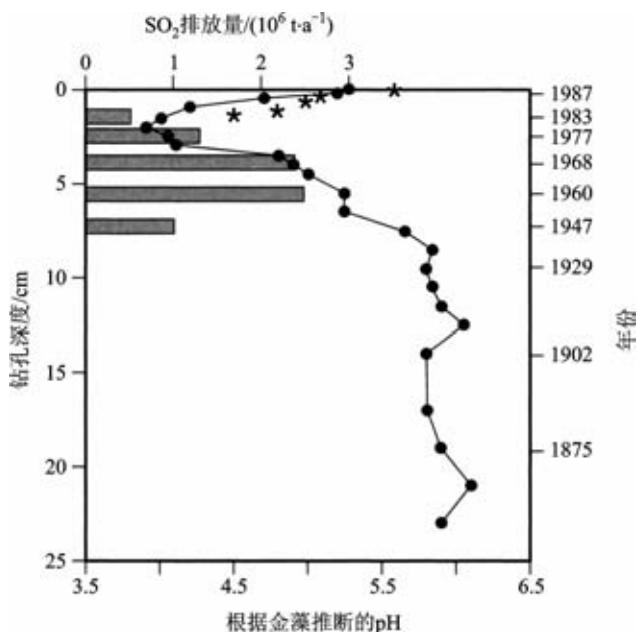


图 27-16 在加拿大萨德柏里, 来自矿业冶炼的  $\text{SO}_2$  排放的变化(条形图)以及天鹅湖 pH 变化的影响(pH 根据岩心中浮游植物(金藻)的组成来推断。\* 表示水中测定的  $\text{pH}_\circ$ ) (Dixit 等, 1989)

### 恢复的证据

到目前为止, 这种经过强有力处理后得到的明确结果还没有在北美和欧洲整个湖区范围内观察过 (Stoddard 等, 1999)。在发电厂实施排放量严格控制的政策出台后, 二氧化硫释放量大幅度降低 (30% ~ 50%; Hedin 等, 1987; Rodhe 和 Rood, 1986), 但似乎并没有导致沉积物中硫和氮的总量的变化。由于土壤缓冲能力、水文的年际和系统之间的变化 (Webster 等, 1990)、冲刷速率以及沉积物中碱的再生等方面的不同, 使得体系产生更多的变化, 从而很难形成一个清晰的响应模式。 $\text{NO}_x$  沉降的增加、空气温度的长期变化对土壤风化和相关离子释放的作用以及  $\text{SO}_4^{2-}$  排放和沉降的地区性差异都会影响到响应模式 (Sommaruga-Wögrath 等, 1997)。敏感土壤中阳离子损耗的差异造成酸中和及碱恢复能力的不同, 敏感流域持续接受酸沉降如果太多, 恢复是不可能的。

最后, 在欧洲和北美的部分地区, 缺乏对  $\text{H}^+$  释放量减少的响应, 这部分归因于碱性阳离子沉降到流域中的量同时减少, 这种减少也会导致大气和流域中 ANC 的降低。对飞尘进行控制可以大幅度减少空气中的阳离子负荷, 在北美东部和欧洲西部这些飞尘来自于煤燃烧、石灰石采石场、水泥生产厂、石灰道路以及暴露在风中的裸露土地<sup>2</sup>。

对加拿大东部 111 个湖酸化趋势的评估 (1983—1991) 表明, 有 60 个湖泊没有改变, 17 个湖泊继续酸化, 只有 34 个湖泊当时正在恢复, 尽管其酸负荷大幅度下降 (Clair 等, 1995)。在 20 世纪 90 年代, 欧洲湖泊的恢复已比较明确了。虽然酸化和酸化系统的恢复中有很多问题都没有很好地解决, 导致无法预测, 但是现有的资料足以表明, 长期的恢复是与酸前体排放量减少成比例的。遗憾的是, 没有足够的长期后续研究以及与酸化相关

的研究经费严重减少,已使得这个领域的科研人员将精力转向研究有毒化学物质(见第28章)对人类和生物群落的影响<sup>①</sup>。

## 本章重点

- 通过强酸或酸前体( $\text{SO}_2$ 、 $\text{NO}_3^-$ 、 $\text{NO}_2$ )形成的环境酸化是以酸中和能力的降低来定义的,环境酸化对北美洲东北部大部分地区、欧洲北部和中部以及其他一些空间较小区域的化学和水生生态系统中的生物群落有巨大的影响。
- 20世纪,欧洲和北美洲的工业化国家及日本的降水中pH降低了10~30倍,按体积加权获得的降水中pH由5~6降低到4.1~4.7,但是目前由于 $\text{SO}_2$ 释放量的减少,降水中pH正缓慢增加。
  - 酸前体从释放至大气到沉降,可以长距离地传输。
  - 对人为酸化最敏感的内陆水体具有低ANC(<50 μeq/L)的属性,且这些水体位于小型流域上,这些流域具有:①高度不溶性的岩床以及来自同一地质情况的表层物质;②硅质砂;或者③泥炭层因其上层的土壤而不能同水体接触。
  - 位于石灰质流域的水生系统含有一些沉积地石灰质,这些石灰质通常可以很好地保护水生系统免受酸性降水的影响。
  - 受影响地区一小部分水体的酸化是由泥炭沼泽及富含有机物的土壤释放有机酸而非人为排放导致的。
  - 随着pH降至低于5.5时,土壤及沉积物中的铝和微量元素的溶解性也会相应增加,同时也会形成对生物群落有剧毒的活性铝。
  - 生物类群会对酸化和有毒活性铝含量升高的敏感度不同,当pH下降至6.0以下,物种丰富度就会有降低的可能。其中最敏感的生物类群是大量营底栖生活的甲壳类和软体动物以及一些特殊的鱼类物种。
  - 通过石灰处理法(添加 $\text{CaCO}_3$ )使得酸化湖泊得到暂时的恢复,提高ANC和pH。长期的恢复取决于酸前体排放量的减少,目前在欧洲和北美洲,酸前体的排放量正在减少。
  - 长期恢复要求酸前体排放量成比例地减少,但是这个比率非常复杂,它受众多因素的影响,包括流域地质情况、土壤缓冲力、酸化持续时间和程度、水文学、温度、沉积物中微生物的碱再生能力、生物的世代时间以及物种的扩散能力。
  - 目前,北美洲和欧洲的负荷指标需要进一步降低,以便使众多最敏感湖泊及相关溪流的恢复成为可能。

(陈非洲译)

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<sup>①</sup> “酸雨对水质影响的研究存在两个难题:首先是缺乏大量的数据,从而需要时间和金钱去获得更多的数据;二是有价值的响应需要很长时间(数年到十年)”(Cosby等,1985)。

# 第 28 章 污 物

## 28.1 引言

19世纪60至70年代,氮、磷对水体的污染在流域尺度范围里逐渐显现,这两种营养盐的污染问题引起了湖沼学领域的广泛关注(见第16章和第17章)。20世纪80年代,酸雨成为了另一个主要的环境问题,且主要发生在北美东部及欧洲的大部分地区,覆盖范围在半洲际至洲际之间,主要涉及4种污染元素或化合物( $H^+$ 、 $SO_x$ 、 $NO_x$ 和Al;见第27章)。有毒化学物质所造成的污染是当前的主要环境问题,其影响已从局部逐渐扩展到区域甚至全球(图28-1)。

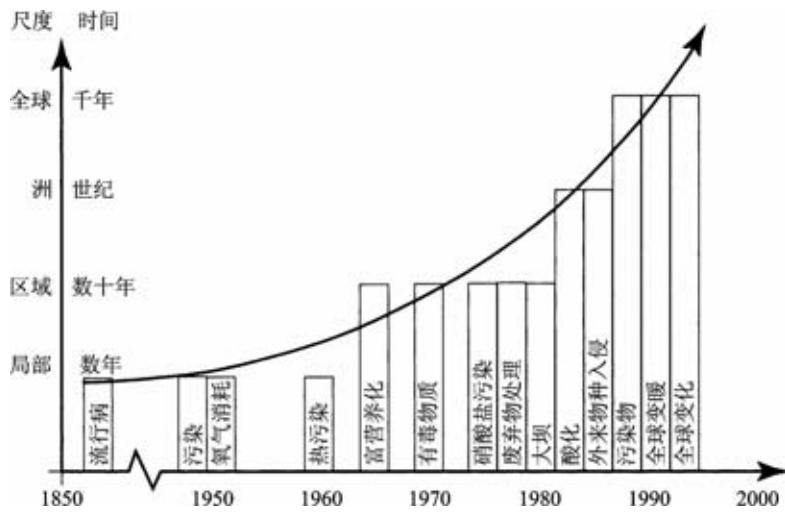


图 28-1 水质新问题增加的速度和广度(改自 Somlyódy, 1995)

有毒化学污染比富营养化及酸雨更复杂从而更难解决。富营养化可通过改进污水处理及农业实践使其逆转,西方国家通过处理发电站及车辆释放的废气也使得 $H^+$ 或可引发

酸雨的气体大幅度减少。而那些人工合成并释放到环境中的有毒合成化学物质的种类和数量都很巨大——接近 80 000 种,包括小部分目前每天仍在使用的有毒的金属(Stumm 等,1983)。

许多污染物是在工业生产过程中附带生产出来的,包括可以扰乱水生无脊椎和脊椎动物内分泌系统的干扰物。还有一些是微生物分解无害化合物时产生的,或无害的天然有机化合物氯化过程中所产生的。

最受关注的化学物质中有许多是被广泛使用的杀真菌剂、杀虫剂、除草剂及生物杀灭剂等,它们曾经在迅速增长的人口所需的食物生产和保护方面起到了极其重要的作用,但其使用却对物种多样性、群落结构以及人类健康产生了严重的负面影响。每年有 500 ~ 1 000 种新合成的有机化合物在没有任何毒性效应信息的情况下,被加入到用于商业目的的有机物中,在已使用的化学物质中仅有 79% 具有毒性效应信息(Postel,1987)。即便绝大多数有机物无毒,但剩余有毒的物质危害却非常大。北美五大湖国际联合委员会(IJC)在劳伦系五大湖中鉴定出 362 种对植物、动物包括人在内具有潜在危害的化学物质(IJC,1987),其中有 11 种化学物质或化学物质组被认为是“关键污染物”,2001 年联合国制定的禁止或高度限制使用的 12 种持久性有机污染物(persistent organic pollutants, POPs)条约中罗列的名单与此几乎完全一致(表 28-1)。这些关键污染物的结构差异非常大,即便仅描述很少一部分对湖沼学教材来说也很难完成,可以参考专门描述单种化学物质的专著或论文集。一些存在于废水和工业生产中的化学物质(如塑料、洗涤产品、杀精子剂以及少量杀虫剂),通常被认为是“影响性别”的内分泌干扰素,要具体论述它们对环境的影响也是不可能的。这些物质能够改变脊椎动物(鱼、鳄鱼等)个体及其后代的荷尔蒙和免疫系统,并有可能产生致癌物。本章着重描述小部分有机化学物质及少数几种重金属的行为。所幸的是这些物质及其他潜在有毒化学物质的毒性一般都与其物理化学结构有关。因此,这些化学物质以及那些正在用于商业用途的化学物质的可能的毒性可以首先从它们的结构了解一些。污染物的结构和功能之间的关系是本章的重要基础。化学物质的物理化学结构为湖沼学家提供了一些一般共性以及进一步搜索文献的基础。

所受关注的大多数化学物质,在湖泊水体中的含量非常低,通常为兆分之一克( $10^{-12}$  g/L,或 ppt),如此低含量的测定技术是最近才可以做到的,且费用昂贵。此外,野外采样、储存、浓缩、消化及样品分析均要特别谨慎以免样品受到污染。另外还有一个更大的问题,那就是这些化学物质的含量在水体和空气中存在较大的时空变化。

与前一章相比,这一章更侧重于单个区域的研究:北美劳伦系的五大湖流域。这并不是因为其他地方没有好的研究,而是因为五大湖区的一系列研究非常卓越并得以坚持,而且在美国和加拿大边界地区,两国的研究均采用了标准方法,其联邦政府也都提供了必要的财力支持,邻接的州和省也进行了空前合作。

劳伦系五大湖的污染状况有很大差异,较偏远的苏必利尔湖较原始,下游的安大略湖污染最为严重。后者与尼亚加拉河相连,而尼亚加拉河又与上游的伊利湖相连。尼亚加拉河流域曾因其水力发电站成为大型化工厂基地,至今仍有许多化学物质倾倒点,其中

66 个最大倾倒点掩埋了约 120 万吨化学污染物,这些化学污染物中的相当部分或向安大略湖渗漏或存在潜在渗漏的风险。

**表 28-1 2001 年签订的联合国公约中全球禁止或严格控制的 12 种持久性有机污染物 (\*) 和北美五大湖国际联合委员会 (IJC) 在劳伦系五大湖鉴定并列出的 11 种关键污染物 (Δ) (注:以其化学稳定性、影响的持续性、所使用的种类和数量、在生物体内的富集趋向性及其毒性而入选。)**

化学物质	生产及释放	来 源
二氯(杂)芑 (* Δ)	无意的	多氯联二苯二噁英 (PCDDs, 75 种同源物) 和多氯联二苯呋喃 (PCDFs, 135 种同源物) 是制造用于农业和森林管理中的除草剂时的副产品,也是含氯化石燃料和用氯漂白医用或城市废物,如塑料和用作木材防腐剂的五氯苯酚 (PCP) 燃烧时产生的副产品,以及纸浆和纸张生产过程中采用氯漂白的副产品;一些同源物毒性很强(图 28-2),但多数具有低毒性
呋喃 (* Δ)	无意的	
苯并(a)吡 (Δ)	无意的	化石燃料和木材不充分燃烧时的产物,如森林大火、自燃、废弃物焚化等,是多环烃 (PAHs) 大家族的一员
DDT 及其分解物,包括氯甲桥萘 (DDE, * Δ)	有意的	热带地区用于控制蚊虫的杀虫剂,在温带地区的半沉降期为 10~15 年
氧桥氯甲桥萘 (* Δ)	有意的	广泛使用的杀虫剂,尤其用于水果保护及白蚁防治;在土壤中的半衰期是 5 年,氯甲桥萘能迅速衰变成氧桥氯甲桥萘
六氯苯 (* Δ)	无意的	HCB 是含氯化石燃料燃烧、含氯废弃物焚化及生产过程中产生的含氯副产品;主要作为杀虫剂使用(自然半衰期为 3~6 年)
烷化铅 (Δ)	有意的	主要用作燃料添加剂、焊料、管道以及油漆添加剂;
	无意的	含铅燃料、废弃物、燃烧的香烟以及管道、油漆罐和油漆碎片均可释放此污染物
灭蚊灵 (* Δ)	有意的	用作控制蚂蚁的燃烧延缓剂和杀虫剂,在光照下分解成更具毒性的光灭蚊灵,当前的来源主要是工厂残余物、渗漏及垃圾处理点,半衰期为 10 年
汞 (Δ)	有意的	主要用于冶金行业
	无意的	局部或区域中含氯的碱、油漆、电器生产过程中以及垃圾焚化和煤炭燃烧时产生的副产品
多氯联苯 (* Δ)	有意的	PCBs 用作电容器和转换器的绝缘液体、液压机液体、润滑剂、油漆添加剂、塑料添加剂和复写本用料,此外也曾用于杀虫剂的媒介物;209 种同源物的毒性各不相同,半衰期从几周到数年不等
八氯莰烯 (* Δ)	无意的	主要通过渗漏、溢出以及废弃物的储存及处理释放到环境中
	有意的	通常用作棉花的杀虫剂,也用作谷物、水果、坚果和蔬菜杀虫剂,在土壤中的半衰期为 1~14 年,最重要的同源物中含 16 个氯;替代物为 DDT,相对不稳定,全球分布

续表

化学物质	生产及释放	来 源
七氯 (*)	有意的	用于控制土壤害虫、白蚁、蚊子以及农作物害虫
一种强力杀虫剂 (*)	有意的	主要用于控制白蚁,在土壤中的半衰期约为 1 年
异狄氏剂 (*)	有意的	用作棉花、稻谷、玉米等的杀虫剂和灭鼠剂;在土壤中的半衰期高达 12 年

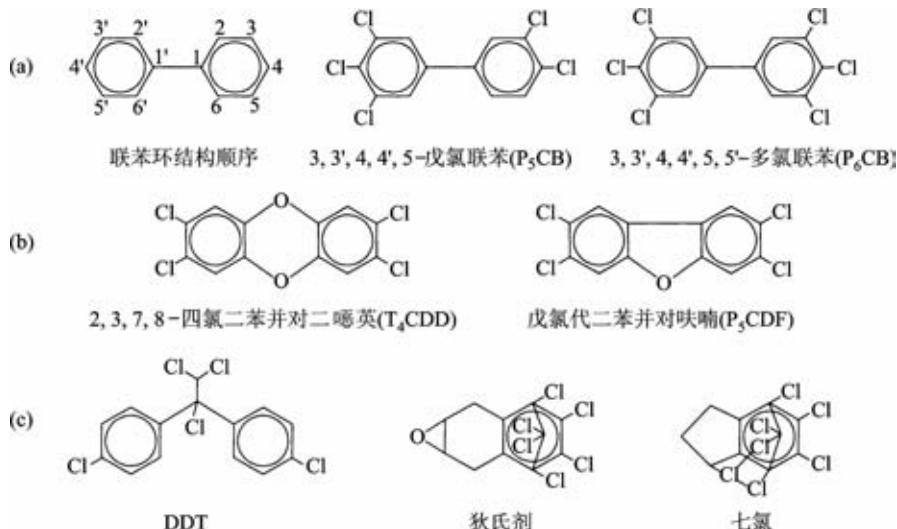


图 28-2 (a)一些 PCBs 的联苯环结构和化学组成;(b)两个密切相关的剧毒多氯二氧芑及呋喃;(c)DDT、狄氏剂和七氯(表 28-1)

### 最受关注的污染物

全球范围内受到广泛关注的化学物质许多是富含氯的有机分子,即所谓的“有机氯”(organochlorines, OCs)。这些有机氯与其他持久有机化学物质一起被称作“持久性有机污染物”(POPs)。从定义来看,持久性有机污染物指那些在水体或土壤中半衰期大于 8 周的污染物,也就是说在这期间其活性将衰减到小于原始浓度的 1/2。这些物质具有多种多样的化学结构,其中的大多数水溶性较低,在脂肪中易积累,且很难降解(高稳定性)。这些高稳定性的化学物质或者是人工有意合成的生物杀灭剂(如杀虫剂或除草剂),或者是在工业生产过程中不经意地生产并释放出来的。其中一个例子是多氯联苯(polychlorinated biphenyls, PCBs),是一组主要用于工业用途的多氯化烃(表 28-1)。多氯联苯混合物的成分及物理特性变化非常大,取决于氯与联苯的结合率及生产温度(图 28-2)。氯分子的数量及其在环上的位置影响着它们的特性及生物活性。商业上所用的混合物中也含有一些副产品以及一些毒性很强的多氯化联苯 - P - 二氧芑和多氯化联苯 - P - 呋喃(PCDDs, PCDFs)。

