电子电器废弃物拆解区蔬菜多氯联苯污染及其健康风险

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摘要 对某电子电器废弃物拆解污染区、拆解污染修复区和非拆解对照区蔬菜多氯联苯(polychlorinated biphenyls, PCBs)污染水平和特征进行了研究, 并与蔬菜种植农业环境土壤、大气和灌溉水3种介质的PCBs污染进行对比源解析, 同时评估了居民食用当地蔬菜的PCBs暴露健康风险. 结果表明, 拆解污染区蔬菜中PCBs浓度显著高于非拆解对照区, 拆解污染修复区和非拆解对照区蔬菜污染水平相当. 蔬菜中PCBs污染均以低氯代同系物为主, 叶菜中PCBs污染水平显著高于地下根茎类和豆类蔬菜. 大气沉降和土壤吸收可能为蔬菜中PCBs的主要来源. 健康风险评估结果表明, 拆解污染区居民摄入蔬菜的致癌风险为 1.01×10^{-4} , 超过可接受致癌风险2个数量级; 非致癌风险达到参考剂量的2.54倍, 建议当地调整种植结构或进行替代种植.

关键词 多氯联苯, 蔬菜, 土壤, 大气, 灌溉水, 健康风险

多氯联苯(polychlorinated biphenyls, PCBs)是环境中典型的持久性有机污染物, 曾被广泛应用于工业领域, 全球PCBs总产量约为120万吨, 其中有30%都进入了环境中^[1]. 研究表明, PCBs具有生物毒害性, 能致癌、致畸和致突变^[2]. 长时间暴露在低剂量PCBs环境中可能干扰内分泌、造成生殖系统紊乱、甲状腺激素失调及癌变等病症^[3]. PCBs具有亲脂性和生物累积性, 从北极的海豹到南极的海鸟蛋及各国人乳中都检测到含量不等的PCBs.

饮食是人体PCBs暴露的主要途径, 研究发现, 人体中超过90%的PCBs是通过饮食途径暴露的^[4]. 其中, 由于PCBs的亲脂性, 对动物性食品关注较多. 国外的调查表明, 动物性食品的PCBs浓度为 10.92 ng/g ^[5], 鱼类对膳食摄入总PCBs贡献比例达80%^[6], 而农作物产品中PCBs浓度仅为 1.90 ng/g ^[5]. 有些学者甚至认

为经谷物、蔬菜等植物性食品摄入的PCBs风险可忽略不计^[7]. 我国人群消费的蔬菜、稻米等植物性食品比重较大, 高达60.8%^[8], 但对通过植物性食品暴露于PCBs的健康风险研究较少.

根据前期调研, 该地居民动物性食品食用比重较小, 本地已不养殖畜禽, 市场出售的禽肉来自外地, 且基本检测不到PCBs^[9]. 而该地居民植物性食品食用比例高达76.3%, 在电子电器废弃物拆解污染区, 稻米中PCBs残留水平较低, 而蔬菜中PCBs含量较高^[9]. 但前人研究中未对蔬菜品种进行分类, 也未进行源解析. 本研究调查了拆解污染区及拆解污染修复区中蔬菜PCBs污染状况, 同时对叶菜、地下根茎类和豆类不同品种蔬菜中PCBs污染水平和特征进行分析, 并结合种植农业环境各介质的PCBs污染现状调查, 进行蔬菜中PCBs来源初探, 为该地区开展

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PCBs污染农田土壤管控提供依据。

1 材料与方法

(i) 研究区域概况. 研究区域位于我国东南沿海典型电子电器废弃物拆解区(东经121°13′, 北纬28°27′). 当地固体废弃物拆解行业始于20世纪70年代, 拆解的固体废弃物主要以国外进口为主. 由于拆解含PCBs变压器、电容器等, 导致当地成为典型的PCBs污染区. 2009~2014年, 当地政府选择典型PCBs污染农田进行了土壤污染修复示范, 修复面积为12500 m², 主要采用微生物修复技术, 修复后土壤中PCBs浓度低于100 ng/g. 本研究选择拆解污染区典型成片农田, 面积约8600 m²; 修复农田中选择与拆解污染区农田毗邻区块, 面积约2000 m²; 选择距拆解污染区7.6 km的非拆解对照区成片农田, 面积约为7600 m². 本文隐去具体地名、详细GPS数据。

