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电子垃圾拆解地翠鸟对多氯联苯的累积及风险评估

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摘要: 粗犷的电子垃圾拆解活动已造成当地野生生物多氯联苯(PCBs)严重污染,但 PCBs 在野生鸟类中的生物累积特征及潜在的毒害作用研究较少。本研究采集了广东省某电子垃圾拆解地翠鸟(*Alcedo atthis*)及其食物(各种小型鱼类)样品,研究翠鸟对 PCBs 的累积特征、生物放大效应及毒性风险。翠鸟肌肉中 PCBs 中值含量为 220 $\mu\text{g}\cdot\text{g}^{-1}$ 脂重,比其他报道值高 1~3 个数量级。计算的生物放大因子(BMF)显示,大部分 PCB 单体的 BMF 值都大于 1,表明翠鸟对 PCBs 具有生物放大效应。计算的共面 PCBs 毒性当量(TEQs)范围为 39~23 600 $\text{pg}\cdot\text{g}^{-1}$ 湿重,已经达到或超过了影响某些鸟类生殖或发育障碍的报道值。上述结果表明,电子垃圾拆卸活动已经造成了当地翠鸟 PCBs 严重污染,PCBs 污染物对电子垃圾拆解地翠鸟及其他野生生物的毒性效应尚需进一步研究。

关键词: 多氯联苯; 鸟类; 生物积累; 生物放大; 电子垃圾

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Bioaccumulation and Risk Assessment of Polychlorinated Biphenyls in the Common Kingfisher (*Alcedo atthis*) from an Electronic Waste Recycling Site in South China

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Abstract: The wildlife from electronic waste (e-waste) sites have been heavily polluted by polychlorinated biphenyls (PCBs), due to the primitive e-waste recycling activities. However, information on the bioaccumulation and the toxic effects of PCBs in wild avian species from e-waste sites is limited. In the present study, we investigated the levels and congener profiles of PCBs in the common kingfisher (*Alcedo atthis*) from an e-waste recycling site in Guang-

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dong Province, South China. Additionally, PCBs in the diet items including three fish species collected from the same sampling site were also examined, to evaluate the potential biomagnification of PCBs in the common kingfisher. Finally, we assessed the potential toxic effects of PCBs to these birds by estimating the toxic equivalent quantity (TEQ) of the co-planar PCBs. Elevated PCB residues (median = 220 $\mu\text{g}\cdot\text{g}^{-1}$ lipid weight for total PCBs) were detected in the kingfishers, which were one to three orders of magnitude higher than the values previously reported in the species from other sampling sites. The calculated predator/prey biomagnification factors (BMFs) were greater than unity for most of the PCB congeners examined, suggesting biomagnification of these chemicals in the common kingfisher. The TEQ concentrations estimated in the common kingfisher ranged from 39 to 23 600 $\text{pg}\cdot\text{g}^{-1}$ wet weight, with some of these values reaching or exceeding the levels known to impair bird reproduction and survival. Our results revealed that the common kingfisher from the e-waste recycling site has been heavily contaminated by PCBs. The need for further examination is warranted to determine the potential adverse effects resulting from the PCBs exposure, in the common kingfishers and other wildlife that are habitants of e-waste sites.

Keywords: polychlorinated biphenyls; bird; bioaccumulation; biomagnification; electronic waste

多氯联苯(polychlorinated biphenyls, PCBs)是一类人工合成的多氯芳香烃类化合物。由于 PCBs 具有物理化学性质稳定、耐热性、电绝缘性等特点,常用作热载体、绝缘材料、溶剂等广泛添加于电子电器等产品中^[1]。这些产品在使用过程中或废弃后 PCBs 很容易进入到环境。研究证实,PCBs 在环境中具有持久性、可生物累积性和较高的生物毒性^[2-3]。2001 年 5 月 PCBs 被列入《斯德哥尔摩公约》持久性有机污染物(POPs)首批受控名单,在全球禁用^[4]。

