峨眉山冷杉衰亡与土壤铝活化的关系研究*

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摘要 通过模拟酸雨对峨眉山土壤中活性铝的溶出试验, 考察了铝离子溶出量及 Ca/Al 比值, 并研究其与冷杉生长的关系. 研究结果表明: 峨眉山土壤中铝离子活化严重, Ca/Al 比值远远小于 1, 铝中毒是峨眉山酸沉降危害冷杉的重要原因之一.

关键词 酸沉降, 活性铝, 土壤, 冷杉, 峨眉山.

活性铝是限制土壤中植物生长的一个重要因素, 被认为是一种新的毒性元素[1-4]. Ulrich[5-6]研究报告指出, 土壤中 Ca/Al 摩尔比是衡量铝对植物危害的一个有用的指标, 当 Ca/Al 比小于 1 时, 铝能对植物吸收水分和养分的根毛产生损害, 进而引起植物枯萎和死亡.

自 70 年代以来, 峨眉山酸沉降严重, 森林中冷杉发生大面积衰败. 本文通过研究峨眉山不同区域冷杉土壤的活性铝溶出量及在酸雨淋洗下 Ca/Al 比值的变化趋势, 比较系统的分析研究了峨眉山酸沉降引起的土壤铝活化与冷杉衰亡的关系, 以期为揭示冷杉衰亡原因, 为峨眉山酸雨环境效应的研究提供科学依据.

1 实验部分

1.1 土样及冷杉样采集

(1) 土壤样点布置 调查表明, 在峨眉山不同海拔高度, 以及同海拔的不同地形, 冷杉衰败程度也不相同, 有着明显的小区特点. 因此, 在冷杉受害严重的七里坡、金顶、中度受害的雷洞坪变电站, 以及冷杉长势良好的千佛顶设置了土壤采集点. 同时, 为了进行对比, 在冷杉长势良好、未受酸雨侵蚀、相近海拔的贡嘎山设置了采样点 2 号、3 号.

(2) 土样采集及制备 土样采集: 在选定区域的样方中, 根据地形特点, 按梅花形、蛇形或三角形布点[7]. 在样点处将土壤挖一剖面, 自下而上分 3 层采集土样, 见表 1.

土样制备: 将土样置于洁净瓷盘中, 剔除石粒、草根等杂物, 自然风干, 再用石英研钵磨成 20-60 目粉末, 装瓶待用.

表 1 土样采集点情况[1)]

样点	贡嘎山 2 号	贡嘎山 3 号	千佛顶	雷洞坪变电站	金顶	七里坡
海拔/m	2820	2940	3099	2355	3077	2900
冷杉长势	良好	良好	较好	中度受害	大片死亡	大片死亡

1) 土层厚度(cm): 上层 0—20; 中层 20—40; 下层 40—60

(3) 冷杉根采集及制备 冷杉根采集: 在峨眉山七里坡冷杉死亡带采集死根, 每个样点采集湿重不低于 1kg 的死根; 在贡嘎山 2 号地, 每样点采集湿重不低于 1kg 的活根. 根样制备: 将冷杉根洗净, 弃去泥土及杂物, 凉干, 再于 80℃烘箱中干燥 12h, 取出研磨, 装瓶待用.

1.2 实验方法和结果

(1) 土壤中活性钙铝溶出静态试验 浸取液选择: 根据文献[8]研究结果, 选用 1mol/L HCl 作为浸取液. 试验方法: 按 1.00g 土样加入 10 ml 1mol/L HCl 的比例, 将配制液置于离

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心管中, 在振荡器中振荡 30min 后静置 16h, 离心分离, 收集上层清液, 分析溶液中活性钙及活性铝含量. 以相近海拔的贡嘎山土样作为对照试验, 其结果见表 2.

表 **2** 土壤中活性钙铝的溶出比

地点	海拔/m	pH	冷杉生长状况	活性铝溶出量/mg·g^{-1}	活性钙溶出量/mg·g^{-1}	Ca/Al(mol/mol)
金顶	3050	4.7	大片死亡	3200.76	12.00	0.0026
贡嘎山 3 号	2940	6.97	生长良好	12.96	1201.2	62.56
七里坡	2700	4.35	大片死亡	121.97	9.4	0.054
贡嘎山 2 号	2820	7.04	生长良好	30.96	3001.00	665.43

从土壤活性钙铝溶出静态试验结果(表 2)可以看出, 峨眉山土壤活性铝溶出量比贡嘎山高得多, 而钙溶出量比贡嘎山低得多, 如金顶与同海拔的贡嘎山 3 号相比, 它的活性铝溶出量为贡嘎山 3 号的 246.9 倍, 而活性钙的溶出量仅为贡嘎山 3 号的 0.01 倍. 因此, 两者 Ca/Al 溶出比相差极大, 贡嘎山 3 号的 Ca/Al 比为金顶的 24062 倍; 同样贡嘎山 2 号与同海拔的七里坡相比, 其 Ca/Al 溶出比为七里坡的 1258 多倍; 峨眉山地区的金顶与七里坡相比, 金顶 Ca/Al 比约为七里坡的 1.2 倍, 说明冷杉死亡严重区域土壤 Ca/Al 比相差不大.