(ii) 样品采集. 于2014年5月采样, 按网格布点法设置蔬菜采样点, 采用GPS仪进行定位, 每个单元采集4个子样品, 每个子样品采集点又采用五点法采集5个样品, 所有样品合并成一个混合样. 同一采样时段内, 共采得蔬菜样品22份. 其中, 拆解污染区叶菜(青菜)、地下根茎类(胡萝卜)和豆类(毛豆)样品各3份; 拆解污染修复区叶菜(青菜)2份, 地下根茎类(胡萝卜)和豆类(毛豆)样品各1份; 非拆解对照区叶菜(青菜)5份, 地下根茎类(胡萝卜)和豆类样品(毛豆)各2份。

将所有蔬菜样品根部附着的土壤轻轻抖落, 即为根际土, 共获得22份根际土壤样品. 非根际土壤样品采样也按网格布点采样, 得到土壤混合样, 共获得8份非根际土壤样. 其中, 拆解污染区非根际土壤样3份、拆解污染修复区2份、非拆解对照区3份。

大气采样点选在研究区块内部, 每个研究区块各设1个采样点. 选用大流量空气采样器, 内部装有聚氨酯泡沫(PUF)和石英纤维滤膜, 分别捕捉气态PCBs和大气中颗粒物. 实行24 h连续采样。

用自制采样器采集表层河水, 每个采样点采集4 L水样, 置于棕色磨口玻璃瓶中, 加入0.5%甲醇, 共获得4个样品. 其中, 拆解污染区与拆解污染修复区灌溉水源及河段相同, 样品重叠, 共2个水样, 非拆解对照区2个水样。

采集的蔬菜、土壤样品经密封袋封装, 大气样品用锡箔纸包裹, 灌溉水样于棕色磨口玻璃瓶闭光放置, 运送入实验室, -20℃保存待测。

(iii) 标准物质和材料. 实验所用丙酮、正己烷、浓硫酸、无水硫酸钠、佛罗里硅土均为分析纯, 聚氨酯泡沫(0.022 g/cm³, Ø90×50 mm), 石英纤维滤膜(孔径0.3 μm, 85 g±4 g/m², 8×10 英尺(1英尺=0.3048 m)), Sep-pak C₁₈型固相萃取小柱(0.5 g/6 mL)。

标准样品: PCBs标准品Aroclor 1254, Aroclor 1242, 回收率指示物2,4,5,6-四氯间二甲苯(TMX)和PCB209, 定量的PCBs单体共57种, 分别为: PCB6, 7, 8, 16, 17, 18, 19, 22, 24, 25, 26, 28, 31, 32, 33, 37, 40, 41, 42, 44, 45, 49, 52, 56, 60, 64, 66, 70, 74, 82, 83, 85, 87, 97, 99, 100, 101, 108, 110, 118, 128, 129, 136, 138, 137, 141, 146, 149, 153, 159, 170, 175, 177, 178, 180, 185, 187。

(iv) 样品处理. 蔬菜样品取可食部分清洗, 剪成小块后经高速粉碎机粉碎, 称取约5 g蔬菜样品, 加2倍样品质量的无水硫酸钠混匀. 添加回收率指示物, 平衡12 h后, 加入30 mL正己烷/丙酮(体积比=1:1)提取液超声萃取, 低速离心后转移至平底烧瓶, 再以20 mL提取液重复操作2次. 提取液经旋转蒸发浓缩至1 mL, 经固相萃取(SPE)处理, 收集正己烷洗脱液, 浓缩定容至1 mL, 转移至进样小瓶, 气相色谱-质谱联用仪(GC-MS)上机分析。

土壤样品经冷冻干燥研磨过筛(60目)处理, 称取5 g土样, 处理步骤与蔬菜样相同, 但不经SPE净化, 而是加入浓硫酸磺化后过层析柱, 收集洗脱液, 浓缩、定容、转移, GC-MS分析。

空气样品采用索氏提取方法. 将石英滤膜和PUF分别加入回收率指示物, 平衡24 h后, 剪碎, 放入索氏提取器中. 加入正己烷:丙酮(1:1)混合液和铜片, 连续抽提48 h后, 将溶剂倒入平底烧瓶中, 再进行旋转蒸发浓缩、磺化、过柱、氮吹、定容、转移, GC-MS分析。