随着 PCBs 的禁用,全球 PCBs 主要生产和使用地区(主要为北美和欧洲)环境中 PCBs 含量显著下降^[5]。然而,作为全球废弃电子电器产品(电子垃圾)主要集中地亚洲和非洲一些国家环境中 PCBs 含量却有上升的趋势^[5-6]。PCBs 在电子垃圾集中地的环境行为及其生态风险评估已引起了广泛关注。我们的初步研究发现,广东省某电子垃圾拆解地野生鱼类体内的 PCBs 含量很高^[7]。这些污染物是否传递到高营养级生物(如食鱼鸟)及其对这些生物可能的毒害作用尚不清楚。本研究在广东省某电子垃圾拆解地同时采集了翠鸟(*Alcedo atthis*)及其食物(3 种小型鱼类)样品,通过测定这些样品中 PCBs 的含量,研究了翠鸟对 PCBs 的生物放大效应,并评估了这些污染物对翠鸟潜在的毒性效应。

1 材料与方法 (Materials and methods)

1.1 样品采集与前处理

翠鸟是一种食鱼性鸟类,主要是以其栖息地附近水体中各种小型鱼类为食^[8]。翠鸟(*A. atthis*)样品($n = 22$)于 2010 年 5 月到 2010 年 7 月在广东省某电子垃圾拆解地池塘边用网捕法采集,鸟类采集经

广东省林业局批准。同时在池塘中采集了中国斗鱼(*Macropodus opercularis*, $n = 9$)、食蚊鱼(*Gambusia affinis*, $n = 11$)和马口鱼(*Opsariichthys bidens*, $n = 9$) 3 种小型鱼类。鸟类样品采集后用 N_2 进行安乐死。所有样品低温运输至实验室后, $-20\text{ }^\circ\text{C}$ 冷冻保存待分析。

翠鸟样品解剖后,取肌肉组织。每种鱼类样品(整鱼样)随机混合成 3 个混合样。取约 4 g 翠鸟肌肉组织和 8 g 鱼类样品,冷冻干燥并混匀后,加入回收率指示物 CB 30、CB 65 和 CB 204 后,用正己烷/丙酮混合溶剂(1/1, V/V)索氏抽提 48 h。抽提液一部分用于测定脂肪含量(重量法)。余下抽提液浓缩至 1 mL 左右,经凝胶渗透色谱柱(GPC)去除脂肪和其他干扰物。洗脱液浓缩至 1~2 mL 后,过复合硅胶柱(酸性硅胶:中性硅胶 = 8:8)净化,最后浓缩定容至 200 μL ,加入内标(CB 24、CB 82 和 CB 198)。样品的抽提及净化具体方法参见文献^[7]。

1.2 仪器测定

75 种 PCBs 单体用安捷伦气相色谱质谱联用仪(Agilent 6890 GC-5975B Series MS)测定。采用 EI 源、选择性离子扫描模式(SIM),使用色谱柱 DB-5MS (60 m \times 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA)进行分离。选择无分流进样,进样量为 1 μL 。载气为高纯氦气,柱流速为 1.50 $\text{mL}\cdot\text{min}^{-1}$ 。升温程序:起始温度 120 $^\circ\text{C}$, 6 $^\circ\text{C}\cdot\text{min}^{-1}$ 升温至 180 $^\circ\text{C}$, 1 $^\circ\text{C}\cdot\text{min}^{-1}$ 升温至 240 $^\circ\text{C}$, 然后 6 $^\circ\text{C}\cdot\text{min}^{-1}$ 升温至 290 $^\circ\text{C}$ 并保留 17 min。进样口、离子源温度和界面温度分别为 290 $^\circ\text{C}$ 、250 $^\circ\text{C}$ 和 290 $^\circ\text{C}$ 。目标化合物采用内标法(6 点校正曲线)定量。

1.3 质量保证与质量控制(QA/QC)

QA/QC体系主要包括回收率指示物添加、程序空白、加标空白、基质加标、样品重复样测定等。程序空白样中有少量PCB 118和PCB 138检出,实际样品进行了相应扣除。样品中PCB 30、PCB 65和PCB 204的回收率分别为83% ± 16%、94% ± 17%和94% ± 15%,定量结果未经回收率校正。空白加标和基质加标中PCBs单体(20种PCBs)的回收率范围分别为75%~107%和75%~104%。样品平行样中所有目标化合物的相对标准偏差均小于15%。PCBs的最低检测限(LOQs)按方法空白中各单体的含量平均值加3倍标准偏差计算。对于空白中没有检测出的目标化合物按5倍信噪比(S/N)计算。样品中PCBs的检测限为0.01~0.20 μg·g⁻¹脂重。

