ISSN 1000-0933
CN 11-2031/Q

生态学报

Acta Ecologica Sinica

第32卷 第1期 Vol.32 No.1 2012

中国生态学学会
中国科学院生态环境研究中心 主办
科学出版社 出版

中国科学院科学出版基金资助出版

生 态 学 报

(SHENGTAI XUEBAO)

第 32 卷 第 1 期　　2012 年 1 月　(半月刊)

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专论与综述

研究简报

期刊基本参数:CN 11-2031/Q * 1981 * m * 16 * 332 * zh * P * ¥70.00 * 1510 * 36 * 2012-01

封面图说: 白鹭展翅为梳妆,玉树临风巧打扮——这是大白鹭繁殖期时的美丽体态。大白鹭体羽全白,身长 94—104cm,寿命 20 多年。是白鹭中体型最大的。繁殖期的大白鹭常常在湿地附近的大树上筑巢,翩翩飞舞吸引异性,其繁殖期背部披有蓑羽,脸颊皮肤从黄色变成兰绿色、嘴由黄色变成绿黑色。大白鹭是一个全世界都有它踪迹的广布种,一般单独或成小群,在湿地觅食,以小鱼、虾、软体动物、甲壳动物、水生昆虫为主,也食蛙、蝌蚪等。

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DOI: 10.5846/stxb201011091604
汪青. 土壤和沉积物中黑碳的环境行为及效应研究进展. 生态学报,2012,32(1):0293-0310.
Wang Q. A review of the environmental behavior and effects of black carbon in soils and sediments. Acta Ecologica Sinica,2012,32(1):0293-0310.

土壤和沉积物中黑碳的环境行为及效应研究进展

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摘要:土壤和沉积物是全球黑碳排放的主要归宿,土壤和沉积物中黑碳具有复杂的环境行为和环境效应。分析了黑碳的概念,指出应以环境意义为出发点去理解黑碳概念的丰富内涵;描述了黑碳形成过程及其对黑碳理化性质的影响,以及基于此的黑碳分类;总结了黑碳来源辨析的若干种常用方法;讨论了黑碳在土壤/沉积物与其他环境介质之间的迁移循环过程,以及在土壤和沉积物内部的迁移行为;探讨了土壤和沉积物中黑碳的降解行为与稳定性,及其与地-气碳氮温室气体通量、土壤稳定碳库的关系,以及在土壤碳循环模型中的作用;综述了土壤和沉积物中黑碳对有机物、重金属和营养盐的吸附行为及主要机制;提出了今后研究的主要方向,以供相关研究者参考。

关键词:黑碳;分类;来源辨析;分布迁移;降解;吸附机制

A review of the environmental behavior and effects of black carbon in soils and sediments

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Abstract: Soils and sediments are major global sinks of black carbon (BC). BC in soils and sediments has complex environmental behaviors and effects. Because of its ability to resist decomposition, BC captures and sequesters carbon from the bio-atmospheric cycle, which, in the long term, reduces greenhouse gas emissions and thus mitigates the greenhouse effect. Meanwhile, resistant BC adds organic matter to soils, thus enhancing soil fertility. Because of its high adsorption capacity, BC adsorbs organic pollutants, heavy metals, and nutrients thus decreasing pollution risks and further enhancing soil fertility. Based on analysis of the concept of BC, it is concluded that BC should be studied in the context of its environmental effects. Variation in the formation of BC leads to its varied properties and classification. Several frequently used methods for identifying sources of BC are summarized. $\Delta^{14}C$ and stratigraphic analysis can be used to identify BC sources (biomass, fossil fuel or rock); $\delta^{13}C$ analysis can distinguish between C3 and C4 plant sources, and fresh water and ocean organisms; particle size analysis can identify local and exotic sources; while analysis of the ratio of polycyclic aromatic hydrocarbon (PAH) isomers, the ratio of BC to total organic carbon, the ratio of benzene polycarboxylic acids, and morphological properties can identify biomass and fossil fuel sources. Transfers of BC between soils/sediments and other pools as well as those within soil and sediment pools are discussed. Global BC reserves in pools and the fluxes between pools are estimated, and it is noted that dissolved BC eroded from soils and transferred by rivers is an important part of the BC global cycle. Decomposition and stability of BC in soils and sediments are discussed in relation to fluxes of greenhouse gases between the land surface and atmosphere, the stable carbon pool in soils, and carbon cycle models in soil.

基金项目:国家自然科学基金项目(41101502, 41001369); 安徽省高等学校优秀青年人才基金项目(2011SQRL028ZD); 自然地理学省级重点学科和安徽师范大学国土资源与旅游学院科研团队资助项目(Asdgl104, Asdgl0903)

收稿日期:2010-11-09;　**修订日期**:2011-05-03

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Especially, coupled mineralization between BC and native or added labile organic carbon in soil is introduced, and adsorption and related mechanisms of organic matter, heavy metal and nutrient retention by BC in soils and sediments are also summarized. Three adsorption mechanisms of PAHs by BC are described: adsorption on surfaces, capture in micropores, and occlusion inside the BC structure. Correlations between BC and PAH concentrations should not be simply explained as a result of adsorption, since environmental adsorption of PAHs by BC is affected by complex factors. Finally, some future directions in BC research are recommended. More fundamental surveys of BC concentrations and its distribution in different kinds of soils/sediments in different areas are needed. More studies should concentrate on key processes related to the stability of BC in soils/sediments such as coupled mineralization between BC and labile organic carbon, losses of particulate and dissolved soil BC, and transformations between BC and other forms of stable carbon in soil. More studies are also needed on BC's specific surface area, porosity, functional groups, and surface morphology, and their roles in the environmental behavior of BC, with a change from concentration measurements or correlation analysis to mechanistic analysis. More application studies should focus on the possibility of applying manufactured BC as part of agricultural management.