自然界中一些倍受关注的 POPs 自身并不具有高毒性,但是它们难以降解(对微生物

及化学分解来说)和容易在生物中富集(见 28.2 节)。一些 POPs 在大气或水流的作用下,已广泛分布于工业区和城市释放区之外。塑料及其他自然或人工合成物以及医疗器具等的燃烧或垃圾掩埋等均能将氯、聚氯乙烯(PVC)、酸性气体(HCl)、二氧化碳、铅(如油漆中的)、镉(用于塑料生产过程中的)等释放到大气中。HCl 与环境中其他有机物质结合会产生多氯化和致癌的二氧芑和呋喃以及其他有毒物质(Piasechi 等,1998)。其他 POPs,如生物杀灭剂,或用于农田、森林及水稻生产中的有机物,具有在空气中广泛分布的可能性。许多 POPs 具挥发性(具有气态形式),能从土壤或水体中释放到大气中并以气体形态存在或吸附于被风吹起的颗粒上。其他持久性有机污染物包括二氧芑和呋喃,可能形成于森林火灾或工业生产过程中有机物的不充分燃烧,也能形成于城市垃圾和医疗废弃物在温度低于 1 200 ℃ 的焚化过程中。内燃机车也能产生有毒有机污染物,这些污染物同样会通过大气输送到河流、湖泊以及湿地中。

## 28.2 有毒物质

有毒物质除具毒性外,还具有潜在的生物富集性、持久性和挥发性(图 28-3)。其毒性可能是急性(能迅速导致死亡)的也可能是慢性的。

### 慢性毒物

大量慢性毒物能导致不正常的荷尔蒙水平或不正常行为,严重的话可使一些物种在一段时间后减少甚至消失。慢性毒物对遗传物质的损坏会影响生育力、功能缺陷或癌症,但是未必会很快致死<sup>①</sup>。这两种类型的区别主要是概念上的不同,如果死亡是终点的话,不同之处只是时间尺度。

一些特殊的慢性毒物对繁殖(生育力)影响很小甚至没有影响,从而使得其在自然界的影响很难被察觉。实际上,慢性中毒可以通过标本上的良性或者恶性肿瘤得以证实,如受污染海湾中慢性中毒的底栖鱼类,尽管未必影响其生育力或者那些没有肿瘤幼鱼的生育力。因此,慢性毒物未必会影响一个物种的丰度,但鱼类或依赖沉积物为生的底栖动物的异常肿瘤丰度或底栖动物口部的功能缺陷可对环境污染提供重要的警示作用<sup>②</sup>。然而,慢性中毒的

<sup>①</sup> 目前,细菌培养作为有机体检测方法广泛用于检测遗传毒物和诱导有机体突变的物质。DNA 损坏、诱变以及致癌性之间的关系被广泛用于沙门氏菌/微粒体分析(“艾姆斯氏试验”)。其他更快的比色分析实验(SOS 比色检验)方法使用遗传性质修改了的大肠杆菌可测定 DNA 损害。这种方法被越来越多地用于工业和生活废水中遗传毒性物质的检测(White 和 Rasmussen,1996),其检测结果同采用艾姆斯氏试验对诱变和致癌性所测定的结果高度一致。

<sup>②</sup> 作为一门科学,毒理学在关注有毒物质对人类的影响方面(实验中通常用暖血动物代替人类)经历了一定的发展过程是有道理的。当少数毒理学家在实验室中进行单种化学物质对鱼类和无脊椎动物的急性实验时,水生毒理学才得以发展。过去的 10 年,实验室中的慢性毒性实验获得了很大发展,其后是野外的生物监测实验。这些科学家主要在野外工作,他们把自己定位为“环境毒理学家”或“生态毒理学家”,主要关注慢性毒物对野生生物种群和“生态系统健康”所产生的影响。

就特别麻烦,因为这种影响会滞后一段时期通过生育力表达出来,这就很难根据某一来源、浓度或样品中某一化学成分来判断因果关系。而且,这种时间上的滞后性使得很难将1种或几种慢性毒性物质与许多其他环境因子对种群或群落的影响区分开来。最后,这些化学物质在水体中的浓度都近于或低于检测限,通常低于实验室观测到的产生影响的浓度。

### 污染物特征

慢性污染物在生物体内的富集(生物富集)是通过从水体中直接吸收或通过食物富集的(见28.8节),加上富集(储存)的速率高于新陈代谢(损失速率)。生物富集的有毒物质的浓度会随时间增加,最明显的证据是寿命长的有机体年龄越大体内毒性物质浓度越高。持久性是许多有毒物质的第二个特点(图28-3)。高持久性的有机污染物,如DDT或一些PCBs,数十年之后才有一定程度的降解。若有毒物质具有气态形式(挥发性),就可以通过大气从生产区域输移到很远的另一个区域(图5-13)。包括少氯的PCB同源物在内的有毒物质均能在低温条件下挥发。河流对有毒物质(无论是挥发性的还是不挥发的)的长距离输移有着重要作用。

过去的氰化物和如今大多数基于有机磷或氮的生物杀灭剂虽然是剧毒却不是持久性的(图28-4)。其他过去使用过的生物杀灭剂类似于持久性的OCs,但其中的一些氯可由氧和硫替代,这些杀灭剂的效果可能更显著,但相对于靶生物的寿命来说,它们的存在时间比较短,因此影响有限。半衰期稍长的物质可能会在一定程度上发生生物富集,但由于降解仍较快,因此限制或避免了在食物链顶端的捕食者的富集。比较麻烦的是那些不仅具持久性而且还可在生物中富集的慢性毒物(图28-3),因其能在一些寿命较长的生物体内达到高浓度。这种化合物的水溶性通常较低(见28.6节),疏水污染物容易吸附在鳃、内脏以及活的有机体和碎屑物的表面,并且一旦被吸收就会不成比例地被停留,其易与含有脂质的颗粒物结合的特性也影响了其在自然界的分布及生物可利用性。而亲水(易溶于水)化合物通常在水中仍以溶解状态存在。关于污染物的理化结构及其在水生生态系统中的关系方面的讨论详见28.6节。



图28-3 有毒物质、毒性、生物富集、持久性和挥发性的定义(改自Kaiser, 1984)

物质	毒性	生物富集	持久性
氰化物离子	×	-	-
氟里昂	-	-	×
有机磷	×	?	-
有机锡	×	?	?
甲基汞离子	×	×	?
PCBs	×	×	×
灭蚊灵	×	×	×
含氯二氧(杂)芑	×	×	×
含氯苯乙烯	?	?	?
六氯丁二烯	×	×	×
含氯苯酚	×	?	×

图 28-4 具有不同毒性、持久性和潜在生物富集程度的环境污染物  
[注:未考虑气压的影响(气压决定了有机污染物从原始生产点被输移往其他区域的可能距离)。]

▲许多在环境方面引起关注的持久性化学物质,如 DDT 和 PCBs,在西方国家已经不再生产和使用,在全球范围内也被逐步淘汰或严格限制,但其高持久性(如 DDT 和分解产物)使得水生生物体内至今仍含有这些物质,虽然含量在慢慢降低。基本上所有已经生产出来的 PCBs 仍在使用、储存或继续以渗漏、溢出等方式释放或从垃圾填埋处逃逸出来。那些经济欠发达国家或区域在 PCBs 使用限制及处置力度方面都很弱甚至没有。

目前,对于在生态系统中从无毒和毒性较小的前物质中合成有毒化合物知之甚少,对某些化学物质降解时所产生的有毒物质也知之甚少,另外,对于单种物质的累加毒性也了解不多,这些起源于工业区和城市的物质通过空气和水流进入水体,通常是没有毒的。最后,对在低纯度工业化学物质或生物灭杀剂生产过程中无意产生的大量低浓度有毒化学物质的释放速率也不够了解。因为,它们不仅在工业生产过程中使用的方法不同,而且使用的原材料也不同。

### 28.3 污染源

湖泊、河流和湿地中出现的高浓度人为排放的污染物通常位于工业区或城市点源污染的下游。很难鉴别和控制的是非点源污染的扩散,如农业生产中使用的生物杀灭剂,会通过径流从流域或通过大气进入水体。流域内点源和面源污染都很少的水生系统常位于“偏远地区”,但仍会受到人类生产活动所制造的污染物通过大气运输的污染。

#### 痕量金属生产及分布

目前,全球范围内释放到大气中的一半以上的痕量金属(大多数为有毒的 As、Cd、Hg、Pb 等)均由人工生产(表 28-2)。北半球的工厂占全球的绝大部分,因此大气中的痕量金属含量最高,从而使得北半球偏远地区的湖泊、湿地等水体和沉积物中的重金属含量升高,这些重金属的唯一运输途径就是大气环流(Nriagu, 1990)。有些情况下,汞是很多偏远地区的湖泊和湿地中最主要的污染物(见 28.9 节),全球范围内人类活动所产生汞的两

种最主要来源分别是煤炭燃烧和垃圾焚化,其他来源包括含氯碱的工业生产过程、废弃物焚化、垃圾填埋、铜和铅的熔炼加工以及水泥生产等。空气中镉的主要来源是金属冶炼而非炼铁,此外,煤炭燃烧以及郊区的垃圾焚烧也是镉及其他痕量金属的重要来源(Nriagu 和 Pacyna,1988)。

表 28-2 1983 年全球范围内通过人类活动与自然界释放而进入大气的痕量金属比较  
[注:中值(括号前数值)及括号内的排放范围为估算值。]

元素	人类活动	自然排放	合计	人类活动的中值/ <sup>②</sup>
As	19 (12~26)	12 (0.9~23)	31 (13~49)	61
Cd	7.6 (3.1~12)	1.3 (0.2~2.6)	8.9 (3.2~15)	85
Cr	30 (7.3~54)	44 (4.5~83)	74 (12~134)	41
Cu	35 (20~51)	28 (2.3~54)	63 (22~105)	56
Hg	3.6 (0.9~6.2)	2.5 (0.1~4.9)	6.1 (1.0~11)	59
Mn	38 (11~66)	317 (52~582)	355 (63~648)	11
Mo	3.3 (0.8~5.4)	3.0 (0.1~5.8)	6.3 (0.93~11)	52
Ni	56 (24~87)	30 (3.0~57)	86 (27~144)	65
Pb	332 <sup>①</sup> (289~376)	12 (1.0~23)	344 (290~399)	96
Sb	3.5 (1.5~5.5)	2.4 (0.1~4.7)	5.9 (1.6~10)	59
Se	6.3 (3.0~9.7)	9.3 (0.7~18)	16 (2.5~24)	42
V	86 (30~142)	28 (1.6~54)	114 (32~220)	75
Zn	132 (70~194)	45 (4.0~86)	177 (74~280)	66

① 广泛分布于含铅汽油但衰减很快。

② 人类活动相对贡献在不同区域变化很大,是主要污染物和盛行风的函数。

资料来源:Nriagu,1989。

### POPs 的生产及分布

POPs 最主要的来源是控制农业和森林害虫的杀虫剂,其次就是石油燃烧过程中产生的副产品或含氯垃圾低温燃烧时产生的氯化烃。在主要的工业化学物质中有 209 种不同形态的多氯化联(二)苯(PCBs),作为商业用途生产的 PCBs 通常含有 70~100 种同源物(具有不同的形态结构,如 P<sub>5</sub>CB 和 P<sub>6</sub>CB;图 28-2),这些同源物具有显著不同的理化性质,其中 13 个表现出类似二氯(杂)芑的毒性。最后要讨论的重要的分布较广的一组持久性化学污染物是多环烃(PAHs),其中苯并芘的毒性最高。PAHs 是石油中有机碳和木头(森林火灾)不充分燃烧时产生的。此外,木材气化、石油裂解和冶金焦炭、炭黑、炭黑沥青、沥青的生产过程中以及垃圾焚烧时也会产生。

### 大气分布

人类活动对大气中污染物分布的影响方面,最典型的证据是在格陵兰岛冰盖中以及

最近在南极测到的铅含量(图 28-5)。工业革命之前,亚洲和欧洲的人类活动使得格陵兰岛的铅含量略有升高,1945 年之后,含铅汽油的大量燃烧则使其迅速升高。最近,格陵兰岛的铅含量迅速降低是全面降低汽油中的铅所致(图 28-5)。镉与锌的负相关变化进一步证明限制环境污染物对工业生产排放控制的有效性(Boutron 等,1991)。

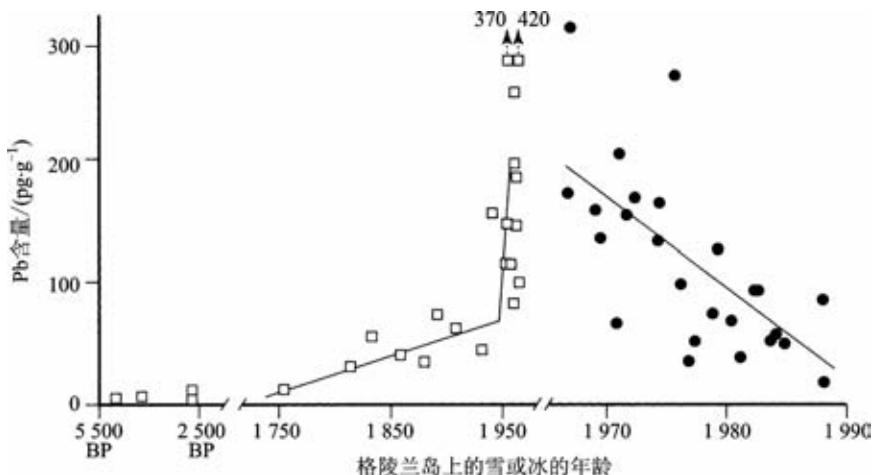


图 28-5 5500 年前(BP)至今格陵兰岛 4 个采样点的冰川和雪中铅含量的变化[注:20 世纪 60 年代中期铅含量的迅速增加(约为几千年前的 200 倍)表明工业革命的开始。从 20 世纪 70 年代开始铅含量迅速降低是由于汽油中铅添加剂的降低所致。现在南极洲的铅含量更低,约为原来含量的 1/10。因开矿和粗炼而使铜含量(未显示出)升高的事实,更早可追溯到希腊的出版物中(2500 年前)和罗马帝国时期(Hong 等,1996)。](引自 Boutorn 等,1991)

大气在提供有机污染物和铅方面的作用,在劳伦系五大湖(美国,加拿大)得到了很好的研究分析。这些湖中,相对偏远的苏必利尔湖(Superior)的数据最易进行解释,因其流域及岸线都仍保持原始状态。主要污染物的排放负荷相对较低,所接受的 60% 的水、66% 的氮(见 18.1 节)、90% 以上的有毒物质是通过大气直接沉降到苏必利尔湖(Superior;表 28-3)。即便大气污染源被控制很久以后,仍有一定份额(小于总释放的 10%)的疏水污染物通过大气沉降到流域并在此滞留,表明大气仍是水体中这些污染物的重要来源。显然,好的数据库及流域-污染物-水体相互作用方面的模型是预测大气污染物在水生生态系统中的空间变化所需要的。

对于一些偏远的水生生态系统来说,大气作为某些持久性有机污染物和有毒微量元素的直接来源,其影响在很大程度上取决于流域与水体的面积比。在具有同样的流域输出系数( $\text{mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ )的前提下,相对于流域与水体面积比大的湖泊和河流,流域与水体的面积比小的湖泊(如苏必利尔湖,CA:LA = 1.6)接受大气沉降相对较多的水量、营养物质以及污染物质。有些污染物极易吸附到颗粒物上,其输出系数相对就较低,这种流域接受的水体中大部分污染物是通过大气沉降而获得的。

从表 28-3 中很容易看出,对于易吸附的 POPs,最多仅有几个百分比通过河流从流

域输入苏必利尔湖。大多数痕量金属被吸附并且很大程度上滞留在非酸化且植被较好的流域内,这就意味着很少有颗粒物输入河流和湖泊(表 28-4)。酸性流域有助于有毒痕量金属的溶解和输出,从而使得接纳水体的重金属含量升高(见 27.8 节; Tessier 等,1985)。

表 28-3 北美五大湖化学物质的大致负荷及通过大气沉降到水面的部分所占的百分比

污染物	苏必利尔湖		密歇根湖		休伦湖		伊利湖		安大略湖		
	$\mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$	%	$\mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$	%	$\mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$	%	$\mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$	%	$\mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$	%	
PCBs	7.4	90	11.8	58	10.6	63	96.9	7	127	6	
t-DDT	1.1	97	1.1	98	1.5	71	12.3	10	5.6	23	
苯并芘	0.9	96	3.6	86	4.8	63	4.7	66	7.8	40	
铅	2 939	97	9 362	99.5	7 167	94	21 808	40	21 300	51	

注:对于下游的两个湖泊来说,上游输入及当地来源都大大低于大气对这些化学物质的贡献。

资料来源:改自 Strachan 和 Ersenreich,1988。

表 28-4 镉(Cd)、铜(Cu)、铅(Pb)在流域内滞留的估算

	滞留百分比/%		
	Cd	Cu	Pb
新罕布夏州(美国)	—	—	95~98
伊利诺依州(美国)	—	—	96
田纳西州(美国)	67~100	72~100	97~99
新泽西州(美国)	—	51	88
德国	69	61	95
安大略省中部(加拿大)	>51~>91	85~90	95~99

资料来源:Schut 和 Evans,1986;Blais 和 Kalff,1993。

## 28.4 污染物的归趋

一些难溶于水的化学污染物进入河流和湖泊后可以通过水流输出,但当换水率降低或水体滞留时间增加时,水体所持留的部分就会增加(见第 8 章)。那些易被吸附的化学物质极易因沉积物吸附而离开水体,因此很难随水流输出。

### 长距离运输

大多数有机氯和有机汞(甲基汞)具有足够高的蒸气压,因此陆地和水体中的一部分

持久污染物会通过挥发散失到大气中去。这个途径在夏季土壤和水体温度最高时尤其重要,但从全年的角度看,对于热带地区的湖泊、湿地及其流域,挥发更为重要。上升气流所携带的挥发性有机物(VOCs)可能以气态形式或吸附在颗粒物上的形式输送到距离释放点几百 km 甚至上千 km 之外。它们以直接输送或者遵循温度—驱动运输—沉降—再挥发—运输的模式(见 5.4 节),被输送到海拔或纬度更高的地方(图 5-13)。在高纬度或低纬度高山区,当大气携带的 POPs(气体和气溶胶形式)达到凝结温度时,沉降就会加强,因此,这些区域的沉降比再挥发(气化)过程更具优势,低纬地区则正好相反。低温会进一步削弱 VOC 的降解速率,从而延长了后者的存在时间。聚集在积雪、植物或土壤表层的 POPs 可能被掩埋、再挥发或随融雪进入水体,在最后一种情况下它们将被生物吸收并在其体内富集(见 28.8 节)。