1.4 生物放大因子(BMF)计算

普通翠鸟体内中各PCB单体的生物放大因子(BMF)按照下式计算:

$$BMF = C_{\text{翠鸟}} / C_{\text{食物}}$$

式中C_{翠鸟}为化合物在翠鸟中的浓度,单位为μg·g⁻¹脂重,C_{食物}为翠鸟食物(3种小鱼)中对应化合物的浓度,单位为μg·g⁻¹脂重。

1.5 毒性当量(TEQ)计算

利用联合国卫生组织提出的鸟类二噁英类化合物毒性当量因子(TEFs)^[7],计算了几种主要的共面PCB单体(包括PCB 77、PCB 81、PCB 105、PCB 114、

PCB 118、PCB 123、PCB 126、PCB 156、PCB 167和PCB 169)的毒性当量(TEQ)。其计算公式如下:

$$TEQ = \sum(PCB_i \times TEF_i)$$

式中PCB_i和TEF_i分别为某种共面PCB单体的浓度(pg·g⁻¹湿重)和其TEF。

2 结果与讨论(Results and discussion)

2.1 PCBs的含量与组成

翠鸟及3种小型鱼类体内7种指示性PCBs及75种PCB单体总含量(ΣPCBs)见表1。翠鸟肌肉中ΣPCBs的浓度范围为4.0~3300 μg·g⁻¹脂重(中值浓度为220 μg·g⁻¹脂重)。目前,仅有一篇文献报道了华南某自然保护区(中值1800 ng·g⁻¹脂重)和农村区域(中值410 ng·g⁻¹脂重)普通翠鸟中PCBs的含量^[7]。但已有不少研究报道了其他食鱼性鸟类肌肉中PCBs的含量。Luo等^[9]研究的电子垃圾区池鹭肌肉中的PCBs的含量达到了120000 ng·g⁻¹脂重。比利时的牛背鹭肌肉中的浓度达到90000 ng·g⁻¹脂重^[10]。Tanabe等^[11]报道了采集于南印度湿地和沿海区域的白胸翡翠(翠鸟)肌肉中PCBs残留浓度为400 ng·g⁻¹脂重。Kunisne等^[12]报道的日本北海道黑尾鸥肌肉浓度为2700~11000 ng·g⁻¹脂重。采自日本Lake Biwa湖区和罗马尼亚Danube Delta区域的普通鸬鹚肌肉中PCBs的浓度分别为2900~77000和700 ng·g⁻¹脂重^[12-14]。Braune等^[15]研究了加拿大西部

表1 电子垃圾拆解区翠鸟及3种小型鱼类中PCBs含量(单位:μg·g⁻¹脂重)

Table 1 Levels of PCBs in the common kingfisher and their prey fish species collected from an e-waste recycling site in South China (Unit: μg·g⁻¹ lipid weight)

样品名称 Sample	普通翠鸟 Common kingfisher	食物 Prey fish		
		中国斗鱼 Paradise fish	食蚊鱼 Mosquito fish	马口鱼 Chinese hooksnout carp
样品数量 Number	22	9 (3)	11 (3)	9 (3)
脂肪含量/% Lipid/%	3.5 (2.2~5.9)	1.8 (1.4~2.5)	1.6 (1.3~1.8)	1.3 (1.0~1.3)
CB 28/31	8.2 (0.69~140)	1.1 (0.92~1.4)	1.9 (1.1~2.5)	2.7 (2.4~3.2)
CB 52	7.3 (0.41~66)	4.3 (3.4~5.5)	3.1 (3.0~3.8)	4.7 (4.4~5.5)
CB 101	18 (0.34~210)	20 (17~20)	16 (13~16)	34 (31~34)
CB 118	32 (0.14~450)	17 (15~18)	21 (17~22)	42 (40~47)
CB 138	15 (0.04~310)	20 (18~28)	15 (13~22)	39 (36~39)
CB 153	17 (0.06~270)	19 (19~27)	15 (13~21)	39 (38~39)
CB 180/193	3.2 (0.006~50)	2.9 (2.3~4.3)	2.0 (1.7~3.5)	8.1 (7.0~8.1)
Σ PCBs	220 (4.0~3300)	210 (100~240)	180 (150~290)	430 (410~570)

注:9(3)表示样品的个数,括号里面的数字表示混合后样品的数量;3.5(2.2~5.9)表示中值和范围;ΣPCBs表示75个PCBs单体的总浓度。

Note: 9(3) is the number of individual samples collected; figures in brackets indicate analyses number of pooled samples when individual were pooled; 3.5(2.2~5.9) means median and range; ΣPCBs is the sum concentrations of the 75 PCB congeners examined.