产生上述差异原因在于, 贡嘎山土壤偏碱性, 且土壤未受到酸雨侵蚀, 可交换的阳离子数量多, 故钙含量高, 固定态的矿物铝被活化的量则少, 因此 Ca/Al 比值较大; 而峨眉山金顶和七里坡土壤已被酸化, 钙离子淋失严重, 大量固定态矿物铝已被活化, 因而土壤中 Ca/Al 比值远小于 1, 故对冷杉毒害较大.

(2) 模拟酸雨对土壤活性钙铝的动态淋溶试验 模拟酸雨配制: 按峨眉山实际酸雨组成, 采用 S∶N= 10∶1 的 H_2SO_4/HNO_3 混合液, 并用去离子水分别稀释为 pH5.6、4.7、3.7、3.1, 再加入按峨眉山降水离子成分的统计平均值配制的电解溶液(K、Na、Ca、Mg 浓度分别为 12.1、25.7、46.7、14.5μg/L)配制成模拟酸雨.

试验方法: 将 50g 土样装入内径为 5.4cm、高 10cm 的塑料圆柱内, 下部筛板垫有玻璃棉防止土粒泄漏, 将土柱置于支架上, 上部设置淋溶装置, 下部用玻璃烧杯收集淋出液.

淋溶量为峨眉山年均降雨量 2000mm, 每淋溶 250mm, 收集 1 次淋滤液, 测其 pH 值, 并按一定比例(1∶10)装入收集瓶中, 测定滤液中 Ca^{2+}、Al^{3+} 溶出量, 其结果见表 3.

从表 3 中看出: ①贡嘎山土壤与峨眉山相比, 它的钙离子溶出量为峨眉山的 12- 14 倍, 而铝离子溶出量仅为峨眉山的 0.01- 0.04 倍, 因此二者 Ca/Al 溶出比相差很大, 贡嘎山的 Ca/Al 比约为峨眉山的 370- 1110 倍, 这与活性钙铝溶出静态试验结果是一致的. ②从峨眉山不同区域来看, 冷杉死亡较严重的七里坡和金顶土壤, 当 pH 值降至 4.2 时, 其 Ca/Al 比便逐渐变得小于 1; 冷杉受害较轻的千佛顶和雷洞坪变电站土壤, 当 pH 值降至 3.7 时, 其 Ca/Al 比才逐渐变得小于 1, 这说明千佛顶和雷洞坪变电站土壤的缓冲能力强于七里坡和金顶, 同时也表明冷杉衰败程度与 Ca/Al 比大小有很好的相关性. ③由表 3 还可看出, 随着酸雨 pH 值的降低, 土壤中 Ca、Al 离子淋出量增大, 但铝离子淋出量增大得迅速, 特别是当酸雨 pH 值降至 4.2 以下时, 铝离子的淋出量几乎是成倍增加.

这种现象可用土壤对酸沉降的缓冲机制来解释. Ulrich[6] 等人对土壤酸化过程研究后, 提出了各 pH 值范围内土壤缓冲系统的几个区间;

pH= 6.2- 8.6: 为土壤第一缓冲阶段, 土壤中 H^+ 在这个阶段主要是通过 $CaCO_3$ 来中和, 其反应为:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2H_2O$$

pH= 5.0- 6.2 此时土壤中的 H^+ 通过原生矿物质中和, 同时释放出碱金属和碱土金属, 其反应为:

$$CaO \cdot Al_2O_3 \cdot 2SiO_2 + 2H^+ + H_2O = Ca^{2+}$$

$+ Al_2O_3 + 2SiO_2 + 2H_2O$

pH = 4.2– 5.0 属于阳离子交换缓冲范围, 输入的 H^+ 离子通过离子交换途径置换出土壤颗粒上吸附的 Ca^{2+}、Mg^{2+}、NH_4^+ 等阳离子.