灌溉水样经过滤后加入回收率指示物, 平衡24 h. SPE浓缩净化, 收集洗脱液, 经无水硫酸钠脱水后, 氮吹、定容、转移, GC-MS分析。

(v) 样品分析. Agilent 7890/5975气相质谱联用仪(GC-MS)分析条件: 毛细管色谱柱19091S-433 (30 m×0.25 mm×0.25 μm), 质谱离子源为电子轰击源(EI), 电子能量70 eV, 离子源温度230℃. SIM模式下升温, 程序为: 初始温度80℃保持2 min, 以8℃/min升温到196℃; 然后再分别以2℃/min的速率升到228℃, 10℃/min升到250℃, 最后保持12 min. 不分流进样1 μL. 通过色谱峰保留时间和检索质谱谱库进行定性分析, 用峰面积外标法定量分析。

(vi) 质量控制及数据处理. 实验采用空白样品、空白加标样品、重复样作为质量控制样品. 以含预估目标物最低检测浓度5倍的基质加标实验计算检测限和回收率, 蔬菜样品基质加标回收率为80%~87%, PCBs检测限为1.43 ng/g; 土壤样品基质加标回收率为63%~101%, PCBs检测限为1.43 ng/g; 大气PUF和滤膜加标回收率为60%~95%, PCBs检测限为0.5 ng/m³; 水样基质加标回收率为71%~80%, PCBs检测限为0.13 ng/L. 实验样品回收率指示物回收率为75%~125%, 蔬菜、土壤和大气颗粒物样品所有浓度均为干重浓度.

本研究所有数据采用Microsoft office excel 2013, SPSS 20.0和Origin 8.0进行统计分析, 采用单因素方差分析法检验平均值差异, 显著性检验水平设为0.05.

(vii) 暴露风险评估. 采用美国国家环境保护局的推荐模型^[10], 对居民摄入当地蔬菜的致癌风险和非致癌风险进行评估, 计算公式如下:

$$LADD = \left(\frac{C \times IR \times ED}{AT \times BW} \right) \times 10^{-6}, \quad (1)$$

$$Risk = LADD \times CSF, \quad (2)$$

$$HQ = LADD / RfD, \quad (3)$$

式中, LADD为生命周期日平均摄入量($\mu\text{g}/(\text{kg} \cdot \text{d})$); C

为蔬菜PCBs浓度(ng/g); IR为蔬菜的日摄入量(g/d); ED为暴露周期, 取30 a^[11]; AT为致癌或非致癌周期, 以生命周期计算, 取72 a^[12]; BW为体重, 按62 kg^[13]计. Risk为致癌风险; CSF为癌症斜率因子, 为2.00 $\text{mg}/(\text{kg} \cdot \text{d})$ ^[10]. Risk小于或等于 1.0×10^{-6} , 为可接受致癌风险水平. HQ为非致癌风险; RfD为EPA参考剂量, 为0.02 $\mu\text{g}/(\text{kg} \cdot \text{d})$ ^[14], HQ不超过1时, 被认为是可接受风险水平.

据统计, 浙江省居民每人摄取的蔬菜约为300 g/d ^[15], 我国居民每日消费的蔬菜中叶菜类占43.92%, 地下根茎类占16.53%, 鲜豆类占1.4%^[16]. 蔬菜含水率按叶菜90%^[17], 地下根茎类90%^[18], 豆类70%^[19]计.

2 结果与讨论

2.1 蔬菜PCBs污染水平和组成特征

对研究区蔬菜可食部分中PCBs污染水平进行分析. 总体上, 拆解污染区蔬菜PCBs污染水平最高, 平均浓度为228.68 ng/g ; 拆解污染修复区和非拆解对照区蔬菜PCBs污染水平相当, 平均浓度分别为58.31和35.65 ng/g . 由图1可知, 拆解污染区以叶菜中PCBs浓度最高, 拆解污染修复区只有叶菜中可检

图1 研究区蔬菜PCBs污染水平与组成特征(拆解污染修复区地下根茎类和豆类样品中PCBs未检出)

Figure 1 The pollution level and characteristic of PCBs in vegetables in study areas (PCBs in underground rhizome and legume samples were not detected)

出,非拆解对照区以豆类蔬菜中PCBs浓度最高.拆解污染区蔬菜中PCBs浓度高于赵冰峰等人^[20]和Xing等人^[21]调查的台州蔬菜PCBs污染水平;非拆解对照区和拆解污染修复区蔬菜PCBs污染水平相比于国内其他非拆解污染区^[22],处于较高污染水平.