北极水体沉积物、湖泊冰层以及生物体内所含的各种 POPs、汞以及由于原子弹试验、核泄露事件等释放的放射性核素的含量均已升高(Lockhart 等,1992)。在冬季,北美北极地区的空气中通常含有来自欧亚大陆以及北美中部的气溶胶颗粒的阴霾(通常是烟灰、碳黑及硫酸盐)和各种气体。此外,阿拉斯加的降雪中也观测到了来自中亚沙漠的尘埃颗粒( $< 1 \mu\text{m}$ ; Lockhart 等,1992),而加拿大北极地区的“棕色降雪”中则含有源自西伯利亚和中国西部地区的吸附了 POPs 的黏土和烟灰颗粒(Welch 等,1991)。然而,随着离北极距离的增加,北方森林湖泊里来自低纬度工业和农业区域的污染物不断增加(图 5-12)。

POPs 在水体中通过微生物、化学或光化学降解的损失程度主要取决于环境条件和特定化学物质自身的物理化学特点(见 28.7 节)。

### 污染物浓度的时间变化

基于物质平衡对最为常见 PCB 的同源物和铅总量的计算表明,这两种污染物在苏必利尔湖(Superior)的流失过程存在很大差异。对于易挥发的 PCBs<sup>①</sup>来说,大气是其主要的汇(92%)。进入苏必利尔湖(Superior)的 PCBs 只有 13% (170 kg/a) 被永久埋藏在沉积物中或通过水流输出而损失,根据平衡关系,通过挥发而损失的 PCBs 占到 87%,约 1 900 kg/a (Strachan 和 Eisenreich,1988)。在 1980—1992,因由大气输入苏必利尔湖(Superior)的 PCBs 减少,全湖的 PCBs 含量每年约降低 20%。如今,苏必利尔湖(Superior)已成为 PCBs 的源而不是汇(Jeremiason 等,1994)。相反,铅易被颗粒物吸附且不易挥发(Strachan 和 Eisenreich,1988),因此铅的汇是沉积物而非大气。

苏必利尔湖(Superior)发现最多的 PCBs 同源物浓度的降低,也在北美无点源污染湖泊(Schmitt 等,1985)的鱼类和沉积物 POPs 浓度的降低中得到验证(图 28-6)。因此,区域或洲际范围内对排放的控制将导致污染物浓度的降低,这一点通过分析不同时间采集

<sup>①</sup> 少氯化联苯(1~3 个氯原子)不仅易挥发,还易因化学、光化学和代谢过程而降解。因此,它的半衰期(数月)比多氯化联苯(4~10 氯原子)同源物短得多,多氯联苯同源物基本上都是持久型的,在活的有机体及靠近污染源的沉积物含量通常比较丰富。

的生物和测年的沉积物就可证实,但对污染物浓度较低和变化较大的水体和空气来说,这个降低并不明显。而同一个观测站大气沉降产生的污染物浓度的年内和年间变化非常大。由于污染物浓度经常(但并非普遍的)随污染源距离的增加而降低,另外大气沉降的污染物浓度因含量很低(往往在检测限附近)而很难准确测定,人们进而利用湖泊、湿地沉积物以及长寿命的肉食性鱼类及其捕食者(如潜鸟)作为污染负荷变化的指示物。沉积物及肉食性鱼类所含有的污染物往往是几年甚至多年富集的水平,这比水体或沉降样品的污染物浓度高得多,可以精确测定过去几十年的变化。

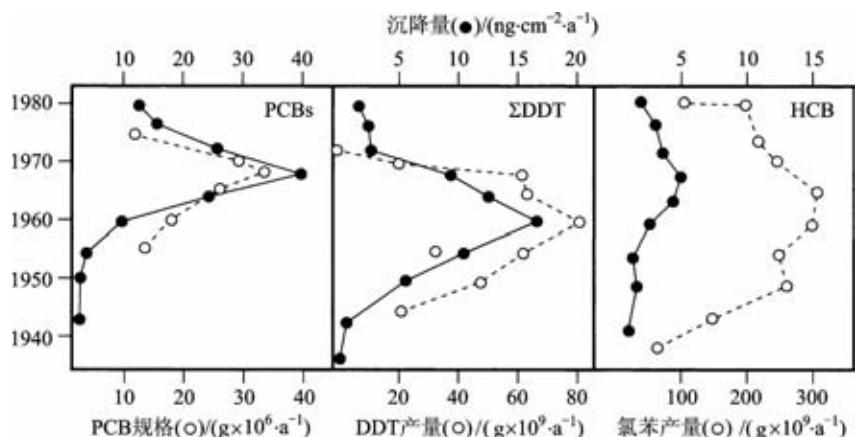


图 28-6 安大略湖沉积物柱状样数据显示沉积物中氯代烃类的含量与美国氯代烃类污染物的产量和销量的关系[注意 PCB 含量及其组成随沉积物深度的变化;随深度增加含氯和易被生物降解的异构体的含量降低,同时含氯和持久性异构体含量随深度增加而增加(Oliver 等,1989)。随着 1972 年美国禁止令的实施,沉积物表面  $\Sigma$  DDT(而不是其中一种需氧或厌氧分解物)的含量明显下降。最近沉降的 PCBs 可能有一半被生活在污染更为严重的深部沉积物中寡毛类的活动混合到沉积物上层。] (引自 Eisenreich 等,1989)

### 污染物的测定

过去数年来分析技术的改进使得污染物的检测限被进一步降低,且更加清楚地了解到样品采集、储存、分析过程中均有可能受到污染。这些变化连同水体、空气中污染物浓度的时空变化一道,也常难以仅从大气和水体样品中得出 20 世纪 70 年代至 90 年代五大湖中的污染物已经降低的明确结论。有两个例子最能说明问题:Coale 和 Flegal(1989)采用最干净的样品、最好的储存方法和最好的分析技术所测定的 Cu、Zn、Cd 和 Pb 的含量比最近采用最现代化的技术在最好的实验室中(但样品是否有污染不是很清楚)所测定的值小 2 个数量级;技术方面的改进给人印象很深的是伊利湖(Erie)湖水中溶解态铅含量的测定结果,1965 年的测定结果是  $< 15\,000 \text{ ng/L}$ ,1988 年该值则迅速降低为  $< 30 \text{ ng/L}$ ,而实际含量似乎没有变化。实际上,20 世纪 80 年代后期才有了比较可靠的测定数据。

1988 年以前,关于有毒 POPs 在劳伦系五大湖及其他地区的分布,几乎没有可信的定量数据,因为先前采集的通常都是小体积样品(1~2 L),几乎所有污染物的含量都在当时

的检测限以下。但通过过滤水样收集到的吸附在悬浮颗粒物上的难溶于水的污染物以及储存在沉积物中的污染物含量较高,获得的数据较好。

## 28.5 沉积物记录

来自柱状沉积物样品的数据能很好地记录持久型难溶于水的有机化学物质和有毒痕量金属浓度的长期变化(见 20.6 节)。由于吸附了大量的污染颗粒物,沉积物中污染物的浓度通常均远高于检测限,特别是痕量金属,其浓度通常更高,且样品在采集、储存和分析过程中几乎不受污染的影响(见 28.4 节)。由于在水体中随时间和空间的变化很小,柱状样也能提供完整而清晰的时间记录。(图 28-6)

柱状样能够记录污染物浓度随时间的变化曲线(图 28-6)。新近形成的沉积物记录的痕量金属浓度比柱状样记录的工业化前的浓度高得多,因为以前沉积物中的痕量金属主要来源于土壤、火山、火灾等自然通量以及不太显著的人类活动的影响。近期沉积物(或大气)中污染物的浓度与工业化前的背景浓度之比称为“富集因子”(enrichment factor, EF)。

### 污染物积聚随时空的变化

位于德国南部工业区下风处湖泊的沉积物中,几种典型金属的富集因子都介于 2.5~9(表 28-5)。这个值与西欧和北美地区所测定的全部 PAHs 和 POPs 的富集因子相比要小得多(表 28-6),主要原因是由生物代谢产生的 POPs 和工业化前人类活动所产生的背景值与 1800 年(图 28-7)前后的欧洲以及 50 年后纽约州北部大规模煤炭燃烧的释放量相比,前者较低。最近这两个区域 PAHs 的下降表明与改为高温煤碳燃烧发电有关,因为高温燃烧所释放的 PAHs 更少(Charles 和 Norton, 1986),这一降低也是对石油、天然气以及在某种监督范围内对核电站使用的增加所致。柱状样记录也表明,单位干重沉积物中的污染物浓度存在较大的年际变化(图 28-7),这一变化幅度未必能确切反映年际间释放量的不同,但与径流及其沉积物负荷有关,沉积物负荷的增加稀释了来自大气的污染物浓度。

在靠近工业区的非点源污染湖泊中,沉积物的富集因子可能会很高(表 28-5),反映出从远处污染源区的长距离输运和附近污染源的运输。通常在点源污染的湖泊中可以发现更高的污染物浓度,在这里不作具体介绍。在温带地区的湖泊沉积物中,干沉降和湿沉降使得污染物浓度随距污染源距离的增大而降低,例如,Windsor 和 Hiters(1979)指出沉积物中总 PAH 的浓度在距波士顿 100 km 的范围内(曼彻斯特,美国),逐渐降低了 3 个数量级。100 km 之外约为  $10^{-7}$ ,这一数值测定于距主要污染源很远的湖泊表面沉积物中,从而也表明了污染的全球性。然而,对具体的 PCB 同源物的研究表明,大气中大多数氯含量较高的物质(大多是不溶于水的、持久性的)比氯含量低的物质(难溶于水的且不易吸附的)更易于被气溶胶吸附从而沉降在距源区较近的地方。气态氯含量低的 PCBs 比例较高,因此在大气中的滞留时间更长、分布更广。

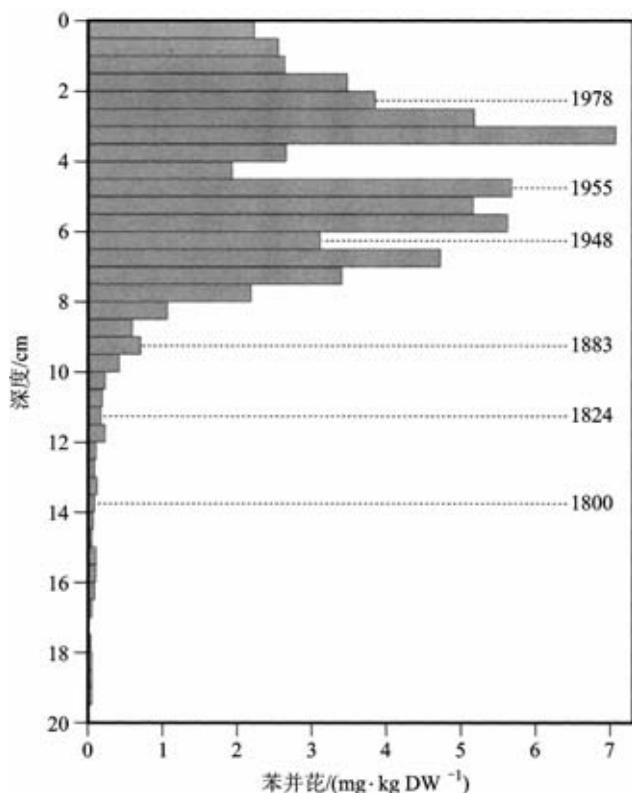


图 28-7 德国南部胡怎巴次湖中苯并芘的垂直分布(以单位干重沉积物表示的污染物含量通常被源源不断的新沉积物所稀释,稀释程度与径流的变化或流域内的建筑活动有关,在一些年份里,径流和沉降负荷的变化幅度比某些颗粒物释放和沉降的变化幅度更大。)(仿 Hilgers 等,1993)

表 28-5 德国西南部山林地区的寡营养湖泊柱状样中污染物的重金属和多环烃的富集系数、背景值及最大值

	干物质/(mg·kg⁻¹)		
	富集系数	背景值	最大值
Zn	7.3	22.8	167.6
Cd	9.0	0.17	1.5
Pb	7.5	13.4	100.2
Cu	3.5	8.0	28.0
Cr	2.5	21.1	53.6
Fl	>520	<0.005	2.60
BbF	>676	<0.005	3.38
BkF	>1 320	<0.005	6.53
BaP	>1 396	<0.005	6.98
BghiPer	>1 900	<0.005	9.50
IndP	>334	<0.005	1.67

Fl: 荧蒽; BbF: 苯荧蒽(b); BkF: 苯荧蒽(k); BaP: 苯并芘; BghiPer: 苯并芘(ghi); IndP: 苛并(1,2,3-cd)。

表 28-6 圣劳伦斯河和沙格奈河(加拿大魁北克省)的 40 个工厂以及弗雷泽河(加拿大的英属哥伦比亚)的两个工厂输出的吸附在悬浮颗粒物上的基因有毒物质及荧光物质的平均百分数[用苯(a)并芘当量表示]

工厂类型	吸附于悬浮颗粒物上的 基因毒物物质百分比/%	吸附于悬浮颗粒物上的 荧光芳烃类物质/%
表面抛光	86	23
无机化学物质生产	85	43
铝精炼	84	92
有机化学物质生产	72	55
石油冶炼	58	92
金属冶炼(不包括铝)	54	77
污水处理	21	22
纸浆及造纸	29	50

资料来源:改自 White 等,1996。

## 28.6 污染物的理化特征及其在自然界的分布

正如前面所提到的,污染物在水体中的溶解度变化很大,易溶于水的污染物被称为亲水(易与水结合)污染物,而在水中溶解度很低的被称为“不溶”(疏水)污染物,后者易被碎屑和生命有机体所吸附。污染物在水体中的溶解性不仅影响它们在水体中的行为,同时也决定了它们被保留在流域中的效率有效性,以及毒素释放到大气中后更易被气溶胶吸附从而以干沉降的方式沉降,或者更易溶解在水中以湿沉降的方式沉降(见 27.2 节)。

### 水溶性

进入水生生态系统中的污染物被生物利用的程度主要取决于其在水体中的溶解度。生物利用度不仅决定了水体中的某种毒物被生物吸收的程度,也决定了这种毒物被生物吸收后的代谢机制。紧紧吸附在胶体或大颗粒物如无机或有机集合体(絮状物)上的不溶于水的污染物与溶于水的污染物相比,更难被生物从水体中直接吸收,而更易通过沉降方式或生物的滤食行为从水体中去除。

平衡状态下某种给定浓度的化学物质被颗粒物吸附而不是溶解在水中,可用分布或分配系数来表示( $K_d$  或  $K_p$ ):

$$K_d \text{ 或 } K_p = \frac{\text{颗粒物上的浓度}}{\text{水体中的浓度}} \quad \text{式 28-1}$$

难溶于水的有机化学物质以及其他一些化学物质,如广泛分布的放射性同位素<sup>137</sup>Cs 具有很高的固体物吸附系数( $K_d$  为  $10^3 \sim 10^7$ )。 $K_d$  通常用对数来表示(即  $\log K_d 3 - \log K_d 7$ ),主要受以下因素的影响:①溶液中化学物质的浓度;②吸附颗粒物的浓度及大小(有效表面积);③悬浮颗粒物是否是有机物或者是否具有利于吸附的有机表层;④温度。

### ▲ 自然界中的分配系数

由于  $K_d$  的概念源于土壤, 我们必须获得水生生物对污染物吸收和污染物毒性在平衡状态下的分配系数。有毒金属可分为溶解态和颗粒态。例如, 在伊利湖(Erie) 和安大略湖(Ontario)之间的尼亚加拉河(Niagara), 吸附在悬浮颗粒物上的镉只占约 5% ( $\log K_d$  约为 3), 而铅和锌( $\log K_d$  约为 7) 则被完全(100%) 吸附(Allan, 1986)。那些吸附在颗粒物上的污染物负荷所占的比例会随颗粒物数量的增加而增加。通常情况下, 难溶于水或易被颗粒物吸附的化学物质在高透明度的湖泊和河流中的溶解比例比在混浊水体中更高。

决定有毒金属分配(吸附)的理化特征主要有颗粒物半径、离子半径、负电量等。负电量表征一个原子通过共价键吸附电子的能力(Forstner 和 Wittmann, 1979; Stumm, 1987), 负电量越多, 元素的溶解度和活度越低。物理特征决定了某种金属或 POP 通过颗粒物沉降离开水体的难易程度(图 28-8)、在水体中的滞留时间、被沉积物束缚的紧密程度以及从捕食者胃中的颗粒物上被释放出来的可能性。需要说明的是, 沉积物的特征、温度、pH 都能改变微量金属的溶解度( $K_d$ ), 其中 pH 的影响特别明显(图 27-8)。不仅大多数有毒金属以及令人讨厌的持久有机含氯污染物具有很高的  $K_d$  并被牢固吸附于颗粒物上, 城市和工厂流出或释放的基因毒素化学物质有时也是这样(表 28-6)。

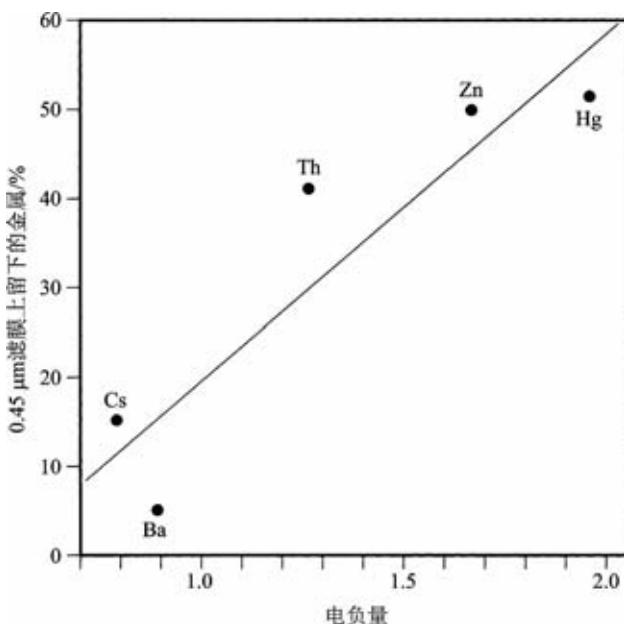


图 28-8 在 20 d 的微生态系统实验中痕量金属特性及通过 0.45  $\mu\text{m}$  过滤的颗粒中标记的痕量金属之间的关系 ( $r^2 = 0.85$ ;  $0.02 < P < 0.05$ ) (仿 Jackson 等, 1980)

## 28.7 毒性及其预测

认识有机持久污染物和有毒金属的结构及其活性(行为)具有系统关系, 从而使得对大量人工合成的不同化合物生物毒性的预测成为可能, 并备受关注。同样, 同源物中不同化合物的生物活性通常不同。