pH< 4.2 属于铝缓冲范围, 土壤中 H^+ 与矿物质晶格中铝氢氧聚合物得以中和, 同时生成游离的 Al^{3+}, 随着 pH 值降低, Al^{3+} 生成越多, 反应为:

$$AlO-OH + 3H^+ = Al^{3+} + 2H_2O$$

从表 3 中可看出, 由于峨眉山土壤普遍有所酸化, 当酸性沉降物进入土壤时, 土壤很容易进入铝氧化物缓冲阶段, 土壤中一些富含营养离子的矿物质会逐渐变枯竭, 最终导致营养离子缺乏. 因此, 土壤若长期处于铝缓冲范围内, Ca^{2+} 将减少, Al^{3+} 将增多, 活化 Ca/Al 比将逐渐降低, 进而导致植物根系受害, 吸收养分能力下降, 最终影响植物生长.

(3) 冷杉根样分析　峨眉山七里坡冷杉死根和贡嘎山冷杉活根测定结果见表 4.

表 **3**　模拟酸雨淋溶钙铝量/ $\mu g \cdot g^{-1}$

地点	冷杉生长状况及死亡率/%	pH	活性铝溶出量/ $mg \cdot g^{-1}$	活性钙溶出量/ $mg \cdot g^{-1}$	Ca/Al (mol/mol)
贡嘎山	生长良好, 死亡率 6.82	5.6	768	0.60	872.7
		4.7	912	0.76	814.3
		4.2	864	0.84	696.8
		3.7	908	1.04	589.6
		3.1	1848	2.16	577.5
七里坡	大片死亡, 死亡率 78.95	5.6	54.26	15.49	2.36
		4.7	48.02	17.32	1.87
		4.7	83.64	53.93	1.05
		3.7	127.16	125.19	0.69
		3.1	148.46	158.76	0.63
金顶	大片死亡, 死亡率 45.07	5.6	51.42	23.74	1.46
		4.7	56.31	25.51	1.49
		4.2	87.73	58.46	1.01
		3.7	115.27	136.63	0.57
		3.1	119.31	145.53	0.56
雷洞坪变电站	长势较好, 死亡率 17.54	5.6	56.54	18.51	2.66
		4.7	42.36	16.61	2.55
		4.2	56.34	22.85	1.67
		3.7	76.32	11.77	1.23
		3.1	96.43	132.17	0.49
千佛顶	生长较好, 死亡率 17.39	5.6	47.21	15.56	2.05
		4.7	53.93	21.65	1.68
		4.2	70.56	25.49	1.87
		3.7	86.45	48.66	1.20
		3.1	117.98	152.19	0.52

表 **4**　元素分析结果/ $\mu g \cdot g^{-1}$

地点	编号	Al	Ca	Mg	K	Na	Fe	Zn	Mn
七里坡冷杉死亡带	峨–7–1	3001	2105	299.3	1272	276.0	406.5	14.65	49.60
	峨–7–2	3301	1682	167.9	761.9	208.8	109.5	7.45	23.32
	峨–7–3	3720	2641	305.1	1328	228.8	98.7	8.01	51.73
	平均	3367	2169	257.4	1120	238.1	204.8	10.03	41.58
贡嘎山二号地	贡–2–1	1488	5715	648.9	4673	180.7	2386	15.85	261.4
	贡–2–2	747.6	1927	713.5	3378	650.3	2062	14.34	196.0
	贡–2–3	470.8	2858	1030	3764	787.1	2893	40.83	162.7
	平均	902.2	3500	797.4	3938	539.4	2447	23.67	206.7

从七里坡冷杉死根与贡嘎山冷杉活根中元素分析研究可以看出:①峨眉山七里坡冷杉死亡带(死亡率为 78.95%),其死根中铝含量为 3.36mg/g,是生长良好的贡嘎山冷杉活根铝含量的 3.73 倍,这是由于七里坡冷杉死亡带土壤已被酸化,土壤平均 pH 值为 4.13,钙、镁等营养离子流失严重,大量铝离子被活化,富集于冷杉根中而使冷杉根系受铝毒害.②由于铝富集于根中,铝离子抑制了根系对钙镁等营养离子的吸收,如表 4 所示,死根中的钙、镁含量分别比贡嘎山活根减少了 38.8%和 67.7%,这与 Thornton. T.C.[10] 观察到生长在铝含量为 250μg/L 稀营养液中的云杉,其根内钙镁含量分别比对照点减少 48%和 60%的结果一致.③铝离子还抑制根系对其它营养元素的吸收,如七里坡冷杉死根中钾、钠、铁、锌、锰含量分别只为贡嘎山活根含量的 28.4%、44.1%、8.4%、42.4%、20.1%.其影响大小顺序为铁> 锰> 钾> 钠> 锌.

