氧化亚氮在森林和草原中的地-气交换*

刘 晔 牟玉静 钟晋贤 杨文襄

(中国科学院生态环境研究中心, 北京 100085)

摘要 采用箱式法, 建立了一套完整的测定森林草原土壤 N_2O 排放方法, 并对我国北方的自然环境中 N_2O 排放作了观测, 得出其最大排放通量为23$\mu g/(m^2 \cdot h)$. 并发现森林草原土壤当温度低于15℃时对 N_2O 有吸收行为, 其最大吸收通量为18.984$\mu g/(m^2 \cdot h)$.

关键词 N_2O, O_3, 排放通量, 源, 汇, 地-气交换.

N_2O 是低层大气中含量最高的含氮化合物, 模式计算显示, 如果大气中 N_2O 浓度增加1倍, 则全球范围内臭氧层柱浓度将不同程度地减少10%—16%[1]. N_2O 的排放源是大量不确定的小的源组成, 包括农业土壤、天然植被土壤、海洋生物源等[2]. 研究 N_2O 的源、汇及其在大气中的化学特性已成为众多学者广泛关注的研究课题. 近年来有研究人员对农作物土壤 N_2O 的排放通量[3]以及生物质燃烧[4]等作了测定. 但是, 作为 N_2O 的天然排放源除农田土壤外, 还有森林和草原土壤等. 而人们对 N_2O 在天然森林和草地土壤的排放情况的研究鲜见报道. Ryder 观测到草原土壤对 N_2O 的大量吸收, 其吸收通量为11.6ng$Nm^{-2}s^{-1}$[5]. Donoso 等也报道了土壤消耗 N_2O 的这个重要现象, 但是还没有足够的数据表明土壤是否会是一个巨大的全球性的 N_2O 的汇[6]. 作为北半球地理地貌的一个主要组成部分, 森林和草原土壤排放 N_2O 的情况无疑是非常重要的. 为今后更好的全面评价 N_2O 在我国的排放情况, 笔者进行了我国森林和草原土壤排放的 N_2O 通量测定的研究.

1 实验部分

1.1 森森土壤和草原土壤 N_2O 排放通量测定

选择位于北京市门头沟区小龙门(39°58′N, 115°26′E)海拔高度为1150m 的中国科学院北京森林生态系统研究站为定点研究森林的实验点. 选择河北省坝上固源县的草原作为定点测定草原土壤 N_2O 的排放通量实验点. 其中无论是森林土壤还是草原土壤均为无任何人为污染(如施肥等)的纯净的自然土壤.

采用静态箱法测定排放通量. 通量箱由薄铁板制成, 内衬 Velton 薄膜, 以减少 N_2O 在器壁上的可能吸附, 其体积为$(47\times52\times42)\ cm^3$. 将此无底箱埋入土内约5cm, 箱上部有一活盖, 侧面有采样口, 有硅胶管通入箱中心位置.

在测点分别放置2个通量箱, 一个通量箱的下垫面为腐植叶土, 另一个通量箱的下垫面为除去表面腐植物的土壤. 在合上活盖后立即用玻璃针筒由采样口采集200ml 气体, 此后每隔15min 采集1次样品, 共6次. 样品存于金属复合膜储气袋中, 运回实验室分析.

1.2 N_2O 浓度检测与分析

气体样品中的 N_2O 浓度分别用 PYE-Unican 304 型气相色谱仪和 HEWLETT PACKARD SeriesII 型气相色谱仪测定的. PYE-Unican 304型气相色谱仪使用配置的^{63}Ni电子捕获检测器和1台 CRIB Chromatopac 进行测定, 载气为超高纯氮(99.999%), N_2O 的

* 国家自然科学基金资助项目
收稿日期: 1997-01-20

二级标准气浓度为644mg·m^{-3}, 由北京标准物质研究所提供. 色谱柱为 porapak Q 填充的玻璃柱, 色谱条件为: 检测器温度300℃, 进样温度120℃, 柱温55℃, 载气流速25ml/min, 在这些条件下 N_2O 的保留时间约为183s. HEWLETT PACKARD SeriesII 型气相色谱仪其检测器是电子捕获检测器(ECD), 色谱柱为 porapak Q 填充的不锈钢柱, 通过计算机来控制定量管(6ml)和十通阀进样, 并将气体样品中的水分在进入检测器之前反吹掉. 载气是高纯氮, 柱温90℃, 进样温度15℃, 检测器温度330℃, 载气流速25ml/min, 标准 N_2O 气体浓度是618.75mg/m^3, 由标准物质研究所提供.