进一步对蔬菜可食部分中PCBs同系物组成进行分析.研究区3类蔬菜中PCBs污染均以二氯到四氯代同系物为主,但非拆解对照区中豆类蔬菜的高氯代同系物比例较高,达46.4%.本研究区蔬菜中PCBs同系物组成与赵冰峰等人^[20]调查的台州卷心菜PCBs同系物组成相似,与贵屿拆解区附近蔬菜中PCBs同系物组成差异较大(五氯到七氯代为主)^[23].

2.2 土壤和大气中PCBs污染水平与组成特征

对研究区农田土壤PCBs污染水平进行分析,发现拆解污染区、拆解污染修复区和非拆解对照区土壤PCBs平均浓度分别为315.90, 19.31和10.80 ng/g(图2).本研究区土壤PCBs污染水平高于Ren等人^[24]报道的全国土壤PCBs污染水平.拆解污染区农田土壤PCBs浓度显著高于其他两个区域($P<0.05$).经微生物修复后,拆解污染修复区土壤PCBs浓度显著降低且与非拆解对照区无显著差异($P>0.05$).本研究区域土壤PCBs浓度低于毕新慧等人^[25]测得的浙江东南某拆解区稻田土壤,高于广州贵屿拆解区露天燃烧点土壤PCBs浓度^[26].

对土壤中PCBs同系物进行分析,发现拆解污染区农田土壤PCBs以低氯代同系物为主,比例达78.5%;拆解污染修复区和非拆解对照区土壤PCBs均以高氯代同系物为主.表明拆解污染区土壤生物可降解性高,而拆解污染修复区和非拆解对照区土壤生物可降解性差.拆解污染区PCBs分布情况与台州温岭拆解区土壤PCBs分布特征一致^[27],拆解污染修复区和非拆解对照区土壤PCBs组成与全球背景土壤PCBs同系物分布情况相近^[24].

对研究区域大气PCBs污染水平进行分析,发现拆解污染区大气PCBs浓度为103.59 ng/m³,其中气相PCBs浓度为37.76 ng/m³,颗粒相为65.83 ng/m³.拆解污染修复区大气PCBs浓度为35.40 ng/m³,气相和颗粒相分别为28.41和6.99 ng/m³.非拆解对照区大气PCBs浓度为13.69 ng/m³,气相和颗粒相分别为8.22和5.47 ng/m³.拆解污染修复区与拆解污染区毗邻,其大气PCBs污染仍处于较高污染水平.本研究区空气PCBs污染高出Zhang等人^[28]研究报道的全国大气PCBs污染水平1~2个数量级,高于Li等人^[29]调查的台州大气PCBs浓度.也远高于国外其他城市大气PCBs浓度,如美国北卡罗莱纳州大气PCBs浓度为2.0 ng/m³^[30],意大利罗马大气PCBs为1.9~5.4 ng/m³^[31].

进一步分析研究区域大气中PCBs同系物组成,拆解污染区大气中气相与颗粒相PCBs同系物以三、四氯代为主,拆解污染修复区和非拆解对照区中大气

图2 研究区土壤与空气中PCBs污染水平与特征

Figure 2 The pollution level and characteristic of PCBs in the farmland soil and the air in study areas

颗粒相以三、四、七氯代同系物为主. 我国城市大气PCBs以四氯到六氯代同系物为主; 邓绍坡等人^[32]发现某电子垃圾拆解区大气PCBs中低氯代所占比超过70.0%; 我国贵屿拆解区大气PCBs也以三、四氯代为主, 且颗粒相中高氯代比例较高^[33].

对土壤和大气PCBs污染水平和特征进行比较, 发现大气PCBs污染浓度与土壤PCBs污染浓度具有一致性, 且大气PCBs同系物组成与土壤PCBs同系物组成相似. 大气PCBs污染可能源于土壤, 土壤PCBs可通过挥发作用影响大气中PCBs浓度和组成.