由于铝对冷杉根系的毒害,降低了营养物质的吸收和转运,从而限制了冷杉地面上部的生长,对叶的伤害较明显,主要表现在针叶黄化、脱落等症状.经调查发现,峨眉山冷杉衰败多呈"鹤颈状",特别是七里坡冷杉死亡带这种症状较为普遍.这与 Papke H.E.[11] 和胁孝介[12]研究酸沉降对杉木衰败的症状一致.随着中毒发展,树叶量不断减少,然后从梢部枯萎发展到下部的树叶也枯萎,直至死亡.但如果在轻度衰败阶段,仍能保持再生能力,从树干及树枝上容易生出新枝,出现暂时性恢复现象.

1.3 分析方法

土壤 pH 值采用 pHS-10A 数值酸度计测定;Al^{3+} 采用羊毛铬花青 R 比色测定[9],其余金属元素用美国 P-E3030 型原子吸收光谱仪测定.

2 结束语

(1)作为对照点、未受到酸侵蚀的贡嘎山土壤,其土壤中活性铝溶出较少,钙镁等营养元素含量较高,Ca/Al> 1,冷杉生长良好;与之相比,峨眉山不同区域土壤,由于酸沉降影响,土壤普遍受到酸化,铝离子活化严重,钙镁等营养离子流失严重,Ca/Al< 1,且以冷杉衰败严重的金顶、七里坡等地表现尤为突出,这说明土壤中 Ca/Al 比值大小与冷杉生长状况有较大的相关性.

(2)峨眉山七里坡冷杉死根中铝含量远大于贡嘎山冷杉活根铝含量,这说明酸沉降引起大量土壤中活性铝进入冷杉植物体内,富集冷杉根中,抑制根系对钙镁等营养离子的吸收,造成根系受铝毒害;同时活性铝还抑制冷杉对其它营养元素(K、Na、Mg 等)的吸收和转运,使峨眉山冷杉衰败多呈"鹤颈状".

以上结果表明,峨眉山冷杉衰败,特别是冷杉死亡严重的金顶、七里坡等地,由于酸沉降使土壤酸化(pH< 4.2),Ca/Al< 1,土壤中活性铝是对冷杉造成危害的重要原因之一.

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Photobacterium phosphoreum was used as the indicator bacteria. The techniques of cell immobilization, luminous bacteria toxicity test and biosensor were combined to develope a bacterial luminescent biosensor. The luminescent intensity of immobilized bacteria film and its stable time were determined. The acute toxicity of 3 metallic ions and 3 organic compounds was detected by this system (based on the EC_{50} value 50% inhibition rate of luminescent intensity of immobilized bacteria film). The kinetic process of toxicants on bacterial luminescence was analyzed. The results showed that the luminescent intensity could reach 250– 300×10^{-7} mW when the immobilized bacteria film was measured in 3.0% NaCl of pH 7.0 at 20℃. The stable time could reach 60– 80min. The toxicity and EC_{50} (mg/L) sequence of toxicants were: Hg^{2+} (0.15) > Cu^{2+} (14) > Zn^{2+} (130), phenol (35) > acetaldehyde (210) > ethyl ester (1200). The EC_{50} sequence was coincident with the LD_{50} of mammal toxicity test and this system had good sensitivity and stability. There was difference among toxicants in the inhibition rate of bacterial luminescence.

Key words: bacterial luminescence, biosensor, acute toxicity, luminescent intensity, stability, sensitivity.

Biodegradation of Poly-β-Hydroxyalkanoates Membrane in Aerobic and Anaerobic Sludge. Gao Haijun, Chen jian et al. (Environ. Biotechnol. Lab., Sch. Biotechnol., Wuxi Univ. Light Industry, Wuxi 214036): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 17—20

Biodegradation process and mechnism of poly-β-hydroxybutyrate (PHB) and poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) were studied in aerobic and anaerobic sludge. Microorganisms in sludge can grow using PHB (V) as sole carbon source. Biodegradation rate of PHB is faster than that of PHBV. Different conditions, such as pH and temperatures, have different influence on microbial degradation abilities of PHB(V) in sludge. Product configuration, especially specific surface area, has close correlation with the rate, and the larger specific surface area is, the faster biodegradation rate is.

Key words poly-β-phydroxybutyrate (PHB), poly (β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV), sludge, biodegradation.