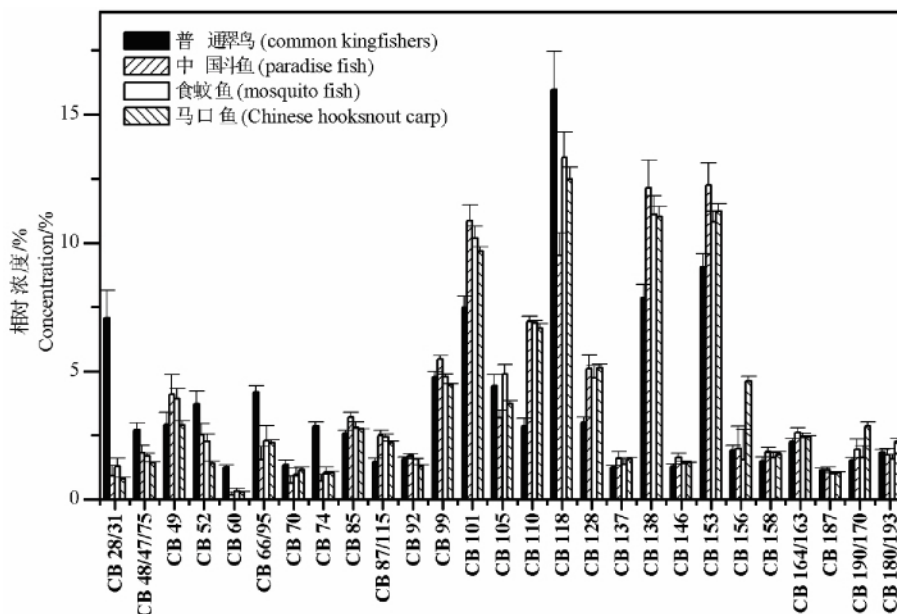


图 1 电子垃圾拆卸区翠鸟和其食物中 PCBs 的同系物分布模式

Fig. 1 Congener profiles of PCBs in the kingfishers and their prey fish species collected from an e-waste recycling site

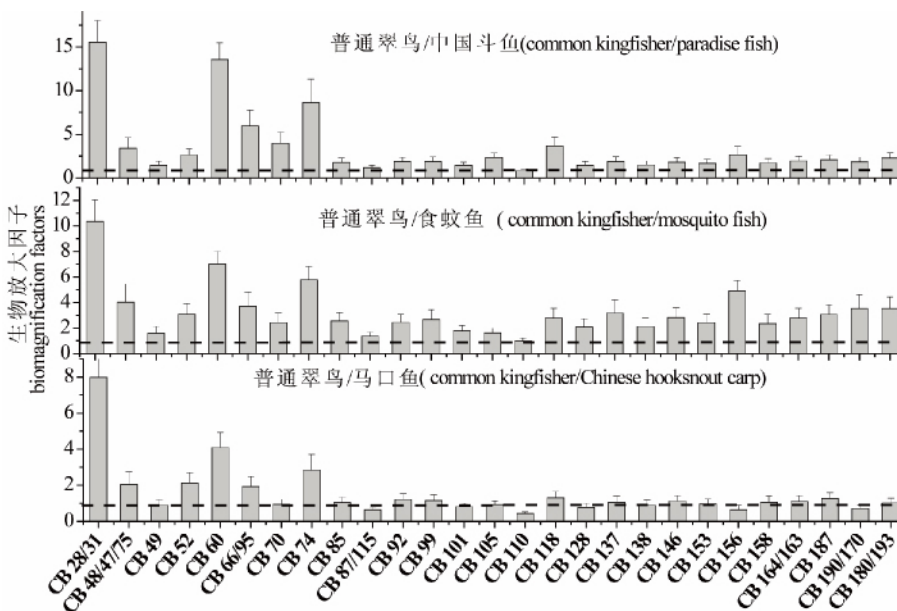


图 2 翠鸟/鱼类的 3 种捕食关系中 PCBs 的 BMFs 值

Fig. 2 Biomagnification factors (BMFs) for PCB congeners derived from the three predator/prey pairs