N_2O 的定性分析是由外标法和保留时间测定的.

用外标法对 N_2O 进行定量分析时, 计算式如(1)式.

$$c_{(2)} = \frac{c_{(1)} V_{(1)} S_{(2)}}{V_{(2)} S_{(1)}} \quad (1)$$

其中, $c_{(1)}$: 标准 N_2O 气体的浓度(mg/m^3); $V_{(1)}$: 标准 N_2O 气体的进样体积(ml); $S_{(1)}$: 标准气在色谱图上的峰高或峰面积; $V_{(2)}$: 样品进样体积; $S_{(2)}$: 样品在色谱图上的峰高或峰面积; $c_{(2)}$: 样品中 N_2O 的浓度(mg/m^3).

2 结果与讨论

2.1 森林、草原土壤中 N_2O 的排放通量测定

N_2O 的排放通量(F)是由箱内气体浓度随时间变化而增加(或减少)来计算的, 计算方法如(2)式.

$$F[\mathrm{mg/(m^2 \cdot h)}] = D \times H \times \frac{\Delta c}{\Delta t} \quad (2)$$

$$H = V/A$$

其中, D 为气体密度, H、V 和 A 分别为箱的高度、体积和底面积, $\frac{\Delta c}{\Delta t}$为单位时间内 N_2O 浓度变化量. 为此首先将测定的通量箱内的 N_2O 浓度对时间作图, 求出起始阶段直线斜率, 由此求出排放通量, 如图1所示.

森林和草原土壤的排放通量结果显示 N_2O 的排放通量随季不同而发生变化. 从6月

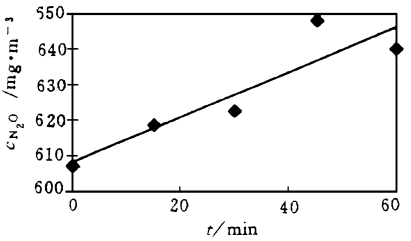

图1 森林土壤的 N_2O 排放通量

到9月其排放通量数值通常为正值, 表明在此期间森林和草原土壤是向大气中排放 N_2O, 此时无论是森林土壤还是草原土壤均表现为一个 N_2O 的排放源. 其最大排放通量为23μg/(m^2·h), 最小排放通量值为1.9μg/(m^2·h).

值得注意的是在1993—1996年的观测记录中发现从9月至来年5月期间 N_2O 的排放通量出现负值, 表明该期间土壤表现为 N_2O 的一个汇, 其最大吸收通量为18.984μg/(m^2·h).

2.2 森林土壤 N_2O 排放通量的日变化

在1h 内, N_2O 的浓度逐渐增大, 表明土壤的 N_2O 正在排放, 随后则观察到明显下降. 在3h 后达到最低点, 然后逐步上升, 此时正值10:00—15:00. 可能与气温变化有关, 待15:00以后浓度又逐渐下降直到第2日8:00. 由此可见, 测定 N_2O 的排放通量, 所选时间应在通量箱加盖1h 内进行.

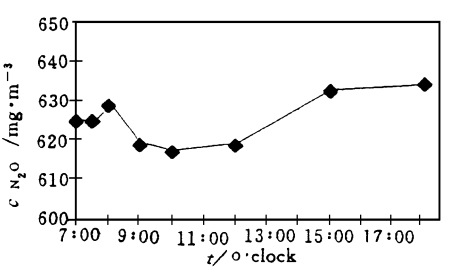

图2 N_2O 排放的日变化

2.3 森林土壤成分对 N_2O 排放通量的影响

小龙门林区的土壤属于褐棕色粘土, 而且没有经过任何形式的人为污染. 表1为其含氮量和有机质含量的一些数据.