Key Words: black carbon; classification; source identification; transference; decomposition; adsorption mechanism

全球每年产生的黑碳中,有 80%—90% 进入到土壤和沉积物[1],并广泛分布于大气、冰雪、水体等环境介质中[2-4]。黑碳在不同环境介质中具有不同的环境行为,表现出不同的环境效应。大气中的黑碳能通过吸热增温[5]和改变云量[6]影响气候和天气,通过形成光化学烟雾和臭氧[2]影响大气质量,通过携带有害物质并进入人体[7]危害人体健康。冰雪中的黑碳能通过降低冰雪反射率[3]影响气候。与这些大体消极的环境效应不同,土壤和沉积物中黑碳往往表现出积极的环境效应。首先,由于其超强的抗降解能力,黑碳可以将从生物-大气碳循环中捕获的碳贮存起来,长期看来可减少大气中温室气体含量以减缓温室效应[8-9];同时增加土壤中有机质含量以提高土壤肥力[10-11]。其次,由于其超强的吸附能力,黑碳可以吸附有机污染物[12]与重金属[13]以降低污染物的环境风险;可以吸附营养盐[14]以增加土壤肥力。此外,土壤与沉积物中的黑碳被认为是全球碳循环中"丢失的碳库"[15];并被用来指示历史火事件[16]。本文首先阐述黑碳的概念、形成与分类、来源与辨析,并在此基础上综述土壤和沉积物中黑碳的迁移、降解和吸附等环境行为及环境效应等方面近年来国内外研究所取得的认识,最后探讨了今后进一步努力的方向。

1 黑碳的概念

黑碳是生物质或化石燃料不完全燃烧[17]或者岩石风化[18]的产物。生物质不完全燃烧产生的黑碳包括一系列物质,如轻微炭化的生物质、炭化物质、木炭、烟炱、石墨态黑碳[19-21]。其中烟炱也可能由化石燃料不完全燃烧产生[17];石墨态黑碳也可能由含石墨岩石风化产生[18]。

尽管这些不同形式的黑碳具有一些共性,如富含碳元素、以芳香结构为主[19]等,但是黑碳的理化性质往往表现出很明显的异质性,如粒径在数毫米到数十纳米之间[19],比表面积在每克数平方米到数百平方米之间[22-23],H/C、O/C 和 N/C 比值的变异也很大[24-25]。由于黑碳的异质性,在不同研究领域中其被关注的侧重点亦不同,有时候被关注的是黑碳的整体,但大多数时候是其中的某一组分或属性,文献中所使用的名称也因此而各异。如大气科学关注其吸光性[26],把它叫做元素碳(元素碳可能包括一些来自类腐殖质、生物气溶胶或焦油的非黑碳物质[27]);生物地球科学关注其火成因,称之为火成碳[28];全球有机碳循环研究关注其抗氧化性,称它为稳定的碳[29],而污染物环境科学关注其吸附性,称它为活跃的碳[30]。土壤和沉积物中的相关研究则倾向于使用黑碳一词,但主要是指木炭和烟炱[31]。工程材料科学中[32]的炭黑指的是碳含量更多、杂质更少、理化性质更确定的一种工业产品,不同于烟炱[33],但是按照 Goldberg 的黑碳定义[17],也可归属于黑碳;另一种常见工业产品活性炭从本质上说是经活化处理的黑碳;近年来备受关注的生物质炭也属于黑碳的一种类型[8,34]。

造成概念和术语不统一的另一个原因在于,许多研究实际上是基于分析方法来定义黑碳的。不同的方法所得到的物质不一样,其环境意义也不一样,如化学高温氧化法[35]、重铬酸盐氧化法[36]及次氯酸钠氧化法[37]、紫外光氧化法[38]所得黑碳分别指的是样品中能抵抗高温氧化、化学氧化、光氧化的物质;显微镜法[39]所得黑碳指的是样品中粒径较大、在光学显微镜下可识别的黑色木炭部分;苯多羧酸(benzene polycarboxylic acid, BPCA)法[40]所得黑碳指的是样品中能被硝酸氧化为苯多羧酸的具芳香结构的物质;热光透射/反射法[41]所得黑碳指的是样品中能吸光的物质。对于氧化法和显微镜法分离所得黑碳的含量测定也有不同方法,如元素分析法测定的是黑碳样品中的碳元素含量;^{13}C 核磁共振波谱法[42]和中红外光谱法[43]测定的是黑碳样品中的稠环芳香烃含量。

为消除这种认识上的不统一,有人开始对黑碳分析方法进行综合对比以寻求标准化方法[44],但后来人们意识到或许并不存在一个万能的、通用的黑碳分析方法[45]。本文认为,此问题的解决可以从黑碳的环境意义入手,黑碳的某些特定环境效应源于黑碳某种特定组分或性质,而不同的分析方法正是针对黑碳的特定组分或性质而设计的,如黑碳的热辐射效应源于其吸光吸热性,相应地就应当用热光透射/反射法;黑碳指示局地历史火事件的依据是粗颗粒的木炭,就应当用显微镜法;黑碳的生物地球化学循环与其稳定性有关,就应当用氧化法或者是能揭示芳香结构含量的 BPCA 法;黑碳的吸附性取决于其表面物理化学性质,就应当结合其比表面积、孔隙度、官能团密度等性质进行研究,而不仅仅是量的多少。这样,在黑碳的大框架之下,根据不同的研究目的选择不同的方法,从不同角度来研究黑碳,有利于研究的深入。当然,为了便于交流,研究者应当明确其所使用的黑碳概念的范畴并加以说明。

2　黑碳的形成与分类

2.1　黑碳的形成

黑碳的形成过程决定了黑碳的理化性质,主要因素有热解过程中最高温度和原料性质。

最大热解温度(highest treat temperature, HTT)是影响黑碳性质的重要因素。Antal 等[46]和 Paris 等[47]揭示了以生物质为原料的黑碳形成的化学过程,热解温度在 120 ℃到 300 ℃之间,羧基及羧基功能团形成并分裂成 CO_2 和 CO,同时发生脱水反应,产生的黑碳主要是炭化物质;300 ℃到 600 ℃之间,焦油形成并挥发,产生的黑碳主要是多孔的木炭;600 ℃以上发生碳化,表现为非碳原子去除,芳香的石墨烯连成整体,这时产生的黑碳以烟炱为主;超过 1000 ℃,位于石墨烯边缘的阻碍石墨烯规则排列的含氧功能团有可能被彻底去除,就形成了石墨态黑碳[48]。

原料性质能影响火焰中烟炱的形成途径,对于脂族化合物,烟炱的前体物质是乙炔和多炔。而对于芳香族化合物,还有另外一种途径,即芳香环直接浓缩聚合成多环芳烃(polycyclic aromatic hydrocarbons, PAHs)直至烟炱:小的芳香环交叉连接,形成石墨烯,石墨烯无秩序排列形成烟炱[49]。但是最新研究发现构成烟炱的不单是六环的石墨烯,还有五环和七环的富勒烯[50],考虑了富勒烯的模型能更好地模拟烟炱的多孔性和强吸附性。