## 结构与活性的关系

有机化合物的理化特征及结构与其活性(包括毒性和分布)之间的关系被称为定量结构-活性相关(QSARs)。在预测某种颗粒物和生物的吸附特征时,最为广泛应用的物理特征是正辛醇水分配系数[ $\log(K_{ow})$ ],它表征水和溶剂(辛醇)之间的平衡浓度,这里正辛醇被用作分离水和生物油脂的萃取剂(图28-9)。可见, $K_{ow}$ 可提供如下信息:①有机体的吸收潜力;②在水中的生物富集潜力(图28-10);③在食物网中的生物放大潜力;④持久性有机污染物在环境中的滞留时间。

▲ 生命周期长的大型有机体中的污染物浓度通常比从 $K_{ow}$ (水体中的溶解度)预测的高,这表明在自然界中,污染物的主要富集方式是食物而非直接从水体中吸收(见28.8节)。用经验模型(基于大范围的毒性及 $K_{ow}$ )获得的 $K_{ow}S$ 表明,急性毒性与细菌、原生动物、藻类、水蚤、小虾及鱼等有机体的 $\log(K_{ow})$ 之间的关系为线性相关(Nendza和Klein,1990)。慢性毒性也与 $K_{ow}$ 有关,但污染物浓度比急性毒性污染物浓度低1个数量级(McCarty和MacKay,1993)。慢性毒性通常被出生缺陷和胚胎死亡率的增加所证实。

水中溶解度低或经膜通道作用后会减少的高度亲脂性毒素[ $\log(K_{ow})$ 约大于5],其毒性和 $K_{ow}$ 之间存在线性关系,结果高 $K_{ow}$ 化合物的毒性比其 $K_{ow}$ 所预测的要小。一些有机化合物的亲脂性(易溶于脂肪)决定了这些有机污染物易于被动物吸收而储存在体内。一些难溶于水的亲脂性有毒烃类化合物及其同源物,因含氯多,不仅不易挥发,毒性也最强,这些同源物不易被鱼类代谢(Niimi,1986)。因此,富含氯的这些同源物不仅容易储存在

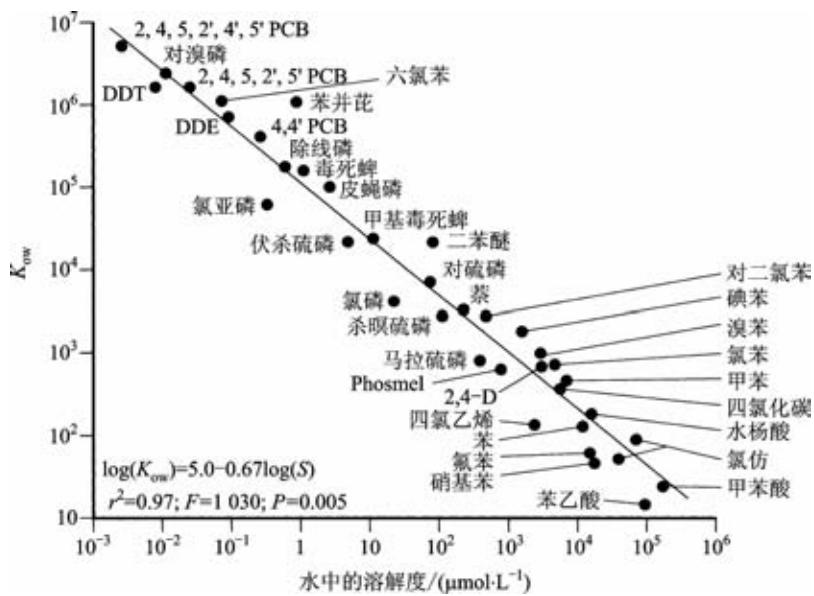


图28-9 一些有机化学物质在水体中的溶解度及其与分溶(水与n-辛醇)之间的关系(分溶系数为 $K_{ow}$ ,为化学物质在水中溶解态和类似脂溶状态的同义词。数据的分散主要是由于温度和分析步骤所致。)(改自Chiou等,1977)

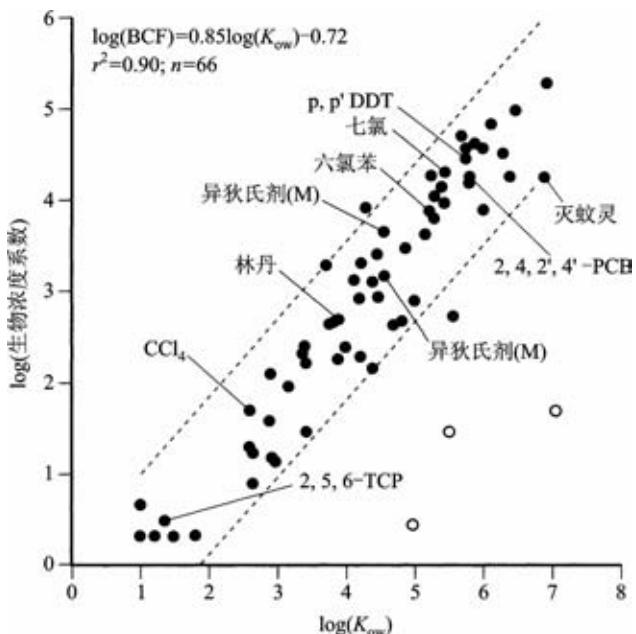


图 28-10 基于 1 个月的实验数据,对胖头鲦鱼(FM)、蓝鳃太阳鱼、虹鳟鱼和食蚊鱼(M)等暴露在非致死化学物质浓度的水中和辛醇:水(1:1)分配系数  $K_{ow}$  的生物富集因子(BCFs)。[图中显示 BCF 的 95% 置信度。回归函数不包括 3 个异常数值(○),原因是尽管  $K_{ow}$  很高,生物富集因子却很低。注意:这里 BCFs 的值来自时间相对短的吸收实验,而非来自在自然条件下相对长期的食物吸收。另外要注意对于同一种化学物质(如异狄氏剂),不同研究者所得的结果会有所差异。](改自 Veith 等,1979;Stumm 等,1983)

有机体中,也不易被代谢(酶解)或被微生物降解。通常情况下,不管在任何地区,氯含量和烃同类物的毒性都会随营养级的升高而升高,但大多数分馏作用看起来多发生在食物网的底部(Oliver 等,1989)。

### QSAR 的局限性

与其他回归模型(包括著名的总磷-叶绿素 a 关系模型;图 8-16<sup>①</sup>)一样, QSAR 模型也存在重要的局限性。 $K_{ow}$  的预测能力随化合物测定间隔的缩短而逐步降低,而 QSAR 揭示了某些格局(规律性)。当测定的  $K_{ow}$  的范围降低 1 个数量级时, $K_{ow}$  的毒性就不能再用  $K_{ow}$  预测(图 28-9)。因此在小尺度间隔范围里,其他通常没测定的变量变得更为重要(见 2.6 节)。QSARs 的另一个局限是要针对具体物种,不同有机体对某些特定毒物的敏感度相差 3 个数量级。这种变化使得很难根据受控条件下的一个或几个物种的实验结果

<sup>①</sup> “对如 QSARD 相关关系的质疑通常是由于它们没有建立在对毒理机制理解的基础上,它们虽能快速给出答案,但并未根本理解其机理所在。只有从根本上理解毒理机制才能真正回答我们所遇到的一些毒理问题。然而,短期内我们仍需一些指导。事实上,将 QSAR 同基础研究结合起来也许会达到这两个目的”(Blum 和 Speece, 1990)

确定某一毒物对群落的影响。这一差别进一步反映出实验条件、有机体年龄及生理条件、中毒行为模式以及毒素被吸收和消除的动力学等都可能影响有机体对毒物的敏感度。

尽管具有局限性,  $K_{ow}$  及其他 QSARs 模型在预测大量人工新合成的有机化合物的毒性时, 作为第一指标起到了关键的作用。因此,  $K_{ow}$  是新化合物核准之前的一个不断调整的替代物。所需要的其他信息包括化合物的理化特征(溶点、沸点、溶解度、水解能力及其他形式的化学降解)及对特定物种的毒性资料。作为其他有毒物质在水体中溶解度的替代指标(图 28-9),  $K_{ow}$  能够反映这些有毒物质吸附于沉积颗粒物( $K_d$ )的程度和能力, 以及这些持久污染物保留在水体中而不是随颗粒物沉降而进入沉积物的程度。

### 生态系统毒性的测定

一些主要的问题仍然困扰着我们, 使得我们无法对化合物的生态系统毒性进行评估(Kaiser, 1984)。在实验室条件下测试几个物种对特定有毒物质的具体反应以及对物种所有发育阶段的毒性实验, 都不能很好地模拟自然界中大多数物种在多变环境条件下对特定有毒物质的反应。只强调短期急性毒性实验对生态系统毒性的评估有失偏颇, 因为即便是内陆水体, 其中有毒物质的浓度也只是偶尔才会达到急性毒性水平。常见的急性毒性实验有两种: 非特定的(没有反应的或麻醉的)和特定的(有反应的或不麻醉的)的急性毒性实验。大多数的 QSARs 使用前一种, 这种实验中毒性是有毒物质积累的函数, 与特定的机制无关。相反, 特定毒素影响特定的机制(如阻止某种代谢途径或酶的生产)。特定毒素的毒性在其阈值浓度以下时表现出非特定毒素的作用(McCary 和 MacKay, 1993)。但对毒性物质的评估仍存在其他两个问题。首先, 即便大多数污染物通常以复杂的混合物形式释放, 但一些特定化合物或元素的急性毒性仍很重要。污染水体通常含有大量不同种类的有机和无机有毒污染物, 我们对这些污染物之间如何相互作用却一无所知。其次, 目前仍缺乏可以测定慢性毒性污染物及其对自然界的影响的先进工具。

通过细菌培养<sup>1</sup>检测环境样品慢性毒性的快速筛选实验是除 QSARs 之外的另一种有前景的环境毒理学方法。这种新方法是环境毒理学家在实验室中基于对同一个物种或其替代物的长期毒性实验, 将自然界中的毒性效应与生物体组织中的污染物浓度结合起来。这种方法比传统的毒理学方法具有更大优势, 传统的毒理学方法是在实验室内将污染物溶解在水中, 然后把有机体简单地暴露在人为升高的特定污染物浓度中, 进行短期(急性)实验, 强调的是剂量反应关系, 而这种通过剂量反应关系获得的死亡率很难外推到自然界。

### 毒性当量系数

自然界中的鱼类及其捕食者常暴露在多种污染物中, 因此有必要测定污染物对生物总体的影响, 毒性当量系数(toxicity equivalency factors, TEFs)是响应这一需求而最近发展起来的。毒性当量系数表示单个或混合污染物如多氯有机物(PCHs)的毒性当量与剧毒四氯二苯并对二噁英(TCDD)的标准相同, 常采用生物测定系统作为化学测定装置。这个方法是基于 PCHs 能够导致特定的肝酶感应, 而这些特定肝酶反过来又代谢(解毒)

有毒的同源物。酶活性的降低程度,即混合功能氧化酶系统(mixed function oxidase system, MFOS),是经验毒性的函数(Ludwig等,1993)。利用TEFs测定自然界中PCHs的毒性,其结果比仅对生物体内PCHs总含量测定得到的结果好得多(图28-11)。在北美五大湖流域对鸬鹚和桑氏燕鸥雏鸟TEFs测定所得的结果可准确地预测雏鸟发生变形的情况。然而,其他生态毒理学家通过测定鱼体内特定的酶或者荷尔蒙水平以诊断自然界中低浓度污染物的浓度(Hontela等,1992)。最后,金属硫因(一种易与痕量金属结合的低分子蛋白质)被用作生物检测以评估有毒重金属对鱼类和无脊椎动物的胁迫(Hamilton和Mehrle,1986)。

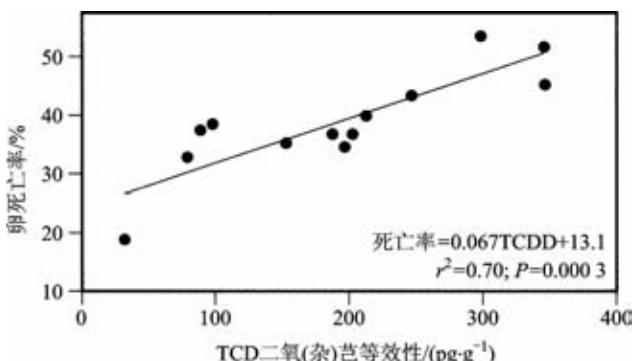


图28-11 基于实验室生物测定的1986—1988北美五大湖TCD二(杂)芑等效性与双冠毛鸬鹚卵死亡率之间的关系(仿Giesy等,1994)

## ▲ 28.8 生物富集及生物放大

生物富集是持久污染物在生物体内的富集比释放更大而导致的净增加。吸收方式包括体表或鳃( $K_{ow}$ 高)对亲脂性或者其他污染物(如有毒金属)的吸附,或者从食物中吸收。对小个体生物来说,吸附富集方式更加重要,因其具有大的表面积与体积比和高的代谢速率。生物体的代谢速率通常比其体重的增长慢得多(代谢=体重 $-0.75$ ;Peters,1983),因此位于食物网顶端的大个体生物从水体中直接吸收的污染物相对较少<sup>①</sup>,而被认为主要从持久污染物所污染的食物中吸收污染物。大型生物降低代谢速率——包括降低排泄速率——使得持久性有机污染物很容易分配至组织器官、油脂及蛋白质中。

湖泊中成年鲑鱼(一种位于水生系统食物网顶端主要供垂钓的鱼),其体内积累的持久性有机污染物有80%~100%来自食物,其余的直接从水体中吸收(见Borgmann和Whittle,1992)。在确定这种供垂钓成鱼的污染物来源时,用来表示动物在污染水体时间长度的个体和年龄的大小,比起鱼类的食物来显得不那么重要。在同一个气候区域,捕食者(如海鸥、潜鸟、鹰、水貂、水獭)身体组织中所含有的持久性有机污染物(包括有机汞)总是比预期的环境浓度或 $K_{ow}$ 值高(5倍;Thomann,1989;Oliver和Niimi,1988)。

<sup>①</sup> 将污染物溶于水,而不是测定生物直接从食物中吸收,这种短期剂量-反应实验室实验使得多数毒理学家认为直接从水中吸收是唯一或基本的吸收方式,直至最近这种观点才得以纠正。

## 生物放大和生物富集

持久污染物的浓度随食物网中营养级的增加而增大的现象称为“生物放大”(biomagnification),可由捕食者与被捕食者浓度的比值得到,而生物富集因子(BAF)表示生物有机体中持久污染物浓度与环境浓度的比值(图28-12)。食鱼性鱼类对PCBs的生物富集一般为 $10^6$ ,食鱼海鸥体内的浓度约大10倍( $10^7$ ),而鹰体内的浓度PCBs则高达 $10^8$ (Ludwig等,1993)。安大略湖食鱼性鱼类(鲑鱼)对PCBs的生物富集因子可用 $K_{ow}$ 通过如下方法进行预测(Oliver和Niimi,1988):

$$\log(\text{BAF}) = 1.07 \log(K_{ow}) - 0.21$$

$$r^2 = 0.86; n = 18$$

式28-2

易被生物富集的物质还包括有机汞(通常与油脂结合)、铯137( $^{137}\text{Cs}$ ,与蛋白质结合)以及锶( $^{90}\text{Sr}$ ,在骨头中通常被钙替代)。这两种同位素均是在原子弹试验以及核泄漏中被释放出来的。

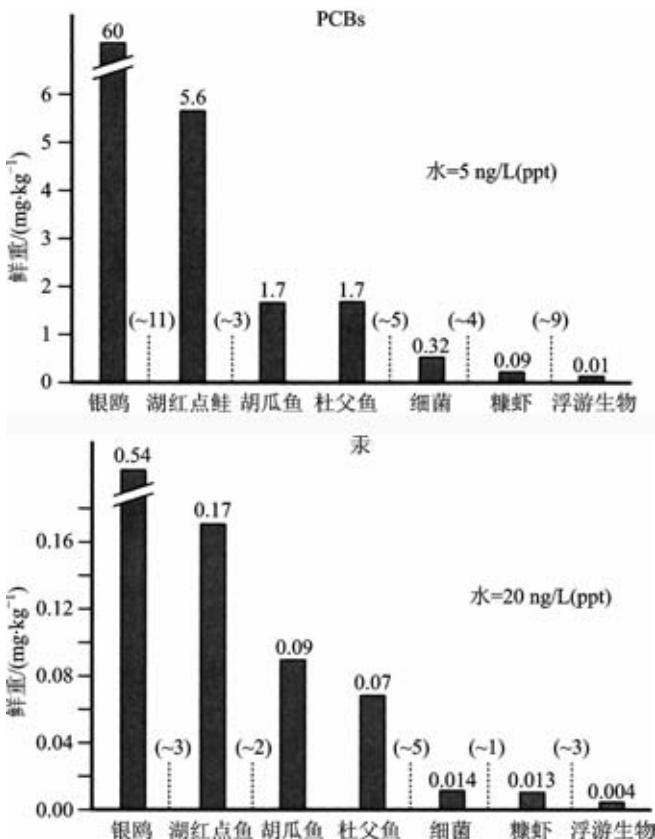


图28-12 安大略湖的PCBs和汞的生物富集因子BAF分别为 $10^7$ 和 $2.7 \times 10^4$ ,代表了污染物从水(包括胶体)到食物网顶端的银鸥(卵)[注:垂直虚线把假定的营养级分开。BAF表示捕食者与其猎物的PCBs浓度比。BMF(显示在括号中)为假设的营养级间的生物放大系数。](改自Anon,1991)

## 食物网结构及生物放大

生物放大能够解释持久污染物的浓度为何在食物网顶端较高,但不能解释偏远的安

大略湖中湖鲑体内的 PCBs 含量 ( $0.015 \sim 3 \mu\text{g/g}$ ) 和汞 ( $0.03 \sim 3.96 \mu\text{g/g}$ ) 为何会相差 2 个数量级 (Rasmussen 等, 1990; Cabana 等, 1994), 也不能解释斯堪的纳维亚地区湖泊中梭子鱼体内的汞含量为何具有同样大的变幅。这种大变幅的存在原因是基础研究的课题, 对人类利用鱼类作为食物具有很高的参考价值。距污染源区等距离的附近湖泊中鲑鱼和梭子鱼体内污染物含量的大幅度变化需要不同的解释, 其中最重要的原因是湖泊内营养级的不同(食物链的长度不同)。

在食物链最短的湖泊中, 湖红点鲑的污染最轻, 在缺少其他猎物时, 这种鱼一般以大型浮游动物(如体型较大的溞)和底栖无脊椎动物为食, 这类湖泊称为第 1 类湖泊(图 28-13)。在有敞水区鱼类(如胡瓜鱼和白鱼)等中介营养级存在时, 湖红点鲑的污染就相对较重, 这类湖泊称为第 2 类湖泊。湖红点鲑在第 3 类湖泊中的污染最为严重, 第 3 类湖泊除了大型浮游动物和浮游生物食性鱼类以外, 也包含糠虾(一种大个体的肉食性甲壳类浮游动物; 图 28-13; 见 23.8 节)。由于具有最长的食物链, 第 3 类湖泊产生了最强的生物放大作用。利用稳定同位素的比值可以测定猎物和捕食者的营养级位置, 其结果比通过测定有限数量的捕食者肠胃内含物(猎物)获得的营养级位置更准确。稳定同位素分析<sup>①</sup>表明, 鱼类和其他脊椎动物的食性并非原本认为那样, 而是更多地表现为杂食性 (Vander Zanden 和 Rasmussen, 1996)。