小龙门森林生态站的土壤含氮量较低, 仅有0.2% —0.3%, 属低氮区, 其数值常年变化不大. 该地区上壤矿物质中可交换元素有 P、Al、

表1　森林土壤的 TN 量[1)]

采样日期	土壤	TN/%
1990-07	3—12cm 土	0.20
1995-09	腐质叶土	0.36
	腐质叶土	0.40
1995-09	土	0.20
	土	0.23
1995-12	腐质叶土	0.15
	腐质叶土	0.20
1995-12	土	0.20
	土	0.25
1996-01	腐质叶土	0.50
	腐质叶土	0.48
1996-01	土	0.26
	土	0.24

1) pH 为6.26, TC 为3.92%

Mn、K、Na、Ca、Mg 等, 可提取元素有 Cu、Zn、Fe 等, 且其组分比较稳定. 由此可见小龙门森林生态站的土壤成分比较稳定, 可以基本排除其为影响该地域 N_2O 排放情况的主要因素.

2.4　地表湿度对 N_2O 排放通量的影响

对比 N_2O 排放通量与地表湿度的变化, 从20%到饱和湿度, 如图3所示. 图中×点为当日降水量, 可以看出在该地区地表湿度与土壤排放 N_2O 之间并不存在什么明显的关系. 图3表明 N_2O 的排放并不随降雨和湿度的增加而增加, 在该地区 N_2O 出现负值时湿度和降水时高时低. 笔者认为这可能与当地土壤成分含氮量低有关. 尽管土壤中由细菌参与的硝化和脱氮过程是产生 N_2O 的原因, 但是在低氮区地表湿度的增加并没有使铵氧化细菌大量繁殖, 从而加剧产生 N_2O 的过程. 由此可见, 地表湿度并非是影响该地区土壤排放 N_2O 的主要原因.

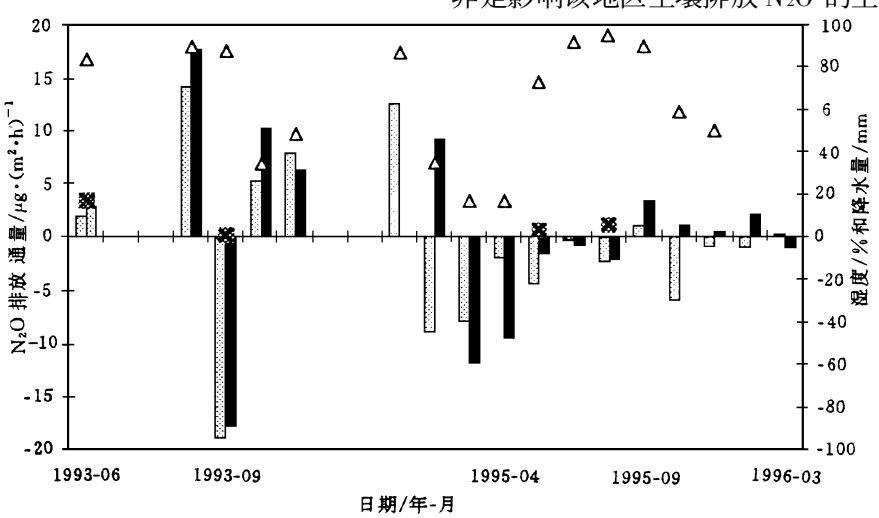

图3　N_2O 排放和森林土壤湿度的关系

□: 土面　　: 叶面 Δ: 湿度 ×: 降水量

2.5　温度对森林土壤排放 N_2O 的影响

用森林土壤 N_2O 排放通量与相对应的地表温度作图时, 发现温度变化影响土壤 N_2O 的排放量, 如图4所示.

很显然当地表温度高于15℃时, N_2O 排放通量通常为正值, 当温度在15—7℃时, N_2O 出现了负排放, 而在0℃以下则几乎停止排放. 结果指出在该地区地表温度是影响其浓度的主要因素. 由此可见, 在低氮区温度是影响铵氧化细菌产生 N_2O 的主要因素. 在对草原土壤 N_2O 的排放通量检测时, 也发现了同样的现象.

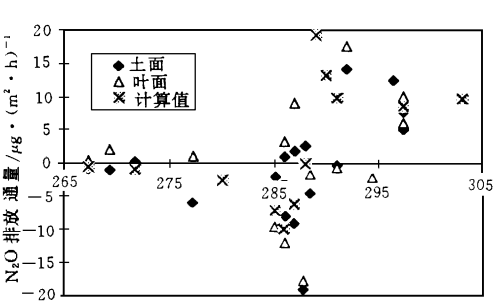

图4　N_2O 排放与温度之间的关系

笔者认为造成该现象的原因主要是因为铵氧化细菌在温度高时, 活动能力比较强, 其硝化与反硝化作用的结果是向外排放过量的 N_2O. 当温度较低时, 铵氧化细菌的活动能力减弱, 其硝化与反硝化作用产生的 N_2O 不足以维持其生存, 其结果就表现为从环境中吸收 N_2O 以供其生存. 而当温度降至0℃以下, 此时的铵氧化细菌几乎处于不活动状态, 其对周围环境中 N_2O 的影响也降至最低.