一般认为,随着 HTT 升高,黑碳的碳含量、芳香程度、吸附能力也相应增加[51-52],但是表面积的变化较为复杂,Pulido-Novicio 等[53]发现,加热生物质产生的焦油会堵塞一部分已经形成的微孔,随着温度升高,焦油挥发掉,这些微孔得以清空,所以表面积升高之前有一个小的低值。Lua 等[54]实验表明,热解温度从 250 ℃增加到 500 ℃,表面积增大,微孔直径增大,但是随着温度进一步升高,黑碳的表面积反而降低[55],其原因可能是高温下相邻微孔的壁被破坏,合并成更大的孔,造成微孔直径增大而表面积下降[56]。

2.2　黑碳的分类

由于成因上的不同,可将纷繁复杂的黑碳分成两大类:残渣态黑碳和浓缩态黑碳[45],前者包括炭化物质和木炭(统称为 CBC),后者包括烟炱和石墨态黑碳(统称为 GBC)[57]。也有学者把烟炱和石墨态黑碳再分开,共分成 3 类[20]。有的文献中 GBC 专指石墨态黑碳[58],并认为其包括烟炱和石墨。本文认为将烟炱归属于石墨态黑碳是不妥的,因为烟炱由石墨烯不规则排列组成,与石墨的规则排列不同,因而属于非石墨态碳。

Joseph 等[59]提出了一种基于黑碳理化性质的分类方法,考虑的因素依次是碳含量、易降解碳含量、表面积和孔隙度、阳离子交换量和官能团。

表 1 残渣态黑碳和浓缩态黑碳的成因及理化性质差异

Table 1 Formation, physical and chemical properties of residual and condensate black carbons

		残渣态黑碳 Residual black carbon	浓缩态黑碳 Condensate black carbon	参考文献 References
形成过程 Formation	成因	固体燃烧物质热解残留而成	燃烧生成气体中的碳浓缩聚合而成	[45,57]
	形成温度	低(<600 ℃)	高(>600 ℃)	[47-48]
物理性质 Physical properties	粒径	大(cm 至 μm)	小(μm 至 nm)	[19]
	BET 比表面积[a]	大(1.3—776 m^2/g)	小(3.6—127 m^2/g)	[60-61]
	平均孔隙直径[b]	小(2.8 nm)	大(9.9—19.5 nm)	[56,60]
化学性质 Chemical properties	元素组成	H/C:0.16—1.52 O/C:0.11—0.72 N/C:0.0016—0.14	H/C:0.1—0.69 O/C:0.08—0.33 N/C:0.016—0.07	[25,62-63]
	官能团	多(0.26—3.02 mmol/g)	少	[61],[63]
	芳香程度	低	高	[51]

a:有研究发现使用氮气的标准 BET 法不能检测孔径小于 2 nm 的微孔表面积,但是用二氧化碳法则能检测出浓缩态黑碳如烟炱有很大的微孔表面积[22,64]; b:不包含<2 nm 的孔隙

3 黑碳的来源与辨析

3.1 黑碳的来源

黑碳的来源一般从 3 个方面讨论。一是类型来源:可分为天然源(包括岩石风化、生物质燃烧)和人为源(包括生物质燃烧、化石燃料燃烧);生物质源又可分为浮游生物、C3 植物、C4 植物等。二是时间来源:可分为现代源、历史源。三是空间来源:可分为陆源、海源;或者是本地源、外来源。

3.2 黑碳来源辨析方法

3.2.1 $\Delta^{14}C$ 分析结合地层年代分析,可辨析生物质源、化石燃料源、岩石源。现代生物质燃烧产生的黑碳中的^{14}C 浓度与现代大气中的值相当,$\Delta^{14}C$ 相应较大,近于 0‰;化石燃料源和岩石源的黑碳中几乎不含^{14}C,$\Delta^{14}C$相应较小,近于-1000‰[18,65-66]。工业化之前的地层中若出现 $\Delta^{14}C$ 很小的黑碳,则可认为是来源于岩石风化[58,67]。利用同位素质量平衡模型可进一步计算出生物质源和化石燃料源各自所占百分比[68]。

3.2.2 $\delta^{13}C$ 分析,可辨析陆地 C3 植物源、C4 植物源以及淡水生物源、海洋生物源。已有的研究表明,C3 和 C4 植物的 $\delta^{13}C$ 的变化范围分别在-22‰—-34‰和-9‰—-19‰之间[69],淡水藻与海水藻 $\delta^{13}C$ 分别在-27‰—32‰和-17‰—-28‰之间。基于生物的^{13}C 丰度在死后保持不变这一假设,通过测定黑碳的 $\delta^{13}C$,可以区分其来源于哪一类生物[18,70]。

3.2.3 粒径分析,可辨析本地源、外来源;粒径分析结合密度分析,可辨析 GBC 的燃烧源、岩石源。由于不同粒径的搬运能力有差异,一般来说,较大粒径如毫米级的黑碳基本源自百米范围之内[71],而更小粒径的黑碳反映的是区域范围内大气背景值。Dickens 等[58]把细而轻(<3 μm、<2 g/cm^3)的 GBC 归于燃烧产生的烟炱,把粗而重(3—63 μm、>2 g/cm^3)的归于岩石风化产生的石墨。

3.2.4 多环芳烃(PAHs)分析,可辨析生物质源、化石燃料源。这是基于 PAHs 与黑碳的同源性(二者都与不完全燃烧紧密联系)和共生性(黑碳大量吸附同源的 PAHs),所以 PAHs 来源辨析的结论可应用到黑碳尤其是浓缩态黑碳的来源分析上[24]。Mitra 等[72]使用 b[*a*]a/chry、b[*b*]f/b[*k*]f、b[*a*]p/b[*e*]p 等几种 PAHs 异构体比率,分析得出密西西比河口颗粒黑碳中的 27% 来自化石燃料的使用。

3.2.5 形态特征分析,可辨析生物质源、化石燃料源。Fernandes 等[73]和 Brodowski 等[74]分析了镜下黑碳颗粒的形态和表面纹理,认为燃油黑碳呈球形,质地均匀;燃煤黑碳呈多孔的球形或者不规则形状;生物质黑碳

呈长形或不规则形状,有细胞和纤维等结构残留,表面光滑,边缘棱角清晰。

3.2.6　黑碳/有机碳(BC/OC)比值分析,可辨析生物质源、化石燃料源。大气气溶胶中 BC/OC 比值可以反映黑碳来源,比值在 0.1 左右反映生物质燃烧,比值在 0.5 左右为化石燃料燃烧[75-76]。在城市土壤和杉木林土壤中也存在这种区分[77-78]。