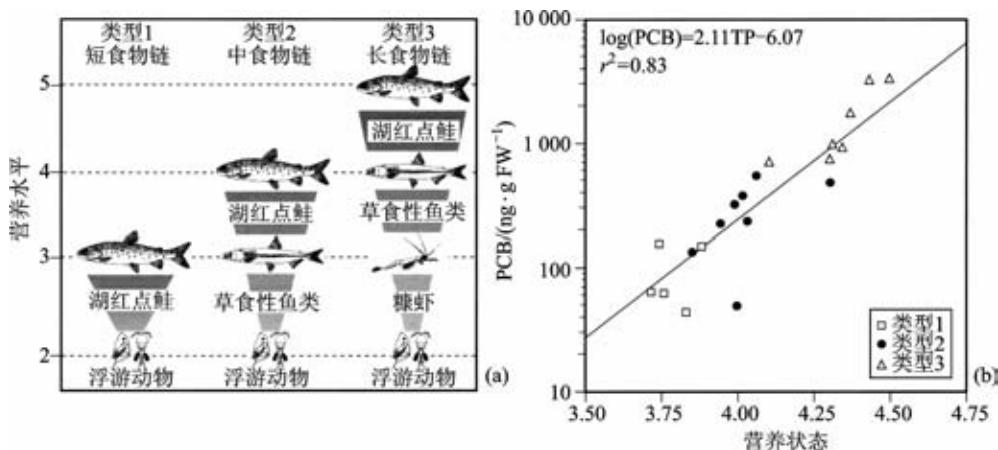


图 28-13 (a) 食性不同的鲑鱼分属 3 个不同的营养级;(b) 基于稳定同位素分析( $^{15}\text{N}:^{14}\text{N}$ ), 鲑鱼的营养级位置及其体内 PCB 水平的关系(仿 Vander Zanden 和 Rasmussen, 1996)

<sup>①</sup> 长久以来, 胃容物一直被用来测定消费者的食性, 但这种方法耗时大, 并仅能提供瞬间的测定结果(除非经常重复测定)。现在湖沼学家越来越多地采用稳定同位素以获得食物网中食物种类、营养结构以及能量流动等信息。其中应用最广泛的是重氮( $^{14}\text{N}$ )和轻氮( $^{15}\text{N}$ )与重碳( $^{13}\text{C}$ )和轻碳( $^{12}\text{C}$ )的比率, 同位素值是相对于参照标准(大气中的氮和石灰石中的碳, 同位素值为 0‰)的千分数, 变率用  $\delta$  为单位表示。消费者的  $\delta^{15}\text{N}$  的丰度通常被认为是高于其食物的  $1.7 \sim 3.4 (\pm 1\%)$ , 被用来确定生物在食物网中的营养级位置。 $\delta^{13}\text{C}$  在食物网碳流动时的变化相对较小 ( $\sim 1\%$ ), 且通常与  $\delta^{15}\text{N}$  一起被用来区分同位素值具有明显差异的能量来源(如浮游植物、大型植被、外来物质)。

不仅湖红点鲑体内的 PCB 和 Hg 含量与其个体大小有关(Cabana 等,1994),许多肉食性鱼类的 PCB 和 DDT 含量也与个体大小有关(Rowan 和 Rasmussen,1992),这表明不同持久污染物具有相同的生物富集与生物放大模式。

## 28.9 汞及汞循环

湖泊汞污染在北温带地区普遍存在。在瑞典的 83 000 个湖泊( $>0.01 \text{ km}^2$ )中,有 40 000 个湖泊的梭子鱼体内汞含量高于  $0.5 \text{ mg/kg}$ ,其中约有 10 000 个湖泊中梭子鱼体内的汞含量非常高( $>1 \text{ mg/kg}$ ),以至于对经常食用这种鱼的人的健康形成了潜在威胁(Lindqvist 等,1991),对那些大部分或全部以这种鱼为食的野生动物种类的威胁更大,因其不像人类可以改变饮食结构。在美国,鱼类体内的汞含量也非常高,以至于 26 个州的一些政府机构不得不发出警告。例如,在威斯康辛州 300 多个偏远湖泊中,有 30% 的湖泊鱼类汞含量超过州政府设定的安全警戒线( $0.5 \text{ mg/kg}$ ; Fitzgerald 和 Watras,1989)。消费者协会还对大约 90% 的安大略地区湖泊、90% 的东北部明尼苏达州湖泊以及 10 000 个密歇根州湖泊发出警告。水体中汞含量升高的地区并不仅局限于北美或欧洲前寒武层湖泊或北部森林地区的湖泊,在佛罗里达州一些缓冲能力低(低 pH)的水体也有鱼类遭到汞污染的报道(Lange 等,1993)。

### 汞中毒

长期以来,人们认为只有职业人员如涉及汞生产的工人有汞中毒的风险。但过去 50 年中两次大规模因食用污染鱼类引起的汞中毒事件(日本和伊拉克)增加了人们对汞污染风险的关注。在 20 世纪 60~70 年代,瑞典在汞的环境污染方面开展了大量研究工作,因为在瑞典有机汞作为生物杀灭剂被广泛使用,至于汞在人类健康方面的影响未得到关注。第二次世界大战之后,一些食草鸟类以及一些以啮齿类食草种动物为食的鸟类的减少引起人们的关注,而这一现象与生物杀灭剂的使用关系密切。之后的 20 世纪 60 年代,人们发现低缓冲湖泊的淡水鱼类体内汞含量也升高了。如今,在北美和欧洲的一些偏远湖泊中,一些较大的食鱼性鱼类体内的汞含量已很高( $>1.5 \text{ mg/kg}$ ),以至于使人类以及以鱼类为食的野生动物体内的汞含量达到了令人担心的水平。根据 Scheuhhammer 和 Blancher(1994)的估算,安大略地区约有 30% 的酸性湖泊中的鱼类体内甲基汞含量很高,并影响到一种潜鸟(*Gavia immer*)的繁殖。

### 污染及与污染源距离的关系

如今,瑞典非酸化湖泊中梭子鱼体内的汞含量已由原来仅能检测出的  $0.05\sim0.3 \text{ mg/kg}$  的背景值增加到  $0.5\sim1 \text{ mg/kg}$ 。这一增加量(3~5 倍)与北美湖泊新增沉积物(图 28-14; Lindqvist 等,1991)相对于背景值的增加量(富集因子 EF)相同(见 28.5 节)。鱼类及沉积物污染的增加归因于:①大气对源于  $1000\sim2000 \text{ km}$  以外工业地区汞的运输的不断增加;②6 个月到 2 年长的大气滞留时间;③位于工厂和城市下风向低缓冲湖泊的不断酸化(见

第27章)。

随着与污染源距离的增加污染降低,这意味着污染物的沉降速率也将随着与污染源距离的增加而降低。事实上,南斯堪的纳维亚污染物的沉降速率比瑞典北部高出近7倍(Johansson, 1985),然而,近年来即使在远离汞污染源的北部森林水库中鱼体内的汞含量也特别高,至少在水库构建后10年是这样。如此高的汞含量至少部分归因于过去几个世纪其他地方汞的释放和近期遭遇洪水的厌氧土壤汞的释放(Bodaly等,1984)。另外,岩石地区汞的来源也很重要。在亚北极区魁北克省的浅水湖泊中,北方梭子鱼(*Esox lucius*)体内的汞含量平均约为3 mg/kg,而这个地区未污染湖泊中的鱼体内的汞含量约为0.4 mg/kg(Chevalier等,1997)。

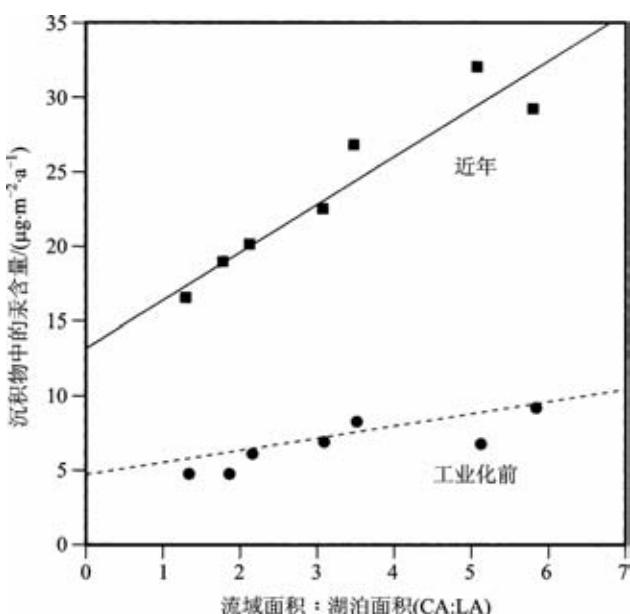


图28-14 在威斯康辛州和明尼苏达州(美国)的几个湖泊中,全流域沉积物中汞的沉降速率是流域面积与湖区面积之比(CA: LA)的函数。[注:“近年”指过去的10年(1982—1992),“工业化前”指大约在1850年以前。在不考虑流域的情况下,回归线描述了大气汞在湖泊的平均沉降速率;斜率与截距的比是对大气沉降占流域输入比例的估算。新近沉积物中汞浓度约为之前的3倍;较大流域内不成比例的高积累速率表明土地利用的变化(引自Swain等,1992)。

### 汞的测定

生物体内及沉积物中汞的高含量与水体和大气中极低的汞含量形成鲜明对比。样品在采集过程中以及分析过程中的污染(见28.4节)妨碍了人们对汞的生物富集速率及通量调节机制的认识。最近的研究采用超洁净微量金属自由收集和储存的方法,结果表明采用这种特别小心的方法得出的总汞的数值仅为以前未采用这一方法所得到的数值的1/100~1/20(Fitzgerald和Watras,1989)。尽管以前没有多少解释甲基汞(MeHg)含量的数据,但在几乎没有可信数据存在的情况下,1989年已经获得了这种毒性非常大的生物富集形态的有机汞(Bloom,1989)。此外,目前仍没有测定现场无机汞甲基化和去甲基化速率的方法。

水生系统中总汞和甲基汞的颗粒活性可以达到( $\log K_dS = 5 \sim 7$ (Watras等,1994)),甲基汞的 $K_d$ 更高,亲脂性使其很少被代谢掉,从而更易被生物富集。处于食物网顶端的游猎鱼体内的汞基本全部(95%)以甲基汞的形态存在(Westoo,1996;Grieb等,1990)。

## 环境因子及污染

对大量鱼体内汞含量数据与环境因子关系的分析发现,北温带地区的偏远水体中,鱼体内汞含量随着水色(水色为DOC替代物)的变深而增加,并且在pH小于6的情况下,随着酸度的增加而增加(Hakanson等,1990;Grieb等,1990)。在大多数北温带的水体中,酸度与水色高度相关,这使得评价每一个因素的相对重要性成为可能。但由于水色基本上取决于流域大小和坡度(式8-2),因为大部分总汞和甲基汞被吸附于溶解态的有机物(DOM)上,因此,腐殖质湖泊不仅接收了更多来自流域的总汞,还接收了比清水湖泊、河流和湿地中更多的甲基汞。

由实验室测定的细菌参与的甲基化和去甲基化,以及测定的大气、水体和沉积物中汞的种类,得到汞循环的概念图(图28-15)。汞离子( $Hg^{2+}$ )是负电性极强的元素,能同有机物形成稳定的复合物。汞的甲基作用常有微生物参与,而且是汞的生物地球化学循环的关键,因为如上所述,甲基汞是生物富集和运输的基本形态。微生物参与汞的甲基化,对汞离子进行解毒,产生更多可溶的(活性)、能从沉积物或土壤中缓慢扩散出来的甲基汞( $CH_3Hg^+$ ),同时通过将 $CH_3$ 转变成为 $CH_3Hg^+$ ,产生更多不溶但可挥发的二甲基汞[( $CH_3$ )<sub>2</sub> $Hg$ ]<sup>+</sup>]。微生物将 $Hg^{2+}$ 还原成更易挥发的 $Hg^0$ (金属)形态,这是微环境的第3个解毒机制(Wood,1987)。汞因挥发从而于沉降之前在大气中滞留很长时间,因此可以在全球分布。最后, $H_2S$ 在和汞发生反应时产生相对易挥发的物质[( $CH_3$ )<sub>2</sub> $Hg$ ],其余的以不溶的非毒性 $HgS$ 沉降(图28-15)。

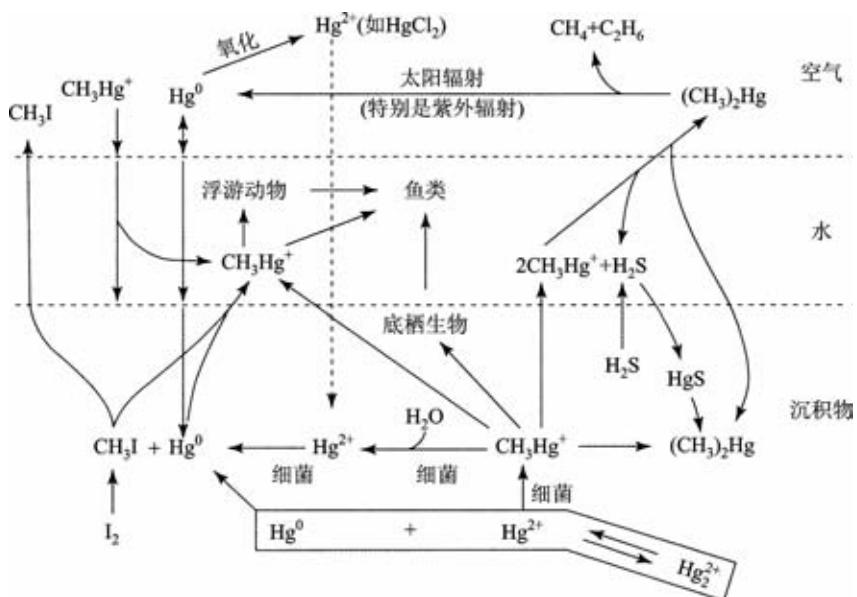


图28-15 水生系统中的汞循环示意图[其中的反应过程包括细菌的催化、 $H_2S$ 的化学还原、有机汞化合物的光化学反应。注意显示的是被吸收的(复杂的)无机汞以及从流域进入水体的 $CH_3Hg^+$ ]。  
(改自Wood,1987)

## 28.10 有毒物质、环境健康和水生系统管理

消减环境中有毒化学物质供给的唯一有效方法是阻止其向大气和水体的释放。有毒化学物质的持续性和生物富集已引起高度关注,因为它们在食物网中存在潜在的生物放大作用。人类对被污染鱼类和野生生物的消费成为一个严重问题,特别是渔民及那些生活在偏远地区且传统上以肉食性鱼类为主食的人,不得不在污染风险与营养结构之间寻求平衡。而肉食性鱼类及以鱼为食的野生动物(如潜鸟、石首鱼、海鸥、鹰、水貂、水獭)不会改变其饮食结构,因此风险更大。

关于肉食性鱼类及其捕食者的污染和对健康的影响严重程度已引起相当多的争论,但是有足够的证据表明劳伦系五大湖中一些野生生物种类至少在重污染地区受到了影响。水鸟中畸形和繁殖缺陷频率的增加,包括胚胎的存活(Giesy等,1994),与实验室研究中所观测到的暴露于PCBs和POPs的相同种类或替代物中的结果类似(Ludwig等,1993)<sup>①</sup>。

### 本章重点

- 有毒化学物质中最受关注的是有机氯分子,称为有机氯,它们是持久性的(难降解),并能在生物体内富集。这些持久性有机污染物(POPs)在一定程度上易挥发或吸附于空气中的悬浮物上,可从源区传播至上百甚至上千km之外的偏远地区。
- 毒性分为急性和慢性,急性毒性可导致快速死亡。但慢性毒性(亚致死的)更常见,其影响因会延滞而更难定量化,很难将慢性毒性与特定的源联系起来。
- 全球范围内释放到大气中的痕量金属(包括有毒的As、Cd、Hg、Pb)一半以上是由人类活动造成的。
- 大气作为水生生态系统中POPs和有毒痕量金属的直接源,其相对重要性受到流域面积与水面积比值的很大影响。
- 易溶于水的污染物被称为水溶性的,而在水中溶解性很低污染物的被称为“难溶性的”。后者很容易吸附于颗粒物或生命有机体上,从而不像水溶性污染物可以在水体中被直接利用,而是更易以沉降方式或因有机体的滤食而离开水体。
- 持久性有机污染物和有毒金属的活性(包括其毒性、吸收、潜在的生物富集)及其分布之间的系统关系已被正式确定为具有预测能力的定量结构-活性相关(QSARs)。
- ▲ 最近发展起来的毒性当量系数(TEFs)使得人们可以对自然界中不同污染物的总毒性进行比较。

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<sup>①</sup> 这项研究表明,野生生物的保护比目前对人类癌症的防治更加需要紧迫措施,应该给予野生动物种群保护和人类防癌以同等的地位。

- ▲ 在偏远地区的水域中,食鱼性鱼类在污染(如 PCBs 或汞)方面存在的显著差别一定程度上均与食物链(食物网)的不同有关,具有不同程度的生物放大作用。
- 消减水生生态系统中有毒物质的唯一有效方法是阻止向水体或大气中释放有毒物质。

(张修峰 译)

# 第 29 章 水 库

## 29.1 引言

现有的大多数水库(reservoirs)体积都相对较小(约小于 100 万 m<sup>3</sup>)——在南非或者澳大利亚,水库被称为蓄水池(impoundments)或者水坝(dams;见 6.8 节),小型水库通常用于解决生活用水、牲畜用水、灌溉或者渔业生产。然而,自 1994 年以来,大约有 948 座大型水库在建设中,其坝高至少为 15 m,按此情况发展,到 2000 年全世界大约就会有 50 000 座大型水库。

水库通常建在蒸发作用接近或超过降雨量的地区的河流上,入库水量主要来自当地河流在雨季的汇水。由于当地的径流量小,并且水库很少有足够的盆地能够保证全年蓄水,因此,永久性的水库较少。在干旱及半干旱地区,水库的河流水量有着较大的季节和年际间的差别。人们在降雨量少的地区修建大型水库主要是为了灌溉、防洪以及为城市提供水源,有时也为了改善航运条件(如伏尔加河;见 5.8 节)、养鱼或者休闲。用于发电的大型水库,建在降雨量大或小的地方均可,前提是那里的地理条件和河流流量允许修建大坝,并且经济效益可观(图 29-1)。