3 小 结

(1) 建立了适用于森林和草原土壤 N_2O 排放通量检测的完整的气相色谱方法.

(2) 观测到低氮含量的森林、草原土壤的 N_2O 排放通量主要与温度有关, 而与土壤的湿度无明显的关系. 一般说, 温度高, N_2O 的排放量大; 温度低, 排放低. 在一定的温度段还出现负排放, 即此时的土壤为 N_2O 的汇. 在评估土壤 N_2O 的释放量时, 不能忽视森林和草原土壤也可做 N_2O 的汇.

参 考 文 献

1 Whitten R C et al.. Atmos. Environ., 1983, **17**: 1995—2000

2 Khalil M A K and R A Rasmussen. The global sources of nitrous oxide. J. Geophys. Res., 1992, **97**: 14, 651—14, 600

3 Skiba U, Hargreaves K J, Fowler D and Smith K A. Fluxes of nitric and nitrous oxide from agricultural soils in a cool temperature climate. Atmos. Environ., 1992, **26**A (14): 2477—2488

4 曹美秋, 庄亚辉. 生物质燃烧释放 N_2O 的测定及其分布. 环境化学, 1994, **13**(5): 395—400

5 Rydne J C. N_2O Exchange between a grassland soil and the atmosphere. Nature, 1981, **292**: 235—237

6 Donoso L, Santana R, Sanhuega E. Seasonal variation of N_2O fluxes at tropical savannah site: Soil consumption of N_2O buring the dry season. Geophy. Res. Lett, 1993, **20**: 1379—1382

• 环境信息 •

书 讯

由国家环保局环境工程评估中心组编的《环境影响评价专辑》已经以《环境科学》1996年增刊出版, 该专辑共128页20万字, 内容包括可持续发展的战略性环评、环评有效性探讨、区域环•评、建设项目环评、生态环评、风险评估、费用效益分析以及完善环评制度的科学探讨和国内外经验介绍等. 本专辑从即日起在评估中心发售, 欢迎环保界同仁和对环境影响评价感兴趣的读者购阅本专辑, 并欢迎提出您宝贵的意见以利于改进工作.

购书办法: 邮购或到单位购买

定 价: 15元/册(包括邮费)

购书地址与联系人: 北京市安外大羊坊8号国家环保局环境工程评估中心 路振山

邮政编码: 100012

电 话: 64232255-268或278

由中国科学技术出版社出版的《资源环境常用数据手册》是集大气、水、土地、自然保护、海洋、城市环境、能源、经济与社会、环境政策与管理以及全球环境问题的常用数据于一体的参考性工具书, 可收到"一册在手, 全局在胸"之效。全书35万字, 定价10元(包括邮费)。

《中国小造纸、小印染高浓度有机废水治理技术交流会论文汇编》(《环境科学》增刊)精选了由国家环保局科技标准司科技处主持的"高浓度有机废水污染防治技术交流会"和"小印染高浓度有机废水污染防治技术交流会"交流的优秀科技论文39篇, 介绍了适用性强、投资少、成本低和能耗低的新型治理工艺、新设备、新药剂等, 包括小造纸厂黑液回收、木素综合开发、石灰法草浆厌氧处理技术, 处理高浓度有机废水的厌氧生物炭技术和处理印染废水的兼氧-好氧-生物炭技术, 高压脉冲电解法新设备等. 《汇编》约20万字, 定价8元/册(含邮费). 编辑部还有刊(书), 欲购后两本书者请将书款汇到北京2871信箱(邮编100085)《环境科学》编辑部, 并请用正楷在汇款单上写清双方地址、邮政编码、姓名、款数、所购书名及数量. 切勿多寄或少寄书款及信中夹邮书款. 也可携款到编辑部购买.