3.2.7　BPCA 比值分析,可辨析生物质源和化石燃料源的比例大小。Brodowski 等[79]假设化石燃料源黑碳的芳香程度高于生物质源的,并且被 HNO_3 氧化后的 BPCAs 中羧酸团数量也更多,先计算只有生物质源黑碳土壤的 B4CAs/B6CA 和 B5CAs/B6CA 比值,再将比值乘以混合源黑碳土壤中的 B4CAs 和 B5CAs 含量,即可得到生物质源黑碳在混合源中的比例。

运用上述方法时,需考虑黑碳的新鲜程度和运输方式,因为氧化过程和累积过程可能会影响来源辨析的准确性,如进入到土壤中的黑碳可能与矿物结合,形态变得更加复杂,而 BC/OC 比值偏高有可能是黑碳稳定性的反映[80]。为了得到可靠的结论,往往需要综合运用几种方法。

4　土壤和沉积物中黑碳的循环与迁移行为

4.1　土壤/沉积物与其他环境介质之间的全球循环

黑碳每年产生量约为 50—270 Tg,其中化石燃料燃烧产生的约 12—24 Tg 黑碳几乎全部排入到大气中[81];生物燃烧产生的黑碳也有 5—6 Tg[49]进入大气,而进入土壤中的则有 40—241 Tg[81]。大气和土壤中的黑碳有可能通过干湿沉降或扬尘等途径再次分配。大气和土壤中的黑碳按各自方式被输送到海洋中,最后沉积于海底并进入成岩过程。大气中的黑碳颗粒主要是烟炱,每年有约 7 Tg 黑碳通过干湿沉降(以湿沉降为主,占 73%—95%)进入海洋颗粒有机物(POM)[82],其中近海沉降 1.35—5.38 Tg,远海沉降 2.40—4.74 Tg。外流河流域内土壤黑碳颗粒可经河流输入到海洋中,年输送量约 12—20 Tg 黑碳[1,82],其中 10 Tg 黑碳进入海洋沉积物,这其中的 90% 沉积在近海,10% 沉积在远海[82]。沉积变质岩石抬升出露地表接受风化产生的黑碳还会重新进入上述循环,但这个过程相当漫长,几乎可以忽略。

以上海陆气之间的黑碳交换量都是基于颗粒态的,近年来,溶解有机物(DOM)中的黑碳越来越受到重视,被认为是黑碳全球循环中的重要一环,可能是进入最终沉积过程前的一个重要中间库。大气中的黑碳颗粒是河流中 DOM 的重要来源之一[83],大气中烟炱可经臭氧氧化而具有水可溶性[84],通过降水进入水体 DOM。土壤中的黑碳也能够进入河流 DOM 中,Kim 等[85]发现河水中的贫氢分子,证明 DOM 中存在黑碳,含有黑碳的土壤渗滤液是水体 DOM 的重要来源[80]。全球河流通过 DOM 形式向海洋每年输送的黑碳总量,若根据有机碳总量和黑碳浓度估算,其数值约为 10 Tg(表 2),而颗粒态与溶解态黑碳之间的转换通量目前还不清楚。

表 2　黑碳全球循环通量

Table 2　Global cycle and fluxes of black carbon

输送途径 Fluxes between pools	年通量/(Tg/a) Annual fluxes	参考文献 References
化石燃料燃烧至大气 Emission from fossil fuel burning to atmosphere	12—24	[81]
生物质燃烧至大气 Emission from biomass burning to atmosphere	5—6	[49]
大气沉降至海洋 Deposition from atmosphere to ocean	7±3	[82]
大气沉降至陆地 Deposition from atmosphere to land	3	根据[82],以海陆面积比例推算
生物质燃烧至土壤 Residue of biomass burning into soil	40—241	[81]
土壤经河流至海洋	12.2—20(颗粒态)	[1,82]
Transportation from soil to ocean by river	10(溶解态)	[1,4]
海洋颗粒物至沉积物 Deposition from ocean particle matter to sediment	9(近海),1(远海)	[82]

用两种方法估算主要库的储量,一是库净通量乘以滞留时间,二是库中有机碳储量乘以黑碳浓度。由表3 可知,土壤、大气、海洋等 3 个黑碳库的储量在两种估算方法中比较吻合,而沉积物储量的两个估算结果之间相差较大。

表 3 黑碳主要库储量的估算

Table 3 Estimation of major pools of black carbon

库 Pools	估算方法一 Method A			估算方法二 Method B		
	库净通量/(Tg/a) Net flux	滞留时间/a Residence time	库储量/Pg^A Reserve	库中有机碳储量/Pg Organic carbon reserve	黑碳浓度/(BC/TOC) Black carbon concentration	库储量/Pg Reserve
土壤 Soil	20—200	500—5000[86]	10—1000	1580[1]	10%—40%[86]	160—600
		50—270[66]	7000[66]	350—1900[66]		
大气 Atmosphere	7—20	0.02[87]	0.14—0.4 Tg	5.1×10^8 *	0.31±0.10[89] * *	(0.16±0.05) Tg
海洋 Ocean	10(颗粒态)			25[83]	10%[86]	2.5
	10(溶解态)	<14000[83]	<140	700[1]	4%—22%[83]	28—154
表层沉积物	9(近海)	10000—20000[86]	90—180	150[1]	20%[1]	30
Surface sediment	1(远海)	10000—20000[86]	10—20			
沉积物 Sediment				30000[88](近海)	5%—38%[68]	1500—10000
				1500[66](远海)	12%—31%[83]	180—450

:全球表面积,单位是 km^2; *:单位面积大气柱中的黑碳浓度,单位是 mg/m^2

4.2 区域/流域迁移

Mitra 等[72]认为密西西比河在 1999 年以总悬浮颗粒物的形式向海洋输出了 0.5 Tg 黑碳。Wang 等[68]在长江口和东海陆架的研究表明该区域的黑碳主要来自长江输送,有 60%—80% 来自化石燃料燃烧。Mannino 等[4]发现特拉华河以 DOM 的形式每年向大西洋输送至少 0.024 Tg 黑碳。Masiello 等[90]研究表明流域面积小于 1 hm^2的山区小河圣克莱拉河年输送 5.9×10^{-6}Tg 黑碳,而全球小型河流在运输黑碳的总量上不亚于大型河流;该河中黑碳主要来自古老岩石和土壤的侵蚀而非化石燃料燃烧,有别于大型河流。