图 29-1 总长度为 200 km 的伊泰普水库  
[面积 = 1 347 km<sup>2</sup>, 平均深度 = 22 m, 最大深度 = 115 m, 平均水滞留时间 = 35 d。伊泰普水库位于巴西和巴拉圭边境的巴拉那河上,泄洪道(正在排洪)防止在汛期大坝漫顶。](照片由伊泰普的 Binacional 提供)

大坝对径流量的控制在不断增长,库容大于  $0.5 \text{ km}^3$  的诸多水库储存了 20% (约  $8\,400 \text{ km}^3$ ) 的世界平均径流量。水库的库容量大约已上升到河流容量的 7 倍 (Vorosmarty 等,1997)。

水库造成水的滞留以及河流流量、沉积物在坝前的积累和营养物质的滞留 (见 9.6 节),这不仅影响到河流和湿地中的生物群落,还对当地居民产生了多方面的影响。人们注意到大型水库对环境和社会的负面影响,预先开始进行大坝环境影响评价 (environmental impact assessments, EIAs),这种评价比原来更加严格。

西方湖沼学家对水库的关注历来就很有限,Thornton 等人 1990 年才出版了第 1 本关于水库的湖沼学英文专著。而用西欧语言出版的最具历史影响的专著,直到现在也就是 3 小卷,其中报道了对几座捷克发电/饮水水库的长期详细的研究 (Hrbá? ek, 1966; Hrbá? ek 和 Straškraba, 1973)。1963 年,共有 613 篇文章是关于伏尔加河 (俄罗斯) 上浅水富营养化的雷宾斯克水库的 (Straškraba 和 Straškrabová)。

## 29.2 天然湖泊和水库

天然湖泊与人工湖泊<sup>①</sup>有很多相似之处,它们拥有几乎相同的生物种类与相近的生境(如敞水区)。在氧化还原反应、捕食 – 被捕食关系、对流混合以及研究这些问题采用的技术等方面,水库均与湖泊相似。但在同一大陆尺度上,温带水库与天然湖泊还是有很大区别的(表 29-1)。有些区别与地理位置相关,例如,比较美国的水库与湖泊,水库大都修建在纬度较低的地区(在  $33^\circ\text{S} \sim 42^\circ\text{S}$  纬度带),而大多数天然冰川湖则处在多水地区,且纬度相对要高。已研究的大多数湖泊是每年发生二次混合,而大多数水库则是多次混合,或者当深度足够分层的时候是单次混合。在另一方面,处于低纬度的水库(或者湖泊)通常经历了较长时间的生长季节,较长的分层期,水温较高,缺乏冰层的覆盖,并且由于水库流域的森林覆盖率低,比起每年二次混合的湖泊,往往会接纳更多的无机颗粒物质。表 29-1 和表 29-2 给出了二者其他方面的差别。

**表 29-1 美国的湖泊和水库所选变量的几何平均值 (geometric means) 以及半干旱地区水库的中位值 (ND = 没有数据。)**

变量	自然湖泊 ( $n = 309$ )	水库 ( $n = 107$ )	世界水库 ( $n = 113$ )
流域面积/ $\text{km}^2$	222	3 228	1 281
湖泊面积/ $\text{km}^2$	6	34	13
流域面积: 湖泊面积	33	93	166

<sup>①</sup> 水库和人工湖泊这两个术语在本章相互替代,但它们并不是同义词。这是因为相当多的天然湖泊的出流受到大坝的调节影响。从技术上这些湖泊也可以称为水库。

续表

变量	自然湖泊( $n = 309$ )	水库( $n = 107$ )	世界水库( $n = 113$ )
最大深度/m	11	20	30
平均深度/m	4	7	10
水力滞留时间/a	0.7	4	1.1
水负荷/( $m \cdot a^{-1}$ )	6.5	19	ND
磷负荷/( $g \cdot m^{-2} \cdot a^{-1}$ )	0.9	1.7	1.3
氮负荷/( $g \cdot m^{-2} \cdot a^{-1}$ )	18	28	ND

表 29-2 干流水库与分层湖泊的特点比较

特点	湖泊	水库
<b>数量(绝对)差别</b>		
来源	天然	人工
地质年代	年代久远(更新世)	大多年轻(<60年)
老化速率	慢	快速(最初的几年)
形成条件	洼地	河流河谷
形状	常规	树枝状
岸线发展系数	低	高
最大深度	靠近中心	极端(在大坝处)
底部沉积物	内源	外源
经度梯度	受风影响	受水流影响
水流输出	表层水流	深层水流
<b>性质(相对)差别</b>		
流域面积: 湖泊面积	低	高
水力滞留时间	长	短
与流域的耦合程度	小	大
形态	U型	V型
水位变化	低	高
水动力	较常规	高度变化
影响产生原因	自然影响	人工影响
水质管理系统	少见	常见

研究比较充分的二次混合湖泊大多数是源头湖泊, 它们一般具有椭圆形外观(见第7章), 最大深度远离出水口。入湖河流在天然湖泊周边的均匀分布导致了外来水与湖水的快速混合(图29-2)。相反, 人工湖(水库)通常位于河谷中, 呈长形。因为众多的小型支流注入水库, 使得水库呈树枝状(图29-3; 见7.5节)。

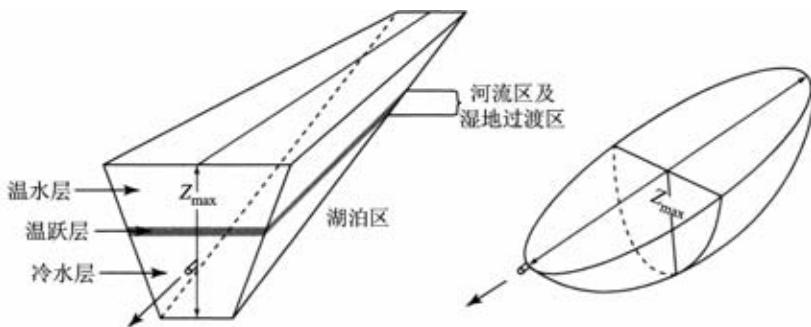


图 29-2 一座位于河谷的干流水库的形状、分区和分层的简化图,及一座典型的冰川湖泊的形状。水库是否分层取决于气候和换水率,换水率很高的水库(水力滞留时间小于 10 d)因水流过急而不能形成分层(Straškraba 等,1993)

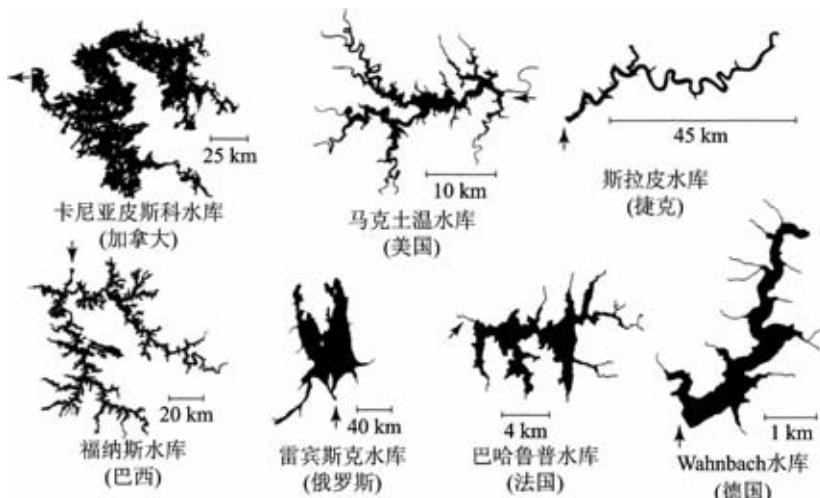


图 29-3 水库的表层形状[位于低海拔平原河流中的水库呈高度树突状。卡尼亚皮斯科水库(加拿大魁北克省)的出水口没有大坝,除此之外,图中箭头表示大坝的位置。坡度小的河流系统(前寒武纪)被拦截,形成了一个大面积的浅水树枝状水库,水库里有许多小岛屿,箭头指示了水流到水库下游的方向。]

为了最大地发挥它们的蓄水潜能,水库通常建在流域的下游。在美国,水库的集水面积比(CA: LA)比湖泊整整大 3 倍,并且在其他方面也有很大的不同(表 29-1;见 9.5 节)。在全球半干旱地区,水库集水面积比更大。大的集水区导致了较高的入库流量、颗粒物(图 9-3,表 29-1,表 29-2)、营养盐和污染物(图 28-14)的入库。

绝大多数入库水量从一个主干河流末端进入水库,主干河流的存在和多数高流量的发电水库的长条形状,说明存在单向的连续水团,称为嵌入水流(plug flow)。而与水库相反,河水入湖后快速混合,类似于一个瞬时混合反应器(instantaneously mixed reactor)<sup>①</sup>。

<sup>①</sup> 我们常常假定大多数天然湖泊的水层混合比较迅速,这可能是湖沼学家极少关注水运动和湖水水平流动的重要原因。

水库的树枝形状或其他不规则的形状,意味着水库的库湾与中心库区在水流、水深、负荷、浊度和生物区系上存在一定的差别。

自然湖泊与人工湖泊的属性高度相似,但二者的差别也十分突出(表29-2)。水库总是在靠近大坝的位置具有稳定的分层,而大多数湖泊在任意位置都可能有1个或多个“深洞”。另一个更重要的差别是大多数水电水库具有亚表层流,这种水流影响了水温、溶氧梯度并且增加了营养盐的滞留时间(表29-2,表9-7)。

与天然湖泊相比,在热分层时期,下层水的输出导致了水库下层水滞留时间减少,其溶解氧浓度下降的时间减少了。比起天然湖泊或者释放表层水的水库,温带地区的水电水库中的底层沉积物含有更多的溶解氧。在高纬度地区,释放冷且营养盐含量低的下层水,会影响下游水库的温度与营养盐水平。在夏天,低温、高密度的水流入库后随即下沉,一直到达温跃层或底层密度相同的水层,然后这股水流作为侵入流(*intrusion flow*)继续水平流动。结果在浅水水库,侵入流所携带的营养盐不能被真光层的浮游植物所利用,减少了浮游植物的生产力。

### 受调节的河流

被上游大坝所影响的河流称作受调节河流(*regulated river*),它显示了大坝对于下游(上千km距离)的影响(Hart和Allanson,1984)。大坝的表层出水或深层出水对河流都有很大的影响。表层出水可以使得大量的浮游动植物、营养盐和大量漂浮植物(在低纬度)随着水流进入到河流中。如果深层出水的话,这些物质就会少很多。当水库底层水在厌氧条件下含有有毒的H<sub>2</sub>S时,水库对于下游的生物群落有更明显的负面影响。

特别是在半干旱地区,由于蓄积大量来自植被覆盖率低的流域的沉积物,水库里的水会出现短周期性或者永久性的混浊。水库里高浓度的沉积物对底栖生物有负面影响,不仅会降低它们依赖视觉的捕食效率,还会导致幼鱼的死亡(Ward和Davies,1984)。出库水流的沉积物负荷大大降低(表9-4),因此,降低了出库水的密度,从而增加了水流的侵蚀能力。侵蚀的增加与河流流态的改变导致了原有河道的退化,影响了沉积物的性质,使得地下水水位降低,影响了鱼类的摄食与繁殖生境,对整条河流的生物群落也有影响(图29-4)。

在水库内滞留的沉积物与所携带的营养盐使河流丧失了“施肥”的功能,河流“施肥”对季节性淹水的湿地、下游农作区和河口是至关重要的。如果不给鱼类一个适合的上下游通道,那么大坝是洄游鱼类(如鲑鱼、鲟鱼)不可逾越的障碍。北美西北地区的鲑鱼和里海(见5.8节)的鲟鱼的减少直接或者间接与大坝建设有关。至于水库对脊椎动物和无脊椎动物在沉积物表面迁移的影响,我们知道的就更少了。

### 流量调节和分流

大坝对河流调节的幅度受河流本身特性和一般性质的影响(图29-5)。人们对于发电和灌溉水库的管理,造成了水流的短期波动,但是减少了季节波动。例如,阿斯旺大坝修建后,尼罗河最大和最小流量的比率从12:1减少到2:1。控制洪水的大坝也减少了水

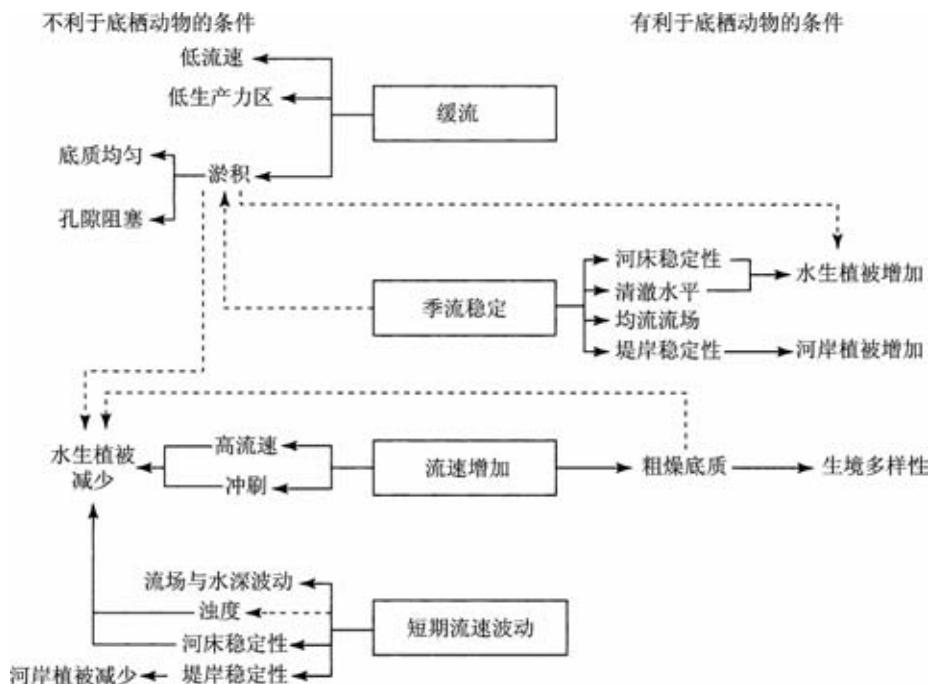


图 29-4 大坝下游的各种河流模式对于生态因子的潜在影响(这些生态因子对于河流的底栖生物有重要影响。虚线表示二者的相关性低。)(Wad 和 Davies, 1984)

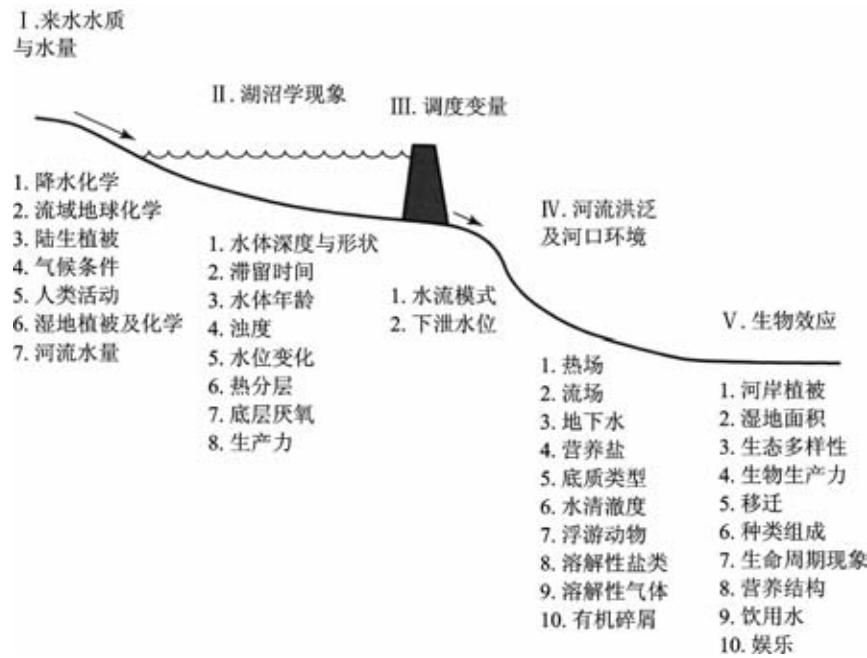


图 29-5 影响大坝下游环境的主要因素和现象及其对生物群落的综合作用(随着水滞留时间和生产力的增加,水库对下游的影响增加了。换水率高的水库对下游的影响最小。)(Ward 和 Davies, 1984)

流的季节性波动。季节性流量波动的降低,减少了因为季节性洪水而淹没的湿地的规模,并将造成下游底栖藻类和大型水生植物的过度生长,因此影响水的流动。流量的减少为无脊椎种类(包括携带疟疾的蚊子)的生长提供了良好条件,它们一般适合在季节性稳定水流的情况下生长<sup>①</sup>(图 29-5)。在景观起伏适当的地区,水库上游的末端往往会造成湿地。

比起流量调节对河流及其生物群落的影响,更大的威胁来源于截流。截流主要用于农业生产,是指建坝将水流截流在水库里,这种情况在干旱或者半干旱区域的河流更为突出。世界上最主要的河流有 37 条流经年降雨量小于 500 mm 的旱地。这些河流的年内流量变化很大,流量的平均变异系数为 99%,而世界另外一些地区则为 20%~30% (Kingsford, 2000)。截流已经造成两条进入咸海的主要河流干涸。另一个例子发生在中国的黄河下游地区,在 1996 年之前的 10 年,平均每年断流 70 d,尤其在 1995 年断流了 122 d。印度恒河的截流导致在一年中的大部分时间,恒河的水都到不了海洋。在美国,截流导致了加利福尼亚中心河谷 90% 的湿地遭到破坏。在澳大利亚的墨累-达令河流域,80% 的水流被截流,导致了大规模的湿地和洪泛平原的消失。因截流导致下游湿地的急剧减少不仅对水生生境、水鸟造成了巨大影响,更影响到依靠湿地支持的农业、牲畜的放养、渔业等人类活动,以及水的贮藏与净化。

### 水库:年龄和生物群落

水库和湖泊最大的不同在于水库(图 29-1)通常很年轻(小于 60 年),而湖沼学家深入研究过的高纬度湖泊是由冰川活动形成于 10 000 年前。水库中通常有很多种类的鱼类,它们来自上游河流和湖泊。这往往使得鱼类得以在静水中保存,虽然河岸带的鱼类通常不能很好地适应静水环境。与之相反的是,天然湖泊里的生物作用是经过了数千万年的演化而形成的(Maclean 和 Magnuson, 1977)。