秋沙鸭和普通潜鸟胸部肌肉中 PCBs 的残留情况，这 2 种鸟类中 PCBs 的残留浓度为 $1.1 \sim 1\,000 \text{ ng} \cdot \text{g}^{-1}$ 脂重。Elliott 等^[16]测定了英国、哥伦比亚和加拿大鸬鹚和棕胁秋沙鸭肌肉中 PCBs 含量，其浓度分别为 $1\,600 \text{ ng} \cdot \text{g}^{-1}$ 脂重和 $78 \text{ ng} \cdot \text{g}^{-1}$ 脂重。相比于前人报道的食鱼性鸟类肌肉中 PCBs 的残留浓度，本研究翠鸟 PCBs 含量与日本 Lake Biwa 湖区的鸬鹚和中国

电子垃圾拆解地池鹭相当(范围为 $4.0 \sim 3\,300 \text{ } \mu\text{g} \cdot \text{g}^{-1}$ 脂重)，但高于其他报道值 1~3 个数量级。翠鸟肌肉中 PCBs 含量也高于采集于同一电子垃圾拆卸区的其他 7 种水生鸟类($1\,800 \sim 18\,000 \text{ ng} \cdot \text{g}^{-1}$ 脂重)和 1 种陆生鸟类($7\,300 \text{ ng} \cdot \text{g}^{-1}$ 脂重)以及华南某保护区 4 种陆生鸟类($45 \sim 1\,770 \text{ ng} \cdot \text{g}^{-1}$ 脂重)肌肉中 PCBs 含量^[9, 17-19]。虽然监测的 PCBs 单体总数量的不同，会

影响本文翠鸟中 PCBs 的残留浓度与其他研究鸟类中浓度的对比,但是这些结果也初步表明,电子垃圾拆解地翠鸟已经受到 PCBs 严重污染。此外,诸多因素如食性和摄食量、迁移性和生态位(营养级)等会影响不同鸟类对 PCBs 的累积。

翠鸟及其食物(3 种小鱼)中 PCBs 同系物组成模式如图 1 所示。翠鸟肌肉中 CB 118 是最主要的同系物,占 Σ PCBs 的 $16\% \pm 1.5\%$ 。CB 28/31、CB 153、CB 101 和 CB 138 也是主要的同系物,共占 Σ PCBs 的

$47\% \pm 1.0\%$ 。翠鸟的食物与翠鸟有着相似的 PB-DEs 同系物分布模式,其中 CB 118、CB 153、CB 101 和 CB 138 是最主要的同系物。本研究普通翠鸟肌肉中的 PCB 同系物组成特征与之前报道的华南某自然保护区和农村区域普通翠鸟中 PCBs 的同系物相同^[7],都以 CB 118、CB 28/31 和 CB 153 为最主要同系物。本研究翠鸟体内 PCBs 同系物组成与电子垃圾拆卸区其他水生鸟类 PCBs 同系物组成也基本相同,都是以 5~6 氯等低氯代的 PCBs 单体为主^[9],

表 2 电子垃圾拆卸区普通翠鸟中共面 PCBs 的毒性当量值(单位: $\text{pg} \cdot \text{g}^{-1}$ 湿重)

Table 2 Toxic equivalent quantity (TEQ) concentrations of major coplanar PCB in kingfishers from an e-waste recycling site (Unit: $\text{pg} \cdot \text{g}^{-1}$ wet weight)

多氯联苯 PCBs	毒性当量因子 TEF _{WHO-Avian} <small>世界卫生组织-鸟类</small>	毒性当量值 TEQ		
		平均值 Mean	中值 Median	范围 Range
CB 77	5×10^{-2}	3 100	1 000	36 ~ 19 000
CB 81	10^{-1}	500	160	1.9 ~ 3 600
CB 105	10^{-4}	39	25	0.27 ~ 170
CB 114	10^{-4}	8	3	0.05 ~ 56
CB 118	10^{-5}	23	11	0.07 ~ 140
CB 123	10^{-5}	0.47	0.22	0.01 ~ 2.3
CB 156	10^{-4}	40	13	0.045 ~ 280
CB 167	10^{-4}	16	5	0.34 ~ 120
Σ TEQs		3 700	1 200	39 ~ 24 000