2.3 灌溉水PCBs污染水平与组成特征

灌溉水PCBs污染水平分析结果表明, 拆解污染区(拆解污染修复区)水样PCBs平均浓度为16.25 ng/L, 非拆解对照区水样PCBs平均浓度为10.78 ng/L(图3), 拆解污染区水体PCBs污染水平略高于非拆解对照区, 与我国主要流域水体PCBs污染水平(0.01~900 ng/L)相比^[34], 处于中等水平. 但高于国外一些河流水体, 如英国Humber河口水样PCBs为1.0 ng/L, 日本东京湾水体PCBs浓度为0.04~0.64 ng/L^[35,36].

分析比较水样中PCBs同系物组成, 研究表明所采集的水样中PCBs均以六氯代同系物为主, 高氯代

占总量的66.5%~99%. 可能是因为土壤中的高氯代PCBs不易降解、挥发而容易吸附在土壤颗粒中, 经雨水冲刷进入河流, 蓄积于底泥, 从而进一步影响水体中PCBs含量和组成. 张祖麟等人^[37]发现厦门港沉积物和表层水体中PCBs污染水平和特征一致. 因此, 灌溉水中PCBs可能是由底泥解吸而来.

2.4 蔬菜、土壤、大气中PCBs污染水平与同系物分布相关性

对蔬菜可食部分、土壤和大气中PCBs污染水平进行分析(图4~6), 总体上, 蔬菜中PCBs污染水平与农业种植环境介质中PCBs污染水平相关联. 各研究区域叶菜和地下根茎类蔬菜可食部分的PCBs污染水平与种植区土壤和大气中PCBs污染水平高低一致. 豆类可食部分中PCBs浓度与种植区土壤和大气中PCBs浓度相比, 无明显规律.

对研究区叶菜可食部分、根际土、非根际土、大气气相、大气颗粒相中PCBs同系物分布特征进行比较. 由图4可知, 叶菜中PCBs同系物组成与大气气相和大气颗粒相中PCBs同系物组成相似, 均以低氯代同系物为主. 表明叶菜受大气的直接影响较大. 赵冰峰等人^[20]研究也表明卷心菜中PCBs污染受大气吸收

图3 研究区灌溉水样PCBs污染水平与特征

Figure 3 The pollution level and characteristic of PCBs in the irrigation water in study areas

图4 (网络版彩色)叶菜、根际土、非根际土及大气中PCBs污染水平与特征

Figure 4 (Color online) The pollution and distribution of PCBs in leafy vegetables, rhizosphere soil, non-rhizosphere soil and the air

图5 (网络版彩色)地下根茎类、根际土、非根际土及大气颗粒相中PCBs污染水平与特征(拆解污染修复区地下根茎样品中PCBs未检出)

Figure 5 (Color online) The pollution and distribution of PCBs in underground rhizome vegetables, rhizosphere soil, non-rhizosphere soil and atmospheric particle phase (PCBs in underground rhizome samples was not detected)

和颗粒沉降影响大。叶菜中PCBs同系物与根际土中PCBs同系物差异较大,根际土中PCBs以高氯代同系物为主,可能是因为叶菜土壤根际微生物降解了大量的低氯代PCBs。叶菜中PCBs同系物与非根际土中PCBs同系物差异较大,可能表明叶菜中PCBs主要不是来源于对土壤中PCBs的直接吸收,邓绍坡等人^[38]研究也表明植物体内PCBs来自土壤的比例很小。Moeckel等人^[39]通过控制实验证实了植物能通过角质层从大气吸收PCBs。Zuo等人^[40]用隔离实验证明了植物叶片中的PAHs主要来自于空气。因此,叶菜中

PCBs污染可能主要受大气的影。

对研究区域地下根茎类蔬菜可食部分、根际土、非根际土和大气颗粒相中PCBs同系物组成进行分析。结果表明(图5),地下根茎类蔬菜中PCBs同系物与根际土中PCBs同系物有很大相似性;地下根茎类蔬菜与非根际土中PCBs同系物分布有较大差异。Azza等人^[41]也发现胡萝卜与土壤的PCBs污染特征一致,张淑贞等人^[42]通过温室种植实验表明小麦可从土壤中吸收PAHs。表明地下根茎类中PCBs可能主要来源于根际土壤中PCBs的吸收。