4.3 剖面/坡面迁移

Leifeld 等[91]研究得出瑞士 Witzwil 泥炭沼泽土壤由于孔隙度大(可高达 92%),黑碳在垂直方向上迁移速度达每年 0.63—1.16 cm。Major 等[92]在热带沙质氧化土的研究发现,添加混合到 0.1 m 深的黑碳在 2 a 内有 0.45% 移动到 0.15—0.3 m 深度之间,有 0.02% 移动到 0.3 m 深度以下,并认为土壤水分流动和土壤动物扰动是黑碳向深层土壤迁移的动力。Carcaillet[93]发现在亚高山草甸土壤中,冻融和动物掘穴是使木炭碎化并进入矿物层的重要机制。Gavin[94]利用模型研究森林灰化土中木炭如何从有机质层移动到矿物层,认为斜坡崩塌、融冻泥流、生物扰动和树木倒根都是可能的动力。

章明奎等[95]在红壤坡耕地的侵蚀研究表明,与土壤其他有机质相比,黑碳较轻,易被侵蚀。Rumpel 等[96]研究表明在东南亚刀耕火种的热带土壤中的黑碳会沿坡面发生迁移。被侵蚀的黑碳大多会就近堆积,比如在坡面和谷底等地[97,98],但是 Guggenberger 等[99]在苔原永冻土流域发现,黑碳成份更易被河水搬运流失。

5 土壤和沉积物中黑碳的降解行为及环境意义

5.1 黑碳的降解过程

早期黑碳被认为是几乎不可降解的[17],但是近来有许多证据表明黑碳是可以降解的[84],一般认为降解的时间尺度约为数千年[100],也有研究表明其尺度可短至数十年[101]。黑碳降解速率随着时间而显著降低。Major 等添加已知^{13}C 值的黑碳到土壤中培养 2 a 时间,有 2.2% 的黑碳转化为 CO_2排放,其中的 75% 发生在第 1 年[92]。Brodowski 将农作物秸杆黑碳与土壤和石英混合培养半年后,发现黑碳损失 5%—50%,但在接下来的 1 年半时间内不再有损失[102]。Smith 等用^{13}C 示踪法确认添加到土壤中的黑碳在 6 d 以内产生了 CO_2 排

放,但之后停止[103]。这些研究表明,黑碳中的一小部分碳是以易降解的形式存在的。土壤和沉积物中黑碳降解的机制主要包括化学降解[104]和微生物降解[62,105]。物理碎化[93]会造成黑碳粒度变小,从而更易于发生化学氧化。

黑碳初始性质、温度、水分和再次火烧对黑碳降解有重要影响。有的黑碳形成之初就有很多的官能团[106],稳定性相对较低。对于低温制备的松木黑碳,120d 之内降解率为 2%—13%[62],而对于中等温度制备的农作物秸秆黑碳在 6 个月内降解率为 5%—50%[28]。玉米黑碳在水分不饱和的情况下培养 1 a,降解率达 16%,橡树黑碳则在干湿交替情况下矿化率最高,约 12%[107]。Nguyen 等对温度的影响做了研究,随着培养温度从 4 ℃增加到 60 ℃,玉米黑碳降解率从 4%—10% 增加到 20%,但是温度系数(温度每增加 1 ℃黑碳降解率的增加量)随着温度的增加而降低[108]。再次火烧会造成黑碳的损失[109],有研究发现在西伯利亚森林土壤中黑碳含量随着火频率的增加而减少[110]。

近年来易降解有机碳在黑碳降解过程中的促进作用正受到越来越多的关注。Brodowski 通过培养实验证实了添加易降解有机物能促进土壤黑碳的生物降解[102]。Hamer 等将玉米黑碳与沙混合培养,并添加^{14}C 标记的易降解有机物葡萄糖,经 60 d 的对比培养实验研究发现,对照组玉米黑碳矿化率为 0.8%,添加葡萄糖组提高到 1.2%[105]。Cheng 等对黑碳和黑碳-土壤混合物分别进行培养,并添加粪肥,结果表明,添加粪肥使黑碳的碳含量比对照组降低、氢和氧含量增加,促进了黑碳的降解[111]。Hilscher 等在培养黑麦草黑碳过程中添加新鲜黑麦草作为共基质,结果表明共基质添加在 3 d 内促使黑碳矿化速率提高 22.8%—31.9%,但在第 48 天培养实验结束时,添加组的黑碳总矿化率增加没有达到显著水平[112]。Kuzyakov 等用^{14}C 标记黑麦草黑碳,与土壤和黄土分别混合培养长达 3.2 a,期间添加葡萄糖作为共代谢基质,结果显示添加葡萄糖在数周内显著增加了黑碳分解速率,他们指出葡萄糖促使微生物酶大量产生,进而影响黑碳降解[113]。

5.2 黑碳与地-气碳氮温室气体通量

由于黑碳的稳定性和相对漫长的降解过程,以黑碳形式存在的碳和氮(主要表现为芳香环结构[19,62]和杂环氮结构[114])得以长期保存,从而退出地-气快速循环。因此,长期看来,黑碳能从地-气碳氮循环中捕获并固定碳氮,减少大气中温室气体含量[8,83]。有人甚至据此提出,可通过人为制造黑碳的途径来实现碳捕获与储存(carbon capture and storage, CCS)以应对全球气候变化[115-116]。

黑碳影响土壤微生物活性与碳氮的生物地球化学循环[117],进而影响温室气体排放。有研究表明黑碳能促进土壤中有机碳降解,前述 Hamer 等实验同时表明黑碳较高的比表面积和较多的孔隙为微生物生长提供场所,促进了易降解有机物产生 CO_2[105]。Wardle 等发现黑碳会造成土壤腐殖质的质量损失[118]。Rogovska 等亦发现添加黑碳会增加土壤呼吸,但黑碳本身并没有矿化[119]。Novak 等将黑碳和柳枝稷添加到土壤中培养 67 d,结果表明黑碳能促进柳枝稷的矿化[120]。Major 等研究发现黑碳添加导致土壤有机碳呼吸量在培养的第 1 年和第 2 年分别提高 40% 和 6%,土壤总呼吸量分别提高 41% 和 18%[92]。但是另一方面,也有研究发现黑碳能抑制有机碳降解,Spokas 等通过添加不同比例黑碳到土壤中培养 100 d,结果表明黑碳抑制了土壤 CO_2的排放[121]。Liang 等向土壤中添加有机质培养,结果表明黑碳含量丰富的土壤总矿化率比黑碳含量少的土壤低 25.5%,他们将此解释为黑碳增加了土壤团聚体结构,保护土壤有机质避免矿化[122]。究竟促进作用和抑制作用哪一种占据主导,目前还存在争议。