联系电话: 62925511-2138 联系人: 万维纲

Impacts of Temperature on N_2O Production and Emission. Zheng Xunhua, Wang Minging et al. (Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 1—5

N_2O emission fluxes from a rice-wheat rotation ecosystem of the Taihu Region in Southeast China and temperature of air and soil were simultaneously measured with an automated system to understand the effects of temperature on N_2O emission. The principle of this automated system for N_2O emission measurement was based on static chamber techniques and gas chromatography with an electronic capture detector. Additionally, some simulated experiments were also undertaken in laboratory to study temperature impacts on N_2O production. Based on the results from this experimental study, conclusions as following could be drawn. N_2O emission flux from fields with suitable moisture is exponentially correlated to top soil temperature. The occurring frequency of significant N_2O emission in a rice-wheat rotation cycle versus top soil temperature is in normal distribution, with 67% of the total N_2O amount emitted within 15—25℃. Temperature is rather a key factor regulating N_2O emisson from wheat fields. However, on significant relationship between temperature and seasonal variation of N_2O emission from rice field was found. Although the diurnal maximum of N_2O emission from rice fields which occurs simultaneously with diurnal temperature peak appears about 3 hours earlier than that from wheat fields, the diurnal variation patterns from both rice and wheat fields are the same.

Key words: N_2O emission, temperature, N_2O production, rice-wheat ecosystem, emission fluxes, farmland.

Calculation of Critical Loads for Acid Deposition with Steady-state Acidification Model. Xie Shaodong, Hao Jiming, Zhou Zhongping (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 6—9

A steady-state soil chemistry model was used to calculate the critical loads of acid deposition for schist red earth and surface water in Liuzhou Area. A complete and systematic approach to collect, measure and estimate the parameters required by the model was established, and some empiric formulas to calculate total deposition from wet deposition for coniferous ecosystems in this area were acquired. The results indicate that schist red earth in this area have reached a steady-state with the acid deposition, whose critical loads of acidity, potential acidity and sulfur deposition are 1.96, 1.88 and 1.1keq$\cdot hm^{-2}\cdot a^{-1}$ (1.8 g $Sm^{-2}\cdot a^{-1}$) respectively, and those of surface water 0.88, 0.80 and 0.61 keq$\cdot hm^{-2}\cdot a^{-1}$ (1.0g $Sm^{-2}a^{-1}$) respectively.

Key words: steady-state acidification model, critical load, red earth, acid deposition, schist red earth, surface water, empiric formula.

Study of Atmospheric Reaction between Isoprene and O_3. Li Shuang, Chen Zhongming, Shao Kesheng, Tang Xiaoyan (The State Key Laboratory of Environmental Simulation and Pollution Control, Center of Environmental Sciences, Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 10—14

The reaction of isoprene-O_3 in the dark was studied by means of the Long Path Fourier Transform Infrared (LP-FTIR) method. Experiments were carried out in the evacuable quartz reactor with the volume of 28.5L under the room temperature. The experiment results indicated that the major products in the isoprene-O_3 reaction systme are methacrolein, methyl vinyl ketone and HCHO, with a yield of 37.4%, 20.2% and 55.1%, respectively. Other products identified in the FTIR spectrum are HCOOH, CO and CO_2, etc. The reaction mechanism for the ozone oxidation of isoprene is briefly discussed.

Key words: isoprene, O_3, LP-FTIR, atmospheric reaction.

N_2O Exchanges between Atmosphere and Territory from Forest and Grassland. Liu Ye, Mu Yujing, Zhong Jinxian, Yang Wenxiang (Research Center for Eco-Environment Sciences, Chinese Acadmy of Sciences, 100085): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 15—18

Nitrous oxide(N_2O) is not only a major greenhouse gas in the atmosphere, but also an important matter that can cause ozone depletion. The emission sources of N_2O are consisted by a large number uncertain minor sources. Besides agricultural soils, grassland and forest soils are also the major natural source of N_2O emissions. In this paper, a completed method to determine the N_2O emission flux from forest and grassland soil by a closed chamber installation was set up, and the N_2O emission at the natural environment was measured in

northern China. The maximum value of N_2O emissions from forest and grassland soil is about 23$\mu g/(m^2 \cdot h)$. A high rate of N_2O loss is observed when the temperature is lower than 15℃. The maximum value of N_2O negative emissions as high as 18.984 $\mu g/(m^2 \cdot h)$ has been measured.

Key words: N_2O, O_3, emission flux, source, sink, exchange between atmosphere and territory.