美国水库中最常见的垂钓鱼的运动种类为大口鲈鱼(*Micropterus salmoides*)、刺盖太阳鱼(*Pomoxis* spp.)和鮈鱼(*Ictalurus punctatus*)。然而,在水库里最普遍的引进种类为砂囊鮈(*Dorosoma cepedianum*),这种鱼占了鱼类总生物量的 30% (Stein 等, 1995)。成年砂囊鮈是植物食性和浮游动物食性的,在游动中依靠鳃的滤水作用获取食物。砂囊鮈幼仔(YOY 或 0+ 龄期)通过减少其他种类鱼的生长率、存活率和丰度来影响鱼类的群落结构。当砂囊鮈幼仔体长大于 3 mm 时,它们就开始摄食原生动物、轮虫和底栖碎屑(包括细菌和藻类)。砂囊鮈和其他杂食性鱼类通过影响食浮游动物鱼类的丰度,间接地影响肉食性鱼类。这是因为在水很混浊的情况下,依靠视觉捕食的食浮游动物鱼类捕食受阻(O'Brian, 1990)。砂囊鮈和其他依靠沉积的食物作为来源的种类在植物营养盐循环中起到重要作用(Vanni, 1996)。

北方温带地区的食物链模式是基于食鱼性种类对食浮游生物鱼类的下行控制,而这种

<sup>①</sup> “在低纬度地区,水流的季节稳定性对多世代(每年繁育多个后代)生物种类,如蚋科(Simuliidae)的黑蝇,比捕食它们的无脊椎动物来说更为有利。水流的季节稳定性导致这些有害种类种群暴发。降低水流的变化有助于底栖藻类和大型植物生长,从而有利于蚊子的繁育。这两个例子支持周期性水流中断造成对河流系统的适度干扰可以防止任何生物成为单一优势物种的观点”(Ward 和 Davis, 1984)。

机制难以解释低纬度湖泊和水库中优势鱼类砂囊鲷或者其他种类的效应。杂食性鱼类,如罗非鱼,对浮游植物、浮游动物和有机碎屑的摄食能力对食物链结构和能流产生影响,但这种影响尚待进一步研究,它与被广泛研究的高纬度模式有很大差异(Vanni,1996)。

### 29.3 河流—湖泊—水库的连续性

人工湖与天然湖都分布存在一些属性的梯度,如气候、地质条件、形态学、换水率、化学环境与生物学,这些属性梯度的存在使我们很难将湖泊与水库截然区分开来。最确切的水库连续属性是从水滞留时间或稀释率方面定义,将水库看成介于湖泊与河流的一种过渡水体类型。

大型水库有3种基本类型(图29-6)。干流型水库(mainstream reservoirs)或者河流型水库(run-of-the-river reservoirs)最接近河流(水滞留时间为数天到数周),这类水库往往用来发电。如果水滞留时间小于10 d,干流水库的温度不会分层(Straškraba等,1993),由于没有季节性的水位变化,位于水库内和下游河流带的生物群落受到干流水库的影响最小。3种类型的水库中,湖沼学家对干流型水库的关注最少,但对干流水库中的梯级水库或串联水库的研究相对较多(如伏尔加河、科罗拉多河和伏尔塔瓦河)。修建在小型河流上的支流蓄水水库(tributary reservoirs)具有很长的水滞留时间(通常为1个月到1年或更长),在地形地貌与气候条件合适时,这种支流蓄水型水库水温分层的可能性最大。这类水库为表层出水,建造目的是防洪和灌溉。当出水远远大于进水时,它们就会出现周期性的水位和水量下降(见29.6节)。然而,水量下降不仅仅限于水库。干旱与半干旱区域的湖泊在少雨季节,由于蒸发作用会出现十分明显的水量自然减少。支流蓄水水库是最常见的水库类型,倍受湖沼学家关注,主要原因是它们在水滞留时间上与天然湖泊高度相似。干流蓄水型水库(mainstream storage reservoirs)在3类水库中处于中间位置(滞留时间为几个月),在大的降雨时期具有河流的特征,其他时期则多具湖泊特征。

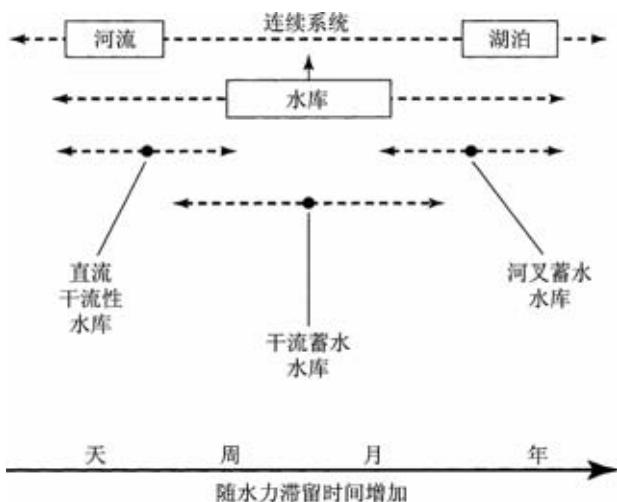


图29-6 水库在水生态的连续系统中处于河流与湖泊的中间位置,河岸影响和水滞留时间的程度决定了在河流——湖泊连续型中的水库类型(如干流水库、干流蓄水水库、支流蓄水水库)

水库与换水快的湖泊在水滞留时间上相似,都对径流与蒸发的季节变化十分敏感。这种影响在降雨少的地区异常明显,典型的例子是麦基尔威恩水库(津巴布韦)。它的平均水力滞留时间为1年,在极度干旱时,最大的理论水滞留时间为12年,而在多雨年份,滞留时间降到了4个月(Ballinger和Thornton,1982)

## 29.4 水滞留时间与浮游生物生长率

在换水率高的水库和湖泊里,浮游生物的多样性会降低,这种情况发生在换水率超过特定温度下生长最快的浮游生物的生长率时,浮游生物还未更新换代就被冲走了。最先受到影响的是淡水中的桡足类,它的发育时间(从卵到卵)在最理想条件下水温10℃的时候需要30d,20℃的时候需要14d,25℃的时候需要7.5d。在同样的温度下,它们的发育时间比枝角类长大约25%。而更小的轮虫则是在理想条件下25℃的时候需要1.5d(Allan,1976)。这就解释了为什么在换水率大的湖泊或者水库,轮虫和生长快的原生动物占绝对优势(Basu和Pick,1996)。在生长快的浮游植物与原生动物受水流影响之前,随着换水率的增加,不同类群浮游动物的流失会对浮游植物与原生动物的群落结构产生影响。如果大型浮游动物出现在换水率高的水体中,它们一定是来自具有比较长滞留时间的库湾或者湿地(图29-7)。当换水率降低,大型浮游动物中最先出现的是个体小、繁殖速率高、行孤雌生殖的枝角类(见23.3节)。例如,当水滞留时间超过18d,一种大型溞属(*Daphnia*)种类出现在苏格兰的一个冷水湖里。当水滞留时间超过4个星期,个体的数量

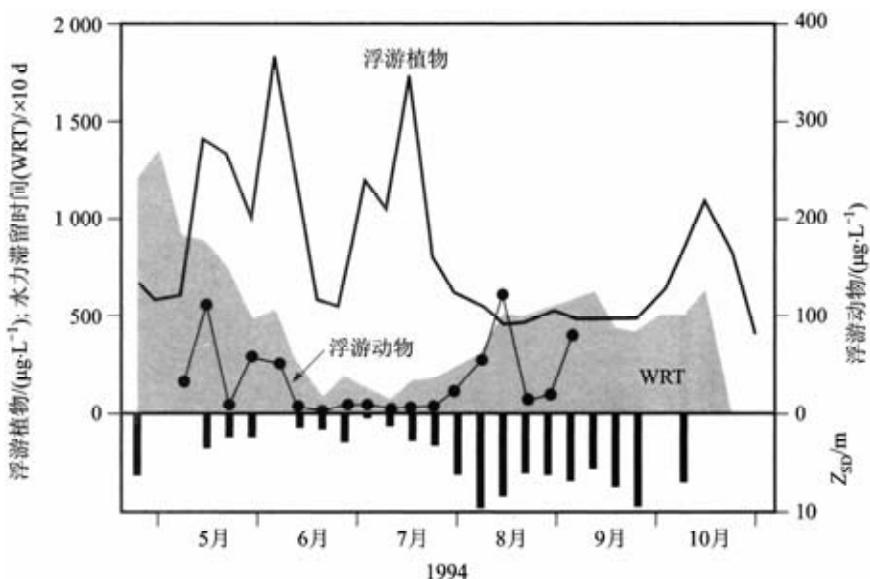


图29-7 多次混合的格伦牟水库(阿尔伯塔,加拿大; $LA = 4.6 \text{ km}^2$ ,  $Z = 6.1 \text{ m}$ )的水滞留时间、浮游植物和大型浮游动物的生物量以及透明度的季节性变化[由图可知,在高换水率时,大型浮游动物的丰度比较低;而在高辐射率、低混浊度( $Z_{eu} > Z_{mix}$ )和最快放水率(最大的营养负荷和浮游生物流失率)时期,浮游植物生物量达到最大。](引自Watson等,1996)

与换水率之间就没有明显的关系了(Brook 和 Woodward, 1956), 这表明在更长的时间尺度上, 除了水滞留时间之外其他影响因素的重要性(捕食或者食物)。

浮游植物的流失出现于混浊的、深层混合的或冷水水库的短水滞留时期, 在这里夏季光合作用的条件远不如混浊度较低的浅水系统。随着系统中或系统之间的水滞留时间降低, 换水率逐渐地超过多数种类的生长率, 生物群落最后仅限于少数潜在生长率高的种类。根据对几座温带湖泊和水库的深入研究, 人们发现在适合的光照、温度、营养条件下, 能够使大部分生物种类达到生物量最大的水滞留时间大约为 7 d(图 29-7; Straškraba 和 Javornický, 1973; Soballe 和 Threlkeld)。

野外观测表明, 在温带水体中, 当水滞留时间降到 60 ~ 100 d 或更短时, 换水率对夏季浮游植物群落组成的影响十分明显(Kimmel 等, 1990)。如此宽的滞留时间变化范围是由于辐照度、水体透明度、混合层的厚度以及  $Z_{eu} > Z_{mix}$  的比值(见 10.11 节)和温度等的不同造成的, 这些因素共同作用决定了浮游植物(见 21.11 节)的倍增时间, 进而直接或间接地影响它们捕食者的生长。

## 29.5 水库的分区:一个概念视图

干流水库呈现突出的纵向分布, 这一点有别于典型的浅水和受风影响的蓄水水库, 后者通常不占据主要的河谷流域。在具有长滞留时间但完全混合的支流蓄水水库, 也很少出现与干流水库相同的分区。没有分支(库湾)的干流型水库在流速、滞留时间、悬浮物、光照、营养盐和生物生产力等方面具有明显的纵向梯度分布。理想化的干流型水库分为 3 个区域:河流区、过渡区和湖泊区(图 29-8)。

### 河流区

在半干旱地区和作物生长区, 由于土壤缺少植被覆盖, 陆地上大量的无机物被冲刷进入河道, 使得浅水河流区在流量高的时期尤其混浊。河流区的无机营养水平最高, 但在流量高的时期光照条件却不适宜, 导致其生产力低。河流区的底栖动物和鱼类群落与入库河流类似。

### 过渡区

在较深的过渡区, 沉积物的对流(输送)强度下降, 透明度和水滞留时间增加, 从而加速颗粒的沉降。由于良好的光线和充分的营养盐条件, 使近表层水体中浮游植物初级生产力增加, 在混浊度下降期间水柱的总初级生产力( $\text{mg} \cdot \text{C} \cdot \text{m}^2 \cdot \text{d}^{-1}$ )达到最大。如果水深、水温和水滞留时间合适, 形成水温分层。分层后, 过渡区的湖下层会变薄并容易缺氧, 这是由于在有机质丰富的集水区里, 水库过渡区常常出现大量有机物的沉降(Cole 和 Hannan, 1990)。如果换水率不超过生长率, 且捕食性鱼类适度, 那么在生长季节里, 较高的初级生产力可以维持大型滤食性浮游动物(Pirozhnikov, 1961)。

在很混浊的水库中, 无机物颗粒对大型浮游动物的摄食活动有负面影响, 浮游动物应对这种影响的相对和绝对能力, 决定了它们的种类组成(图 29-9), 但与此同时, 依靠视



图 29-8 一个理想的温带水库中环境因子的纵向分布(这些环境因子控制光、营养盐、藻类生产力、现有作物、有机物的供应和营养状态。在枯水期,过渡区呈湖泊性质,河流区呈湿地性质;在换水率很高的时期,过渡区的性质更接近于大坝。)(Kimmel 和 Groeger, 1984)

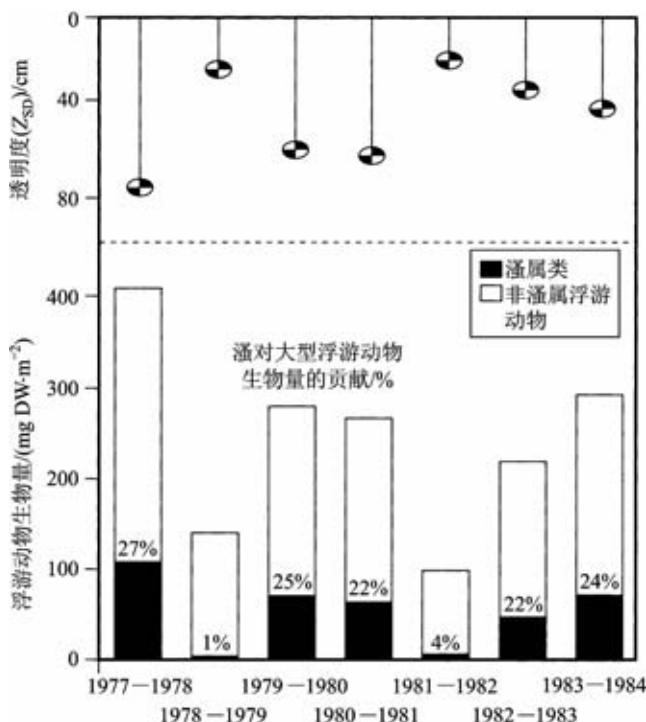


图 29-9 1977—1984 勒鲁水库由大型浮游动物的平均生物量和加权平均透明度之间的相关关系(可以看出在高无机混浊度环境下,水蚤类的滤食效率明显降低。)(Hart, 1988)

觉捕食的鱼类对大型浮游动物造成的损失率也在减少(Marzolf, 1990)。南非学者在无机浊度与生物之间的联系,包括悬浮颗粒对大型无脊椎动物和鱼类产量的负面影响方面,已经进行了大量杰出的研究(Allanson等, 1990)。

### 湖泊区

干流水库湖泊区的透明度通常比过渡区要高,但营养盐浓度要低。尽管如此,其水柱浮游植物初级生产力( $\text{mg C} \cdot \text{m}^2 \cdot \text{d}^{-1}$ )可能与营养丰富但混浊的过渡区相同,甚至更高,这归因于有利的光照分布和 $Z_{eu}/Z_{mix}$ 的比值(式10-6;图10-12)。高透明度有利于大型沉水植物的生长(图24-5)。就像在天然湖泊中,水面下的坡度较低,大型植物比较丰富(图24-6),尤其是在受水位影响不大的湖泊区。

以上提出的概念模型并不适合多数温带和低纬度的支流型水库。在这些水体中,高径流期间河流区有相对较高的换水率,或者紧随高浊度时期之后,出现一个较长时间的低流量和高表面蒸发阶段。于是,浅水的河流区逐渐变成由大型水生植物及其相应的生物群为主的湿地(见第24章和第25章),这时水库不具有明显的过渡区。换水率低的支流型水库与同一个区域的相似深度的天然湖泊并没有明显区别。树枝状的支流水库也并不符合水库分区概念模型,这类水库的库湾在混浊度、分层、水力滞留时间以及生物群落在各个分支流域中均有很大差别。

## 29.6 水位下降

发电或灌溉的需水量的变化具有季节性,从而导致蓄水水库每年经历完整的水位下降期。对于浅水或坡度小的水库,其水位通常会下降2~4 m,甚至更多,这使得水库中大部分的库底裸露。

不管是天然水体还是人工水体,水位的波动都会对大型水生植物、底栖生物群落、鱼类的出现或者消失造成很大的影响。事实上,研究人员曾经在美国的浅水湖泊里运用降低水位来控制沿岸区水生植物(见第24章; Cooke等, 1993)。在温带地区,前一年水位降低持续的时间决定了下一年大型水生植物的生物量和种类组成。这些大型水生植物种类在水位降低期间可以保存它们的根,休眠的种子也可以发芽(Nilsson和Keddy, 1988)。

鱼类丰度和年龄的分布随其产卵水位而变化,因为水库中的许多鱼类利用有植被覆盖的沿岸带来产卵、摄食、隐藏幼鱼(YOY)。在高纬度的水库,水位下降50 cm就会引起大量卵的干燥和脱水,对每年只有1次产卵期的鱼类而言,这就会清除整个年龄段的种群(Duncan和Kubečka, 1995)。美国水库采用在夏季降低水位来增加大口鲈鱼的生长,当水位下降,作为食物的幼鱼被迫远离开大型捕食性鱼类,不敢进入密度很高的大型水生植物区(O'Brian, 1990)。

低纬度地区浅水水库的人为水位降低,以及天然湖泊和湿地中高蒸腾蒸发率导致水位下降,都将出现较大面积的库底暴露干燥,从而出现有机物氧化和反硝化作用、高纬度地区的结冰和陆生植物的生长。这些现象会影响沉积物的化学性质( $E_h$ , pH、营养盐)、生物群落组成及其活动。大量的无机营养盐、有机物和土壤里的细菌在洪水泛滥之后再次释放,而

这一时期,流域输入水体中的无机营养盐和有机物也都达到了最大值。在苏联的浅水水库,细菌的丰度与水位成正相关支持了上述结论(Kuznetsov 等,1966;Procházková 等,1973)。

## 29.7 水库的老化和营养水平上涌

新建水库库底的土壤第一次被淹之后,其湖沼学性质会很快发生改变,改变的程度与土地的功能类型、水位、土地与植被性质和气候条件有关。水库的老化既与陆地植被和被淹没土壤有机物的氧化相联系,也与水库从河流状态转化为湖泊状态期间生物类群的组成和丰度的变化有关。

在水库蓄水的头几年里,水体中营养盐浓度和各个营养级的生产力都有提高,这一现象就是所谓的营养水平上涌(trophic upsurge)。随后的营养(水平)下降(trophic depression)会持续几年至几十年,但会产生较为稳定的生物群落和生产力,表明低营养盐供应速率和新的竞争与捕食关系的形成。

1952—1955,克里萨瓦水库(捷克)开始蓄水后的营养水平上涌现象得到了详细的记录(图 29-10)。1993 年,Straškraba 等人基于下行效应的重要性重新解释了这种演化模式。他们认为食浮游动物的鱼类对于大型浮游动物的捕食压力低,导致在水库开始蓄水初期大型浮游动物的丰度很高,而大型浮游动物又可以对浮游植物施加牧食压力,从而推迟了浮游植物的上涌。在这一期间,水库中鱼类群落由适应能力较差的沿岸带鱼类组成,鱼产量及其对大型水生动物的捕食压力很低,这种情况一直持续到湖泊性种类的入侵或引进。在斯里兰卡的水库中,低的鱼类生产力一直持续到适应性很好的罗非鱼种类的引入(见 26.6 节)。