图6 (网络版彩色)豆类、根际土、及大气中PCBs污染水平与特征(拆解污染修复区豆类样品中PCBs未检出)
Figure 6 (Color online) The pollution and distribution of PCBs in legume vegetables, rhizosphere soil, and the air (PCBs in legume samples was not detected)

进一步对研究区豆类蔬菜可食部分、根际土、大气气相、大气颗粒相中PCBs同系物组成进行分析(图6). 结果表明, 豆类蔬菜中PCBs同系物与根际土、大气气相和大气颗粒相中PCBs同系物组成均相似, 表明豆类蔬菜中PCBs来源较为复杂. 豆类蔬菜油脂占到总量的16%~20%, PCBs具有很强亲脂性, 容易在豆类蔬菜内累积, 且豆类根部有根瘤菌共生, 研究表明, 有根瘤的植物, 其根部和体内PCBs含量显著提高^[43].

2.5 暴露及健康风险评估

对研究区居民通过食用当地蔬菜而暴露于PCBs的致癌风险和非致癌风险进行评估, 见表1~2. 结果表明, 拆解污染区中居民摄入蔬菜的平均致癌风险

为 1.01×10^{-4} , 非致癌风险为2.54; 拆解污染修复区中摄入蔬菜的平均致癌风险为 3.06×10^{-5} , 非致癌风险为0.76; 非拆解对照区中摄入蔬菜的平均致癌风险为 6.19×10^{-6} , 非致癌风险为0.16. 拆解污染区和拆解污染修复区均以摄入叶菜类蔬菜的致癌风险和非致癌风险最高, 该研究区域农田蔬菜中PCBs污染对人体健康存在较大风险.

拆解区居民PCBs食物暴露途径健康风险与该地拆解方式、拆解物类型及食物来源、种类等有关, 朱晓楼^[9]发现浙江某拆解区蔬菜样品的致癌风险为 5.52×10^{-7} . 王慧芬^[44]测得台州蔬菜样品中PCBs致癌风险水平为 $1.32 \times 10^{-5} \sim 5.06 \times 10^{-5}$, 非致癌风险大于1.25. Shen等人^[45]发现龙门蔬菜PCBs的非致癌风险为0.73.

表1 蔬菜样品PCBs暴露量和致癌风险水平
Table 1 The exposure and cancer risk of PCBs in vegetable samples

采样点	样品	IR(g/d)	PCBs浓度(ng/g)	LADD(mg/(kg d))	风险值
拆解污染区	叶菜类	131.76	551.49	4.88×10^{-5}	9.77×10^{-5}
	地下根茎类	49.59	33.04	1.10×10^{-6}	2.20×10^{-6}
	豆类	4.2	101.52	8.60×10^{-7}	1.72×10^{-6}
	总量	185.55	—	—	1.01×10^{-4}
拆解污染修复区	叶菜类	131.76	172.06	1.52×10^{-5}	3.05×10^{-5}
	地下根茎类	49.59	1.43	4.76×10^{-8}	9.53×10^{-8}
	豆类	4.2	1.43	1.21×10^{-8}	2.42×10^{-8}
	总量	185.55	—	—	3.06×10^{-5}
非拆解对照区	叶菜类	131.76	25.96	2.30×10^{-6}	4.60×10^{-6}
	地下根茎类	49.59	4.38	1.46×10^{-7}	2.92×10^{-7}
	豆类	4.2	76.61	6.49×10^{-7}	1.30×10^{-6}
	总量	185.55	—	—	6.19×10^{-6}

表2 蔬菜样品PCBs暴露量和非致癌风险水平

Table 2 The exposure and non-cancer risk of PCBs in vegetable samples

采样点	样品	IR(g/d)	PCBs浓度(ng/g)	LADD(mg/(kg d))	危害商
拆解污染区	叶菜类	131.76	551.49	4.88×10^{-5}	2.44
	地下根茎类	49.59	33.04	1.10×10^{-6}	0.06
	豆类	4.2	101.52	8.60×10^{-7}	0.04
	总量	185.55	—	—	2.54
拆解污染修复区	叶菜类	131.76	172.06	1.52×10^{-5}	0.76
	地下根茎类	49.59	1.43	4.76×10^{-8}	0.002
	豆类	4.2	1.43	1.21×10^{-8}	0.0006
	总量	185.55	—	—	0.76
非拆解对照区	叶菜类	131.76	25.96	2.30×10^{-6}	0.12
	地下根茎类	49.59	4.38	1.46×10^{-7}	0.007
	豆类	4.2	76.61	6.49×10^{-7}	0.03
	总量	185.55	—	—	0.16