Ultrafiltration Membrane Bioreactor for Domestic Wastewater Treatment and Its Hydraulic Behavior. Xing Chuanhong, QianYi, (State Key Laboratory of Environmental Simulation and Pollution Control, Dept. of Environ. Eng., Tsinghua University, Beijing, 100084), Tardieu Eric (CIRSEE-Lyonnaise des Eaux, 38, rue du President Wilson, F78230 Le Pecq.): *Chin. J. Environ. Sci.*, **18** (5), 1997, pp. 19—22

It is proven that Ultrafiltration Membrane BioReactor (UMBR) applied to domestic wastewater treatment, under conditions of hydraulic retention time 5h, sludge retention time 30d, membrane surface velocity 4m/s and membrane flux 75L/($m^2 \cdot h$), is technically feasible and reliable during several weeks. Removal rate of COD, NH_3-N, and turbidity of the systme are equal to or higher than 98%, 97% and 98%, SS and E. coli., 100%. The effluent quality is always better than the quality standard for reuse issued by the Ministry of Construction in China. Furthermore, the hydraulic behavior of UMBR is concisely discussed. The hydraulic boundary layer is about 185—5.9μm thick, and the mass transfer boundary layer, 18.5—0.59μm when the typical Reynolds number is 4×10^3—2×10^5.

Key words: ultrafiltration membrane, bioreactor, domestic wastewater, hydraulic behavior, boundary layer thick.

Soil Sensitivity to Acid Deposition in South China Ⅶ. **Cation Leaching and Buffering Mechanism**. Qiu Rongliang et al. (Department of Environmental Science, Zhongshan University, Guagzhou 510275): *Chin. J. Environ. Sci.*, **18**(5), 1997, pp. 23—27

Acidic deposition is considered an environmental problem that may affect the soil's cation-exchange status. This study used column leaching experiments to examine the influences of simulated acid rain with different pH values on base cation leaching of main soil types collected from South China. The results showed that amounts of leaching base cations increased obviously when the pH value of simulated acidic rain was lower than 3.0 or 3.5, while the amounts almost did not differ when pH higher than 3.5. The leaching of Ca^{2+} and Mg^{2+} was affected evidently by the pH value of simulated acidic rain, compared with the leaching of K^+ and Na^+. The H^+ buffering mechanisms which may vary in different simulated pH acidic rain are proposed for main soils studied. The dissolving reaction of salts was the dominant resources of leaching base cations and H^+ buffering when pH value higher than 3.5. The mechanisms of H^+ buffering treated with acid rain at pH 3.5 were the exchangeable cations and sulfate sorption. Dissolved aluminum on the broken edge of clay and aluminum oxides weathering of original and secondary minerals and sorption of sulfate played a grea role on the leaching of soil cations and H^+ buffering when the soils treated with acid rain of pH lower than 3.5.

Key words: simulated rain, base cations, leaching, soil sensitivity.

Studies on Effect of Water Treated by High-Voltage Electrostatic Field on Oxygen Utilization Rating of Activated Sludge. Yang Feng, Kong Jilie, Deng Jiaqi (Dept. of Chem., Fudan University, Shanghai 200433), Xiang Yang, Gao Tingyao (School of Environ. Eng., Tongji University, 200092): *Chin. J. Enwiron. Sci.*, **18**(5), 1997, pp. 28—30

The microorganisms extracted from activated sludge were selected as the sensitive material to make a BOD biosensor for monitoring the metabolic ability of themselves in high-voltage electrostatic treated water (HVETW). The oxygen utilization rating of the microorganisms which operated in such an aqueous media for appropriate time, could be promoted by at least 20%. At the same working high-voltage, this effect depended on how long the water was treated. The water treated for too long a time would lead to the negative effects. At 5000 V, it took about 6.0 h for the microorganisms to obtain the maximum oxygen utilization rating, whereas it did about 4.0 h at 7000 V. This discovery might offer a great potential for improving the new waste water disposal techniques.

Key words: high-voltage static electricity, activated sludge, BOD, microbial sensor.

Mixtoxicity of 2, 4-DNT and 6 Kinds of Nitroaromatic Compounds to the Algae. Liu Jingling, Yuan Xing, Lang Peizhen (Dept. of Environ. Sci., Northeast Normal Uni., Changchun, 130024): *Chin. J. Enwiron. Sci.*, **18** (5), 1997, pp. 31—33

In order to evaluate objectively the ecological effects of 2, 4-DNT mixed with 6 kinds of ni-