Lehmann 等[123]发现黑碳添加到土壤中后减少了氮的淋失。DeLuca 等[124]和 Berglund 等[125]研究发现黑碳增加了土壤硝化速率和有机氮矿化速率。Novak 等[120]研究认为黑碳能固定土壤中的氮,从而可能会造成 NO_3^--N 的暂时性短缺。Yanai 等[126]的培养实验发现黑碳减少了土壤中 85% 的 N_2O 排放。Rondon 等[127]研究发现黑碳减少了土壤中 50% 的 N_2O 排放和几乎全部的 CH_4 排放。Spokas 等[121]也发现黑碳抑制了土壤 N_2O 的排放。Knoblauch 等[128]则认为将秸秆制成黑碳还田能比秸秆直接还田减少约 80% 的 CH_4排放。

5.3 黑碳与土壤稳定碳库

有机质稳定性的机制有 3 种:内在稳定性;与土壤与沉积物中的矿物相互作用;缺乏微生物[129],其中第

一种机制主要适用于黑碳和化石碳[130],因此,黑碳在土壤稳定碳库中具有非常重要的地位。

腐殖质也被认为具有内在稳定性,是土壤稳定碳库的重要成份,其结构模型包括杂聚物和聚合体两种[131],前者指单核或多核的芳香环上的羟基和羰基结合了醚、酯、脂族等成分,具有大分子量[132];后者指处于不同降解阶段的小分子的生物聚合物在氢键结合和弱色散力作用下形成超分子结构[133]。二者都认为芳香结构是腐殖质的重要成份[134-135]。Haumaier 等[136]研究发现黑碳氧化后的腐殖酸和土壤中高芳香性的腐殖酸在光谱特征和化学组成上有显著的相似性,认为黑碳是土壤腐殖质可能来源之一。Chiou 等[137]根据胡敏素的高表面积,认为黑碳是胡敏素的组成之一。Poirier 等[138]利用高分辨率透射电子显微镜对法国一处森林土壤中胡敏素结构进行研究,发现了黑碳成份。

5.4 黑碳与土壤碳循环模型

土壤碳循环模型大多包含有一个惰性有机质(inert organic matter, IOM)库[139]。RothC 模型中的 IOM 滞留时间长达 50000 a,完全不参与降解过程。CENTURY 模型中的 IOM 滞留时间在 1000 a 以上,参与降解。IOM 库的大小确定有 4 种方法:人为给定;根据土壤有机碳(SOC)换算;根据^{14}C年龄换算;用黑碳代替。Lehmann 等[140]指出根据 SOC 换算的方法在黑碳含量较高的地区可能会得到不正确的结果。Leifeld[141]指出普遍使用的基于^{14}C质量平衡方程计算土壤 IOM 的方法,其准确性受到黑碳的影响,如现代木炭具有高的^{14}C值但是却属于稳定碳。Skjemstad 等[142]通过测定木炭含量来确定 IOM 的大小,并据此成功利用 RothC 模型模拟了长期实验的结果。Rethemeyer 等[143]将 BPCA 法所得黑碳作为 IOM 的代表,利用 RothC 模型模拟土壤有机碳变化,结果表明,对于以近期有机质为主要碳源的土壤有较好的模拟效果,但是对含有以褐煤为源碳的土壤则效果不佳。

6 土壤和沉积物中黑碳的吸附与解吸行为及环境意义

6.1 黑碳对有机物的吸附与解吸

黑碳可强力吸附憎水性有机物(hydrophobic organic compounds, HOCs)和持久性有机污染物(persistent organic pollutants, POPs),具体包括多环芳烃(PAHs)、多氯联苯(polychlorinated biphenyls, PCBs)、多氯二苯并-对-二恶英(polychlorinated dibenzodioxins, PCDDs)等[23],其中以 PAHs 的研究最多。在很多土壤和沉积物样品中,黑碳和 PAHs 具有显著的相关性[144-146],这种相关性多数被解释为是黑碳对 PAHs 的吸附,其理由是基于黑碳对 PAHs 吸附能力的室内实验[12,60],这些实验表明黑碳对 PAHs 的吸附能力要比一般有机质对 PAHs 的吸附能力强几十到几千倍。而且被黑碳吸附的 PAHs 很难解吸[147-148]。因此黑碳的存在能影响 PAHs 在环境中的分配行为和被生物利用累积的状况[23,149]。

黑碳吸附 PAHs 的机制包括吸附于黑碳表面、捕获于黑碳微孔中,对于火成 PAHs 来说,还包括锢囚于黑碳结构内部[60,150-151]。

黑碳吸附 PAHs 的一个非常重要的机制是表面吸附,因为黑碳的比表面积(specific surface area, SSA)很大,可以提供很多的吸着点。因此,面对某些研究发现的不同类型黑碳以及不同方法测定的黑碳对 PAHs 的吸附能力有很大不同这一问题[149],有人提出把黑碳标准化到 SSA 可以明显消除这种变异性[152-153]。而在分析黑碳的 SSA 时,样品是否磨细代表了不同的环境意义,磨细的样品代表潜在有效的表面积和吸附能力,不磨的样品代表实际有效的表面积和吸附能力。

微孔捕获机制也很重要。根据 Rouquerol 等[154]的分类方法,微孔是指直径小于 2 nm 的孔隙,相当于烟炱结构中的石墨烯层间距大小[155],与许多 POPs 分子厚度亦相当[156]。Rockne 等[22]发现烟炱中微孔的孔隙容积占颗粒内部总容积(微孔加中孔,<50 nm)的 10%—20%,并指出这些微孔可能是烟炱吸附 HOCs 的重要场所。Jonker 等[60]进而发现烟炱的平均孔径对 PAHs 的烟炱-水分配系数有很大的影响,表现为负相关关系。Karanfil 等[157]亦研究表明活性炭吸附 HOCs 过程中,孔隙大小比 SSA 更重要,并且随着微孔数量增加,吸附能力增强。关于其具体机制,Mastral 等[158]和 Jonker 等[60]认为主要是平面的 PAH 分子嵌入黑碳颗粒中的微孔和分子层间空隙,从而接触更多的黑碳表面吸附点,本质上还是表面吸附作用在起作用。

在生物质不完全燃烧的过程中,会同时生成黑碳和 PAHs,而且 PAHs 是烟炱形成的一种前体物质[159],在烟炱颗粒不断增大的过程中会锢囚一部分 PAHs 在其结构内部[160],另一部分 PAHs 则被吸附在黑碳的表面上和微孔中。这些与黑碳同源的 PAHs 往往被称为"原生的"PAHs(native PAHs),与"添加的"PAHs(added PAHs)相对。锢囚的 PAHs 不能释放到水中但是可以被 PAHs 测定时使用的化学试剂提取,因此,锢囚的 PAHs 会导致黑碳-水分配系数表象性地增加[60]。黑碳对原生 PAHs 的吸附系数与 PAH 的分子体积呈负相关关系,这也与锢囚机制有关:PAH 分子体积越大就越难从黑碳结构内部逃脱。