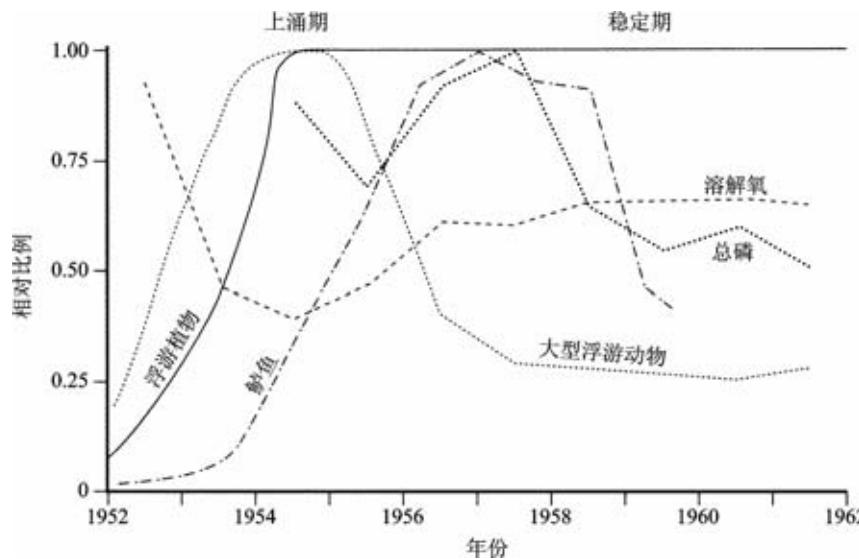


图 29-10 1958 年后,克里萨瓦水库(捷克)的老化过程[达到最大值的是:湖下层溶解氧( $13 \text{ mg/L}$ )、总磷( $25 \mu\text{g/L}$ )、浮游植物( $10^6 \text{ 个/L}$ )、浮游动物( $7 \text{ kg N/ha}$ )和鲈鱼( $15000 \text{ 条/ha}$ )。](改自 Straškraba 等,1993)

### 热带水库

在克里萨瓦水库营养水平上涌期间,其湖下层的溶解氧仅下降到最低值 $5\text{ mg/L}$ ,下降的原因是建库之前对树木、灌木的清理和普遍的低水温。这种湖下层较高的溶解氧与多数水库库底完全厌氧和经常的湖上层缺氧形成了对比。一般在湿润并且植被良好的热带地区,新建水库后,那里的森林植被仍是以保留(图 29-11; Tundisi 等,1993)。

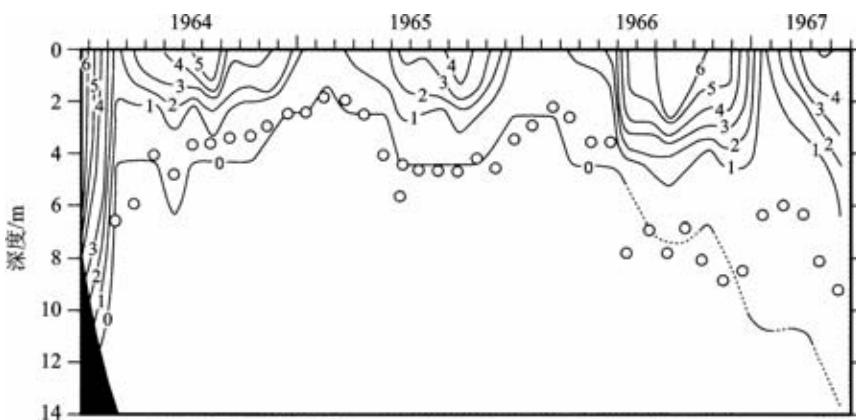


图 29-11 苏里南的布罗科蓬多水库( $\text{LA} = 362 \text{ km}^2, Z_{\max} = 19 \text{ m}$ ) [ 经过第 1 个 4 年蓄水之后,其溶解氧( $\text{mg/L}$ )在深度和时间上的分布。空心圆表示真光层的深度,真光层的深度大致与溶解氧为 0 的等高线吻合。 ]

热带水库普遍缺氧是由于大多数水库呈树枝状的特性所决定的(图 29-3),原因与风浪的减少、高温时氧的低溶解度还有代表热带大陆区域性的相对较低的风速等有关(图 5-11)。溶解氧的跃式变化开始于库底的表层,光合硫氧化细菌利用表层下高浓度的还原性硫形成一个薄层。这些还原性硫是植被中富硫的氨基酸被细菌分解后释放出来的(见 22.10 节; Dumester 等,1999)。甚至是在被淹没的植被分解之后,湖下层依然缺氧。

大多数年代久远、被严重侵蚀的热带水库通常相对较浅,因此是多次混合的(见 11.2 节)。周期性的混合导致大量鱼类的死亡,这是由于下层缺氧水的混合,同时底层中大量的有毒气体  $\text{H}_2\text{S}$  和还原性化合物进入到水表层。通过周期性的混合,输出水缺氧对于河流生物群落的组成与系统功能有长时间的副作用。许多新建的热带或者亚热带水库不仅大范围缺氧,并且部分或者全部覆盖了大型漂浮性植物(如水葫芦 *Eichhornia crassipes* 和假水蕨面具 *Salvinia molesta*, 图 24-1),这些植物可以从营养水平上涌中获得营养盐。

### 伏尔加河水库

对伏尔加河(俄罗斯)上的大型浅水( $Z = 7 \text{ m}$ )梯级水库的研究比较充分。这些水库蓄水之后,并没有出现在热带水库湖下层所普遍观察到的厌氧条件,原因是只有部分的陆地有机物被淹没,加上高换水率和低水温等因素。这些水库沉积物的氧化充足,在水体营

养水平上涌期间,大型底栖生物群落形成并促进了鱼类的生产力。在大范围的湖沼区和湿地区,浅水水库形成了大面积的大型水生植物带(Straškraba 等,1993)。但并没有出现类似于低纬度水库中普遍出现的水葫芦等漂浮植物的大规模发展。然而,肥沃的土壤和农业活动导致了上涌期结束后富营养状态的维持(夏天  $Z_{sd} = -1.5$  m, TN =  $-1$  mg/L, TP =  $-110$   $\mu$ g/L; Litvinov 和 Mineeva, 1994)。

### 北方水库

最后讨论一组大型浅水型发电水库,这些水库是近几年在美国北方和欧亚大陆森林覆盖率低、地势比较平缓的地方建造起来的。那里土壤贫瘠,所以营养水平上涌的空间也小。在夏天,由于风力作用的混合,水体中往往溶解氧含量高,但是冬天浅水地区冰层下会出现缺氧现象,浅水地区往往是有机质丰富的沼泽。

水库刚建成的十几年间,水库中寿命较长的捕食性鱼类体内汞的浓度大大增加,如鳟鱼、狗鱼等,这是一种出乎意料的负面影响。根据对一些加拿大水库的研究表明,在水库被淹没7年之后,捕食性鱼类的主要食物的体内汞含量降低了,包括水库中寿命较短的食浮游动物鱼类——白鱼。鱼体汞含量的降低是由于土壤中汞含量的耗竭,但肉食性鱼类的体内汞含量依然没有改变(Chevalier 等,1997)。即便如此,天然湖泊中沉积物里汞含量的增高表明了水体中汞含量依然很高,尤其能在食物链顶端的肉食性鱼类的体内积累。

## 29.8 大型水库及其影响

修建大型水库获得的利益十分模糊,尤其是在世界上低纬度经济不发达的地区。水库的发电效益十分明显,但主要是面向水库下游的城市和地区。世界上的灌溉耕地面积为2.71亿ha,其中30%~40%都依靠水库供水,这部分地区对于世界粮食供应起到了重要作用,但取得这些利益是以大量的环境成本为代价的,而且这部分环境成本没有引起必要的关注。这些成本包括河流的破坏,由于季节性洪水消失所带来的大量湿地和生物群落的消失,由于灌溉截流造成下游河道干涸。更为严重的是,大坝干扰了鱼类和其他水中脊椎动物正常的迁徙,导致了生物多样性的降低,同时,入海的水流量减少导致了海岸带湿地的盐渍化。其他受损失群体是政治上弱势的土著居民——他们依靠河流、湿地和淹没的土地来打猎、捕鱼、农耕、养殖牲畜和延续文化。因此,为大项目提供基金之前,环境影响评价是必不可少的,湖沼学家及咨询公司可以提供相关技术支持。水库建设有两个难点:建设水库的成本投资者和受益对象通常是不同的,他们很少关注对环境成本的投入(Straškraba 等,1993)。在国际社会的压力下,建造更多库容较小、影响较小的水库是否就能与环境或社会影响达到平衡?这取决于各地具体情况。不管怎样,我们非常需要一批拥有环境前瞻性的湖沼学家,并期待他们能与经济学家、社会学家还有工程师合作,讨论这些环境影响。

## 本章重点

- 水库修建具有不同的目的：灌溉、发电、防洪、对城市的供水、改善航运条件、水产养殖、鱼类或者其中几项的结合。
- 在降雨量低（或者径流量低）的地区，许多拦截河流建造的小型水库是用于灌溉的。
- 水库与天然湖泊具有很多共同点，不过在相同大小与相同地区范围内，水库比天然湖泊的流域要大。另外，水库是新建成的水体，最深的地方位于大坝处。
- 大型的水库有3种类型。干流型水库或者河流型水库主要用于发电，其特点包括快速的换水率、很少或者没有分层、没有水位降低、在深层出水，通常与河流很相似。支流水库通常建在较小的河流中，通常用来灌溉或者防洪。它们的换水率很低，如果深度足够则水体会出现分层，周期性的水位降低，通常是表层排水，大部分的特性与湖泊接近。干流蓄水水库处于中间位置，在降雨量高的时期有河流特征，而在降雨量低的时期则具有湖泊特征。
- ▲干流蓄水水库建于规则的河谷中，在水流速度、水滞留时间、固体悬浮物、混合层的光照和生物群落方面具有明显的经度分布特征。
- ▲当换水率大于浮游生物的倍增速率，会导致浮游生物的损失。
- 大坝建成后，筑坝形成的静水系统严重影响了河流及其生物群落，大坝还阻碍了生物的迁移。并且，径流时间、流量的改变和坝前的沉积物积累影响到下游的生物群落。然而，对于河流及其生物群落以及下游湿地的最严重的威胁来自用于灌溉的大规模引水截流，这会导致下游河流的断流、下游湿地与生物群落的消失。
- ▲水库水位降低而导致的沿岸区的暴露与干燥对于生物群落有显著影响。
- 修建大型水库是一把双刃剑，尤其是在世界上经济不发达的地区。

（韩博平，邓琛，李慧明译）

# 附录 1 国际标准化组织(ISO, 日内瓦)国家代码

代码	国家	代码	国家
AF	Afghanistan	KZ	Kazakhstan
AI	Albania	LA	Laos
AM	Armenia	LK	Sri Lanka
AO	Angola	LT	Lithuania
AQ	Antarctica	LU	Luxembourg
AR	Argentina	MD	Moldova
AT	Austria	MG	Madagascar
AU	Australia	ML	Mali
AZ	Azerbaijan	MM	Myanmar( Burma )
BD	Bangladesh	MN	Mongolia
BE	Belgium	MW	Malawi
BF	Burkina Faso	MX	Mexico
BG	Bulgaria	MY	Malaysia
BI	Burundi	MZ	Mozambique
BJ	Benin	NA	Namibia
BO	Bolivia	NE	Niger
BR	Brazil	NG	Nigeria
BT	Bhutan	NI	Nicaragua
BW	Botswana	NL	Netherlands
BY	Belarus	NO	Norway
CA	Canada	NP	Nepal
CH	Switzerland	NZ	New Zealand
CI	Cote d'Ivoire	PA	Panama
CL	Chile	PE	Peru

续表

代码	国家	代码	国家		
CM	Cameroon	喀麦隆	PH	Philippines	菲律宾
CN	China	中国	PK	Pakistan	巴基斯坦
CO	Colombia	哥伦比亚	PL	Poland	波兰
CU	Cuba	古巴	PY	Paraguay	巴拉圭
CZ	Czech Republic	捷克	RO	Romania	罗马尼亚
DE	Germany	德国	RU	Russian Federation	俄罗斯联邦
DK	Denmark	丹麦	RW	Rwanda	卢旺达
EG	Egypt	埃及	SD	Sudan	苏丹
ES	Spain	西班牙	SK	Slovakia	斯洛伐克
ET	Ethiopia	埃塞俄比亚	SL	Sierra Leone	塞拉利昂
FI	Finland	芬兰	SR	Suriname	苏里南
FR	France	法国	SE	Sweden	瑞典
GB	United Kingdom	英国	SY	Syrian Arab Republic	叙利亚
GH	Ghana	加纳	TD	Chad	乍得
GN	Guinea	几内亚	Th	Thailand	泰国
GT	Guatemala	危地马拉	TJ	Tajikistan	塔吉克斯坦
HF(CN)	Hong Kong	香港	TM	Turkmenistan	土库曼斯坦
HR	Croatia	克罗地亚	TR	Turkey	土耳其
HU	Hungary	匈牙利	TZ	Tanzania	坦桑尼亚
ID	Indonesia	印度尼西亚	UA	Ukraine	乌克兰
IE	Ireland	爱尔兰	UG	Uganda	乌干达
IL	Israel	以色列	US	United States	美国
IN	India	印度	UY	Uruguay	乌拉圭
IQ	Iraq	伊拉克	UZ	Uzbekistan	乌兹别克斯坦
IR	Iran	伊朗	VE	Venezuela	委内瑞拉
IS	Iceland	冰岛	VN	Vietnam	越南
IT	Italy	意大利	YU	Yugoslavia	南斯拉夫
JO	Jordan	约旦	ZA	South Africa	南非
JP	Japan	日本	ZM	Zambia	赞比亚
KE	Kenya	肯尼亚	ZR	Zaire	扎伊尔
KG	Kyrgyzstan	吉尔吉斯斯坦	ZW	Zimbabwe	津巴布韦
KH	Cambodia	柬埔寨			

资料来源：国际航空运输协会航空编码目录，IATA Airline Coding Directory。

## 附录 2 正文中所提及的特定元素和化合物的换算系数

( 毫克/升  $\times F_1$  = 毫克当量/升 ,  
毫克/升  $\times F_2$  = 毫摩尔/升 )

	元素及其化合态	$F_1$	$F_2$
Aluminum( $\text{Al}^{3+}$ )	铝( $\text{Al}^{3+}$ )	0. 111 19	0. 037 15
Ammonium( $\text{NH}_4^+$ )	铵( $\text{NH}_4^+$ )	0. 055 44	0. 055 44
Arsenic( As )	砷( As )	—	0. 013 34
Barium( $\text{Ba}^{2+}$ )	钡( $\text{Ba}^{2+}$ )	0. 014 56	0. 007 28
Bicarbonate( $\text{HCO}_3^-$ )	碳酸氢根( $\text{HCO}_3^-$ )	0. 016 39	0. 016 39
Boron( B )	硼( B )	—	0. 092 50
Cadmium( $\text{Cd}^{2+}$ )	镉( $\text{Cd}^{2+}$ )	0. 017 79	0. 008 90
Calcium( $\text{Ca}^{2+}$ )	钙( $\text{Ca}^{2+}$ )	0. 049 90	0. 024 95
Carbonate( $\text{CO}_3^{2-}$ )	碳酸根( $\text{CO}_3^{2-}$ )	0. 033 33	0. 016 66
Cesium( $\text{Cs}^+$ )	铯( $\text{Cs}^+$ )	0. 007 52	0. 007 52
Chloride( $\text{Cl}^-$ )	氯( $\text{Cl}^-$ )	0. 028 21	0. 028 21
Chromium( Cr )	铬( Cr )	—	0. 019 23
Cobalt( $\text{Co}^{2+}$ )	钴( $\text{Co}^{2+}$ )	0. 033 94	0. 016 97
Copper( $\text{Cu}^{2+}$ )	铜( $\text{Cu}^{2+}$ )	0. 031 47	0. 015 74
Fluoride( $\text{F}^-$ )	氟( $\text{F}^-$ )	0. 052 64	0. 052 64
Hydrogen( $\text{H}^+$ )	氢( $\text{H}^+$ )	0. 992 16	0. 992 16
Hydroxide( $\text{OH}^-$ )	氢氧根( $\text{OH}^-$ )	0. 058 80	0. 058 80
Iron( $\text{Fe}^{2+}$ )	铁( $\text{Fe}^{2+}$ )	0. 035 81	0. 017 91
Iron( $\text{Fe}^{2+}$ )	铁( $\text{Fe}^{3+}$ )	0. 053 72	0. 017 91
Lead( $\text{Pb}^{2+}$ )	铅( $\text{Pb}^{2+}$ )	0. 009 65	0. 004 83
Magnesium( $\text{Mg}^{2+}$ )	镁( $\text{Mg}^{2+}$ )	0. 082 29	0. 041 14
Manganese( $\text{Mn}^{2+}$ )	锰( $\text{Mn}^{2+}$ )	0. 036 40	0. 018 20

续表

	元素及其化合态	$F_1$	$F_2$
Mercury( Hg )	汞( Hg )	—	0.004 99
Molybdenum( Mo )	钼( Mo )	—	0.010 42
Nickel( Ni )	镍( Ni )	—	0.017 04
Nitrate( NO <sub>3</sub> <sup>-</sup> )	硝酸盐( NO <sub>3</sub> <sup>-</sup> )	0.016 13	0.016 13
Nitrite( NO <sub>2</sub> <sup>-</sup> )	亚硝酸盐( NO <sub>2</sub> <sup>-</sup> )	0.021 74	0.021 74
Phosphate( PO <sub>4</sub> <sup>3-</sup> )	磷酸盐( PO <sub>4</sub> <sup>3-</sup> )	0.031 59	0.010 53
Potassium( K <sup>+</sup> )	钾( K <sup>+</sup> )	0.025 58	0.025 58
Selenium( Se )	硒( Se )	—	0.012 66
Silica( SiO <sub>2</sub> )	二氧化硅( SiO <sub>2</sub> )	—	0.016 64
Sodium( Na <sup>+</sup> )	钠( Na <sup>+</sup> )	0.043 50	0.043 50
Strontium( Sr <sup>2+</sup> )	锶( Sr <sup>2+</sup> )	0.022 83	0.011 41
Sulfate( SO <sub>4</sub> <sup>2-</sup> )	硫酸盐( SO <sub>4</sub> <sup>2-</sup> )	0.043 50	0.043 50
Sulfide( S <sup>2-</sup> )	硫( S <sup>2-</sup> )	0.062 38	0.031 19
Zinc( Zn <sup>2+</sup> )	锌( Zn <sup>2+</sup> )	0.030 59	0.015 30

资料来源: 仿 Hem, 1985。

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