表 3 文献报道的 PCBs 的 TEQs 对鸟类的毒性参考值

Table 3 Reported toxicity reference values in birds exposed to TEQs of PCBs

物种 Birds	毒性参考值/($\text{pg} \cdot \text{g}^{-1}$ 湿重)	参考文献 References
	Toxicity reference values /($\text{pg} \cdot \text{g}^{-1}$ wet weight)	
实验室研究 Laboratory avian toxicity data		
原鸡(Gallus gallus)	66	[24]
美国隼(Falco sparverius)	230	[25]
环颈雉(Phasianus colchicus)	710	[26]
双冠鸬鹚(Phalacrocorax auritus)	3 670	[27]
火鸡(Meleagris gallopavo)	10 000	[28]
绿头鸭(Anas platyrhynchos)	35 360	[29]
灰雁(Anser anser)	50 000	[29]
鹊鸭(Bucephala clangula)	50 000	[24]
红嘴鸥(Larus ridibundus)	50 000	[30]
银鸥(Larus argentatus)	50 000	[29]
野外研究 Field avian toxicity data		
林鸳鸯(Aix sponsa)	5	[31]
大蓝鹭(Ardea herodias)	13	[32]
鸮(Pandion haliaetus)	140	[33]
加拿大燕鸥(Sterna forsteri)	350	[34]
红嘴巨鸥(Sterna caspia)	1 440	[35]

但与陆生鸟类 PCB 的同系物组成特征(主要是以 5~8 氯为主 PCBs 单体为主)具有较大的差异^[17,20]。水生鸟类和陆生鸟类生活环境和食性的不同,可能是导致这种差异的主要原因。相对于高氯代的 PCB 单体,低氯代的 PCBs 具有较高的水溶性,更容易在水生生物体内富集,造成翠鸟体内较高含量的低氯代 PCB 单体。

2.2 PCBs 的生物放大

为了调查 PCBs 单体在普通翠鸟食物链中可能的生物放大效应,我们计算了这些化合物的生物放大因子(BMFs)(图 2)。大部分的 PCB 单体的 BMF 值都大于 1(Σ PCBs 的平均 BMF 值为 1.1~2.5),表明翠鸟对这些 PCB 单体产生了生物放大效应。通过对比 PCB 单体在 3 种捕食关系中的 BMFs 发现,翠鸟/中国斗鱼和翠鸟/食蚊鱼之间 BMF 值都大于 1,而 PCB 少数单体(CB 49、CB87/115、CB110、CB156、CB190/170)在翠鸟/马口鱼之间 BMF 值小于 1,通过查询文献,普通翠鸟其食物中 99%都是以 2.3 cm 左右小型淡水鱼类(最大也能达到 12.5 cm)^[8],但是本次样品中马口鱼的平均长度为 7.0^[21] 较其他 2 种鱼类长。因此,马口鱼可能不是翠鸟的主要食物之一,不同鱼类在翠鸟食物中的比例可能是造成这种差异的原因。本研究计算的 PCBs 的 BMF 值与之前报道的华南某自然保护区普通翠鸟对这些污染物的 BMF 值基本相似(Σ PCBs 的平均 BMF 值为 1.1~1.4)^[7]。Drouillard 等^[22]采用肠道累积放大的方法预测了环鸽(*Streptopelia risoria*)对 PCBs 的生物放大效果,预测的 BMF 范围为 18.5~33.8,高于我们当前的研究值。野外实验条件和实验室预测条件的差别以及物种间对于 PCBs 不同的累积特性,可能是导致不同研究 BMF 值不尽相同的主要原因。

2.3 TEQ 值

目前还未见 PCBs 对于翠鸟的毒性风险评价数据。我们计算了几种主要的共面 PCB 单体(包括 CB 77、CB 81、CB 105、CB 114、CB 118、CB 123、CB 156 和 CB 167)的毒性当量(TEQ),并通过对比 TEQs 对其他水生鸟类的毒性参考值(TRVs)或风险评估的阈值,评估 PCBs 对普通翠鸟潜在的毒害作用。计算的 TEQs 范围为 39~24 000 $\text{pg}\cdot\text{g}^{-1}$ 湿重,平均值为 3 700 $\text{pg}\cdot\text{g}^{-1}$ 湿重(表 2)。较多研究报道了 TEQs 对鸟类的 TRVs(表 3),超过这些参考值将对鸟类产生胚胎死亡和发育障碍等方面的影响^[23]。与这些结果比较,电子垃圾拆卸区翠鸟体内的 TEQs 含量超过

了大部分水生鸟类的 TRV 值。这一结果预示着电子垃圾拆卸区翠鸟体内的 PCBs 可能对其生殖和发育方面带来潜在的毒害作用。

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