环境中黑碳对 PAHs 的吸附能力要小于理论上的由分配系数实验得到的新鲜黑碳对 PAHs 的吸附能力,原因主要是(1)原生 PAHs 会降低黑碳对添加 PAHs 的吸附能力,因为它优先占据了黑碳表面的高能吸着点和微孔。(2)环境中有竞争吸附剂吸附 PAHs;(3)环境中有竞争吸着物占据黑碳表面的微孔和吸着点;(4)环境中粗粒的黑碳真正起作用的比表面积小于实验中磨细的黑碳的比表面积。实验表明,新生成的黑碳中含有高浓度的 PAHs,而环境中 PAHs 与黑碳之比要小得多(表 4)。该表暗示黑碳在环境中可能会解吸一部分原生的 PAHs(由于吸附竞争)。综上所述,黑碳吸附 PAHs 的过程受诸多因素影响,其与 PAHs 含量的相关性不能简单地解释为黑碳对 PAHs 的吸附。

表 4　环境黑碳和新鲜黑碳中多环芳烃浓度对比

Table 4　PAHs concentrations in fresh and environmental black carbons

采样地点/物质类型 Sampling sites and sample types	PAHs PAHs /(ng/g)	黑碳 Black carbon /(mg/g)	PAHs/黑碳 PAHs/BC /(ng/mg)	环境样品 数量 *n*	黑碳测定方法 BC analyzing method	PAHs 种 类* PAHs type	参考 文献 Reference
环境样品 Samples from soils and sediments							
渤海湾沉积物 Bohai bay sediment	946.77±1007.18	2.18±0.21	421.83±433.01	12	10% HCl+375℃/24h	16 种	[161]
北黄海沉积物 North Huanghai sediment	224.55±346.41	0.37±0.28	907.38±1542.38	9	10% HCl+375℃/24h	16 种	[161]
珠江口沉积物 Pearl river estuary sediment	712.14±877.50	0.47±0.45	2126.77±2756.55	15	10% HCl+375℃/24h	16 种	[161]
上海市水稻田表层土壤 Top soil of paddy field in Shanghai	3092.39±3641.23	2.68±1.53	1221.63±1165.45	17	1M HCl+375℃/24h	16 种	[147]
上海边滩沉积物 Shanghai foreshore sediment	498.28±543.97	0.62±0.15	798.35±885.07	10	1M HCl+375℃/24h	16 种	[147]
汕头红树林湿地沉积物 Shantou mangrove wetland sediment	136.75±55.15	6.01±3.63	28.66±16.57	14	文献[36]	16 种	[146]
澳门河口远岸沉积物 Macao estuarine offshore sediment	1909.29±409.77	1.29±0.20	1466.58±102.63	7	10% HCl+375℃/24h	16 种	[162]
澳门河口近岸沉积物 Macao estuarine inshore sediment	2069.67±715.06	1.27±0.26	1593.52±370.71	9	10% HCl+375℃/24h	16 种	[162]
澳门城市近岸沉积物 Macao urban inshore sediment	6490.78±2806.78	1.48±0.47	4715.73±2125.60	9	10% HCl+375℃/24h	16 种	[162]
澳门郊区近岸沉积物 Macao suburban inshore sediment	2003.83±678.77	1.27±0.37	1568.70±144.40	6	10% HCl+375℃/24h	16 种	[162]
澳门乡村近岸沉积物 Macao rural inshore sediment	2026.93±923.29	1.31±0.49	1509.54±426.79	14	10% HCl+375℃/24h	16 种	[162]
波士顿港沉积物 Boston harbor sediment	7733.33±4051.34	6.00±0.70	1288.89	3	文献[163]	3 种	[164]
纽约港沉积物 New York harbor sediment	516.67±215.48	3.40±0.20	151.96	3	文献[163]	3 种	[164]

续表

采样地点/物质类型 Sampling sites and sample types	PAHs PAHs /(ng/g)	黑碳 Black carbon /(mg/g)	PAHs/黑碳 PAHs/BC /(ng/mg)	环境样品数量 *n*	黑碳测定方法 BC analyzing method	PAHs 种类* PAHs type	参考文献 Reference
新鲜黑碳 Fresh black carbon							
乙烯燃烧产物 Ethylene soot	—	—	51441.00		—	16 种	[151]
煤油燃烧产物 kerosene soot	—	—	23155.00		—	17 种	[165]
燃油烟囱内物质 Oil soot	59400.00	1.2	49500.00		文献[163]	11 种	[60]
燃木材烟囱内物质 Wood soot	112600.00	2.6	43307.69		文献[163]	11 种	[60]
燃煤烟囱内物质 Coal soot	799200.00	67.5	11840.00		文献[163]	11 种	[60]
树皮燃烧所得木炭 Charcoal	43200.00	41.8	1033.49		文献[163]	11 种	[60]
汽车排气管内物质 Traffic soot	124300.00	0.38	327105.26		文献[163]	11 种	[60]
柴油机烟炱 Diesel soot	232600.00	361	644.32		文献[163]	11 种	[60]

*16 种:美国环保署(EPA)16 种(萘、苊稀、二氢苊、芴、菲、蒽、荧蒽、芘、苯并[*a*]蒽、屈、苯并[*b*]荧蒽、苯并[*k*]荧蒽、苯并[*a*]芘、二苯并[*a*,*h*]蒽、茚并[1,2,3—*cd*]芘、苯并[*g*,*h*,*i*]苝);17 种:EPA16 种+2-甲基萘;11 种:菲、蒽、芴、芘、苯并[*a*]蒽、屈、苯并[*e*]芘、苯并[*b*]荧蒽、苯并[k]荧蒽、苯并[*a*]芘、苯并[*g*,*h*,*i*]苝;3 种:菲、芘、苯并[*a*]芘