3 结论与建议

(1) 拆解污染区蔬菜中PCBs平均浓度高达228.68 ng/g, 以叶菜类蔬菜中PCBs浓度最高。经修复后, 蔬菜中PCBs平均浓度为58.31 ng/g, 与非拆解对照区持平。蔬菜中PCBs污染均以低氯代同系物为主。

(2) 拆解污染区农田土壤以低氯代PCBs为主, 生物可降解性高; 拆解污染修复区土壤以高氯代PCBs残留为主。拆解污染区大气PCBs平均浓度远高于拆解污染修复区和非拆解对照区; 以低氯代同系物为主, 而高氯代PCBs则在颗粒相中较为显著。拆解污染区、拆解污染修复区及非拆解对照区灌溉水PCBs污染水平较低, 且均以六氯代同系物为主。

(3) 蔬菜中PCBs污染主要来源于土壤和大气,

叶菜类受大气直接影响较大, 地下根茎类受土壤直接影响较大, 豆类蔬菜中PCBs来源较为复杂, 需进一步探究。

(4) 拆解污染区和拆解污染修复区中居民通过摄取蔬菜暴露PCBs的致癌风险分别为 1.01×10^{-4} 和 3.06×10^{-5} , 均高于可接受致癌风险水平1~2个数量级。拆解污染区非致癌风险为2.54, 高于可接受风险水平。研究区以叶菜类蔬菜致癌风险和非致癌风险最高。

(5) 建议当地政府加强对含PCBs废物的管理, 切断污染源; 调整种植结构, 特别是停止种植叶菜类; 或采取替代种植, 改种对PCBs低富集的蔬菜品种; 进行全区域多介质的PCBs污染控制与修复。

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Summary for “电子电器废弃物拆解区蔬菜多氯联苯污染及其健康风险”

The pollution and health risk of polychlorinated biphenyls in vegetables in e-waste recycling pollution area

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Polychlorinated biphenyls (PCBs) are one of the typical persistent organic pollutants, which have carcinogenicity, neurotoxicity and endocrine disrupting effects. Due to the crudely electronic waste (e-waste) recycling, the environment in study area was seriously polluted by PCBs. It posed a threat to human health by environmental and dietary exposure. According to our previous survey, the proportion of vegetables in the dietary structure of local residents was very large, and the vegetables were contaminated by PCBs. Samples of farmland vegetables, soil, air, and water were collected from e-waste recycling pollution area, remediated area and non-dismantling control area. By determining and comparing the pollution levels and characteristics of PCBs in these samples, the source of PCBs in vegetables was analyzed. With the help of US EPA risk assessment model, the health risks of residents exposed to local vegetables with PCBs contaminated were assessed. The results showed that the average concentrations in three researching areas were 226.68, 58.31 and 35.65 ng/g. Among them, the PCBs pollution in leafy vegetables was significantly higher than that in underground rhizomes and legumes. The di-chlorinated to tetra-chlorinated congeners occupied largest proportion in the vegetables. The average PCBs concentration of farmland soil samples in e-waste recycling pollution area was 315.90 ng/g, and the main PCB homologs were lower chlorinated. The average PCB concentrations of air in three area were 103.59, 35.40 and 13.69 ng/m³, and the lower chlorinated congeners occupied largest proportion. There was no significant difference of the PCB levels between different irrigation water samples from e-waste recycling pollution/remediated area and non-dismantling control area. Atmospheric deposition and soil absorption were the potential sources of PCBs in vegetables. Risk assessment indicated that the lifetime excess carcinogenic risk and non-carcinogenic risk for residents in recycling pollution area were 1.01×10^{-4} and 2.54, both of them were higher than the acceptable risk level. The local restrictions on vegetable cultivation and the planting structure adjustment were suggested.

polychlorinated biphenyls, vegetables, soil, air, irrigation water, health risk

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