Comparative Study on the Biodegradability of Chlorobenzenes by Chlorobenzene Acclimated Sludge. Qu Fuping, Zhang Xiaojian, He Miao, Gu Xiasheng (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 21—24

A study on the biodegradability of five priority pollutants, which include chlorobenzene, o-, m-, p-dichlorobenzene and 1, 2, 4-trichlorobenzene, was conducted by measuring the respiratory consumption. Seed sludge and chlorobenzene acclimated sludge were used in the test. The experimental observations indicated the respiratory of seed sludge was completely inhibited by the five organic compounds, the degree of inhibitory is linked with the degree of chlorination, the site of chlorine atom substitution and the substrate concentration. The chlorobenzene acclimated sludge not only shows the biodegradable ability for the chlorobenzene, but the cometabolic ability for the o-, and m-dichlorobenzene, while the p-dichlorobenzene and 1, 2, 4-trichlorobenzene presents the strong inhibition, this shows the characteristic of the enzymes induced by chlorobenzene, i. e. they require the substrate must have at least one "continuous three vacant site structure" in the benzene ring. The kinetic biodegradable/inhibitory constants are also presented in this paper.

Key words: chlorobenzenes, priority pollutant, aerobic biodegradability, active sludge, acclimation.

The Study on the Relationship between the Activation of Al in Soil and Decline of Fir Forest

at Mt. Emei. Zhu Xiaofan, Lu Hong, Jing Yan (Dept. of Environ. Sci. & Engineering of Sichuan Union. University, Chengdu 610065): *Chin. J. Enviton. Sci.*, **18**(4), 1997, pp. 25—28

With simulated acid rain, the experiment on leaching of Al in soil at Mt. Emei was done and the amount of Al leached and Ca/Al ration in soil were examined. The aim is to inquire into the relationship between active Al、Ca/Al ration and the growth of Fir Forest at Mt. Emei. The results showed that the phenomenon of Al activation at Mt. Emei is evident, especially in the decline districts of Fir Forest, the Ca/Al ration in soil is much less than 1. Thus, Al poisoning is one of the important factors which resulted in the decline of Fir Forest at Mt. Emei.

Key words: acid precipitation, Al, soil, fir forest, Mt. Emei.

Kinetics of Reaction of OH Radical with C_2H_2Br and the Residual Lifetime in the Atmosphere. Zhong Jinxian and Zhang Deqiang et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Enviton. Sci.*, **18**(4), 1997, pp. 29—31

Brominated alkanes are a destructive substances for the ozone layer. The kinetics of reaction of OH radical with C_2H_2Br were studied. The reaction velocity rate constants were measured by the discharge flow-resonace fluorescence technique over the temperature range of 297- 369K and the Arrenius equation was derived. The atmospheric lifetime of C_2H_2Br has been estimated to be 0.168 year due to the Arrenius equation at condition that the average temperature of atmospheric convection layer is 277K.

Key words: hydroxyl radical, C_2H_2Br, discharge flow resonance fluorescence, atmospheric lifetime.

A Primary Study on the Acid-solatile-sulfide (AVS) in Le An River Sediment and the Effect of Oxygen on the Release of Heavy Metals in the Sediment. Xianghua Wen (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Herbert E. Allen (Civil Engineering Department, University of Delaware, Newark, DE 19716, USA): *Chin. J. Enviton. Sci.*, **18**(4), 1997, pp. 32—34

This research did aeration experiments and the measurement of acid-volatile Sulfide (AVS) and simultaneously extracted metals (SEM) for a set of sediment samples in Le An River to determine the metal release potential. It was found that AVS in Le An River sediment is low and there would be the risk of second pollution in the way of mobilization of sediment bound metals to the overlying water. It is most likely that the iron and manganese oxide are important metal binding components in Le An River sediment.

Key words: sediment, metal release, acid-volatile-sulfide, aeration.

Chemical Oxidation of J-Acid and Tobias Acid Dye Intermediate Waste Liquor. Jiang Zhanpeng, Zhu Wanpeng, Yang Zhihua et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Enviton. Sci.*, **18**(4), 1997, pp. 35—37

After recovering the useful substances from the waste liquor of two kinds of naphthalene series sulfonic acid dye intermediates, J-acid and Tobias acid, it is necessary to have a final treatment of the effluent, remained liquor, according to the National Standard of Industry Wastewater Discharge. The salt recovery-coagulation and sedimentation-chemical oxidation process was carried out for treating the remained liquor (COD_{Cr} 1000mg/L, salt concentration 150- 300g/L) in the paper. Fenton reagent (combination of H_2O_2 and Fe^{2+}) was used for the chemical oxidation and the optimum parameters of the process had been obtained. The dosages of hydrogen peroxide (containing 30% of H_2O_2) and $FeSO_4 \cdot 7H_2O$ are 4L and 1.35kg per m^3 of the remained liquor,