6.2 黑碳对重金属的吸附与解吸

Corapcioglu 等[166]很早就研究过活性碳对 Cu(Ⅱ)、Pb(Ⅱ)、Ni(Ⅱ)和 Zn(Ⅱ)的吸附,认为吸附过程可由配位化合物形成模型解释。现在一般认为,黑碳吸附重金属的机制主要有两种,一是黑碳表面吸附[167],吴成等[168]研究了玉米秸秆黑碳对 Hg(Ⅱ)、As(Ⅲ)、Pb(Ⅱ)和 Cd(Ⅱ)的吸附,发现用 Langmiur 方程拟合黑碳等温吸附过程最佳,表明其主要是吸附位有限的非线性表面吸附,以这种方式被吸附的重金属极易解吸,30 min 内洗脱率均在 85% 以上。二是黑碳上的官能团与重金属之间的静电相互作用,包括离子交换[169]和部分配位反应[170],Qiu 等[171]研究认为稻草黑碳和麦秆黑碳对 Pb(Ⅱ)的吸附属于静电相互作用机制,被吸附的重金属相对较稳定。黑碳阳离子交换量(cation exchange capacity, CEC)与其吸附重金属能力成正相关关系[172],表明第 2 种机制是黑碳吸附重金属的主要机制。尽管吴成等[168]认为黑碳的 CEC 比土壤/沉积物环境中其他吸附剂如腐殖酸和粘土的较小,其对重金属离子吸附量相对不大,但是 Liang 等[173]研究认为黑碳可通过自身氧化或吸附其他有机质提高土壤的 CEC。

土壤中存在的低分子有机酸会影响黑碳对重金属的吸附[174]。张文标等[175]研究了不同炭化温度的竹黑碳对 Pb(Ⅱ)、Hg(Ⅱ)、Cr(Ⅵ)和 Cd(Ⅱ)的吸附,结果表明黑碳的比表面积、孔径及 pH 等均影响到吸附重金属能力,溶液中同时存在的多种重金属离子之间存在着协同和阻碍两方面的效应。

6.3 黑碳对营养盐的吸附

黑碳可吸附土壤溶液中的 NH_4^+-N[125,176]和 NH_3-N[8]。Novak 等[120]研究认为由于电荷正负性的原因,黑碳对 NH_4^+-N 的吸附能力要强于对 NO_3^--N 的吸附能力。添加到土壤中的木炭增加土壤对氮和磷的吸附能力,减少了总氮流失量的 11% 和总可溶磷流失量的 69%[177],还能增加土壤对钾的吸附能力[123]。黑碳可通过间接方式影响对营养盐的吸附,如 Lee 等[178]研究表明氧化了的黑碳表面官能团增多,可以增加对 NH_4^+-N 和 NH_3-N 的吸附。

7 研究展望

目前研究者已对我国部分城市、森林和农业土壤和近海沉积物中的黑碳含量及分布做了一些研究,但是还远不清楚黑碳在各种类型和不同区域土壤和沉积物中的含量,仍需开展大量基础性工作以摸清黑碳的环境本底值及分布特征。

目前对涉及到土壤和沉积物中黑碳稳定性的一些关键过程还不是很清楚,比如黑碳与易降解有机碳的耦合矿化降解过程、土壤黑碳以颗粒态和溶解态的流失过程、黑碳与土壤其他稳定有机碳的转化过程等,这些过程决定了黑碳全球循环的途径和速率、黑碳作为土壤保碳和抑制全球变暖手段的有效性等重大理论与实践问题,亟待进一步深入研究。

土壤和沉积物中黑碳的迁移、降解、吸附等主要环境行为都取决于其理化性质,因此在今后的相关研究中,需要更加重视从微观层次研究黑碳的表面特征如比表面积、孔隙度、官能团、表面形貌特征等在黑碳环境行为中的作用,这有助于将研究水平从含量分析或相关性分析提升到较为深入的机理分析。

为了提高黑碳测定数据的准确性和对比性,需要建立一套标准物质和规范方法,而另一方面,为了提高数据的解释性和针对性,则需要以具体的环境意义为导向选择合适的分析测定方法。

鉴于黑碳在土壤固碳和保肥方面的重要作用,有必要深入研究施用人工制备黑碳在农田管理中的可行性,重新考虑农作物秸秆直接还田方式和焚烧还田方式对土壤固碳的长期、综合影响,开展黑碳在农业领域的应用研究。

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ACTA ECOLOGICA SINICA Vol. 32, No. 1 January, 2012 (Semimonthly)

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国内邮发代号:82-7　国外邮发代号:M670　标准刊号:ISSN 1000-0933　CN 11-2031/Q

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编辑部主任　孔红梅　　**执行编辑**　刘天星　段　靖

生　态　学　报
(SHENGTAI　XUEBAO)
(半月刊　1981 年 3 月创刊)
第 32 卷　第 1 期　(2012 年 1 月)

ACTA ECOLOGICA SINICA
(Semimonthly,Started in 1981)
Vol. 32　No. 1　2012

编　辑	《生态学报》编辑部 地址:北京海淀区双清路 18 号 邮政编码:100085 电话:(010)62941099 www. ecologica. cn shengtaixuebao@ rcees. ac. cn	**Edited** by	Editorial board of ACTA ECOLOGICA SINICA Add:18,Shuangqing Street,Haidian,Beijing 100085,China Tel:(010)62941099 www. ecologica. cn Shengtaixuebao@ rcees. ac. cn
主　编	冯宗炜	**Editor-in-chief**	FENG Zong-Wei
主　管	中国科学技术协会	**Supervised** by	China Association for Science and Technology
主　办	中国生态学学会 中国科学院生态环境研究中心 地址:北京海淀区双清路 18 号 邮政编码:100085	**Sponsored** by	Ecological Society of China Research Center for Eco-environmental Sciences, CAS Add:18,Shuangqing Street,Haidian,Beijing 100085,China
出　版	科　学　出　版　社 地址:北京东黄城根北街 16 号 邮政编码:100717	**Published** by	Science Press Add:16 Donghuangchenggen North Street, Beijing　100717,China
印　刷	北京北林印刷厂	**Printed** by	Beijing Bei Lin Printing House, Beijing 100083,China
发　行	科　学　出　版　社 地址:东黄城根北街 16 号 邮政编码:100717 电话:(010)64034563 E-mail:journal@ cspg. net	**Distributed** by	Science Press Add:16 Donghuangchenggen North Street,Beijing 100717,China Tel:(010)64034563 E-mail:journal@ cspg. net
订　购	全国各地邮局	**Domestic**	All Local Post Offices in China
国外发行	中国国际图书贸易总公司 地址:北京 399 信箱 邮政编码:100044	**Foreign**	China International Book Trading Corporation Add:P. O. Box 399 Beijing 100044,China
广告经营 许 可 证	京海工商广字第 8013 号		

ISSN 1000-0933 01>

ISSN 1000-0933
CN 11-2031/Q　　**国内外公开发行**　　**国内邮发代号** 82-7　　**国外发行代号** M670　　**定价** 70.00 元