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北京地区稻田上空甲烷浓度的监测*

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摘要 通过对北京地区稻田种植区上空甲烷浓度持续2 a的观测发现，该地区大气中1992和1993年甲烷的年平均浓度分别为1.16，1.17 μg/L，且季节性变化规律以及年际变化规律有比较固定的趋势。一年中当地上空甲烷的浓度呈明显的冬春低夏秋高的趋势，且夏季甲烷浓度的变化幅度比较大。该地区甲烷浓度的日变化趋势不明显。在水稻生长期内的7、8月间，稻田上空甲烷浓度和水稻甲烷排放速率有密切的关系，动态分析表明，该地区大气中甲烷浓度年增加速率为0.2%，较以往文献报道要小。

关键词 甲烷，水稻，排放源，生物圈，大气痕量气体。

全世界每年甲烷的排放量估计为240 Tg/a[1]，主要的来源是生物源，其中很大的一部分和人类种植水稻有关。80年代以来，人们在世界各地包括在我国西北民勤地区对于大气甲烷的浓度进行了大量的观测，但是直接针对水稻种植区中大气甲烷浓度的观测研究还鲜见报道[2]。中国水稻的播种面积约为3.2×10^{11} m²，约占全球水稻总面积的22%[3]。北京地区属半干旱地区，温带、季风型大陆性气候，种植习惯多以小麦和水稻间作为主，这种自然和农业条件在北方地区有很大的代表性[4]。通过研究这个地区大气中甲烷浓度的变化和水稻甲烷的排放关系，可以进一步了解本地区乃至全国甲烷排放的情况，并有利于进一步改善相应的测试手段。

1 实验方法

1.1 样品采集

实验点设于北京朝阳区洼里乡的农田中，该区每年的6—10月份种植水稻，以麦茬稻为主，播种总面积为2000 hm²。采样点周围2—3 km范围内除有2条公路外都种满水稻，没有其他明显的人为源。在1991-10至1993-11的2 a期间里，用注射器隔天于每日早中晚3次采集实验地点距地面1—2 m高处的空气样品，同时测定一般的气象条件，并将样品带回实验室以5 ml/min的流速通过3—5 cm长的氯化钙干燥管立刻分析。

1.2 仪器及样品分析

样品分析采用GC-FID，色谱仪为北京分析仪器厂制造的SP2305气相色谱仪，标准气(浓度为3.447 μg/L)由北京分析仪器厂提供，并采用美国NBS提供的标准气(2.561 μg/L)定期标定，相对平均偏差不超过0.02%。分析柱为13X(60—80目)分子筛填充柱，1.5 m×3 mm (i.d)。分析时柱温80℃，载气为高纯氮气，流速40 ml/min，保留时间1.8 min。采用峰高法定量。每个样品重复分析3次，分析相对误差小于0.08%。利用六通阀进样，定量管体积为5 ml。

2 结果与讨论

2.1 稻田上空甲烷浓度的季节变化

在1991-11至1992-10和1992-11至1993-12月期间2个完整的观测区间内，甲烷的日平均浓度曲线呈比较明显的“冬春低夏秋高”的趋势，浓度极差可达1.3 μg/L。而且年际间的重

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复性比较好，如果将 2 a 的月平均值进行相关性检验，其相关系数在置信度为 90%的条件下可达 0.97。冬季浓度变化比较平稳，夏季稻田上空甲烷浓度的变化幅度比较大，2 a 中 6，7，8 三个月的月平均标准偏差均大于 0.35，明显大于一般情况下冬季和春季的月平均标准偏差(见表 1)。

表 1　1991—1993 年间稻田上空甲烷浓度的月平均浓度(μg/L)

月	1991—1992		1992—1993	
	平均	SD	平均	SD
11	1.070	0.1399	1.043	0.1183
12	1.078	0.2099	1.069	0.1243
1	1.063	0.1566	1.082	0.1395
2	1.041	0.2289	1.022	0.1206
3	1.061	0.2146	1.096	0.1416
4	1.028	0.2724	1.064	0.3127
5	1.187	0.2828	1.175	0.2374
6	1.239	0.2546	1.285	0.3182
7	1.312	0.3263	1.332	0.2861
8	1.193	0.2810	1.243	0.3654
9	1.290	0.1294	1.304	0.1282
10	1.358	0.2583	1.329	0.2644
年平均	1.160		1.170	

类似的变化形式 Oregon 研究生院的 Cape Meares 实验点也曾被发现过[5]。但是本地区的波动幅度较大且夏季的浓度较 Cape Meares 的浓度偏高。造成这种季节性变化的原因目前还不十分清楚，初步估计和甲烷的源强度以及有关的光化学汇的变化有关系。从分析各方面的因素来看，造成这种情况的主要原因是：由于夏季气温高，各种生物源的活动比较活跃，且日光强度变化较大；甲烷在大气中通过 OH 自由基和其他过程的消耗量也有很大的不同所致。

除 6、7、8 月以外，2 a 中 4、5 月的平均标准偏差和 10 月的平均浓度也明显偏高，初步分析可能和春季烧荒积肥以及秋季的秸杆焚烧还田有关。

2.2　稻田上空甲烷浓度的日变化

在 1991-10 至 1993-11 期间，对于稻田上空甲烷的浓度进行 24 次间隔为 2 h 的昼夜观测，观测结果表明：该地区大气中甲烷浓度日变化形式有明显的规律性。通常晴天时日变化幅度比较大，下午至晚间出现峰谷，凌晨出现极大值，阴天时变化幅度较小。冬季甲烷的浓度变化比较平缓，夏季变化幅度稍大，且出现“日高夜低”的情况比较多。一般情况下甲烷浓度的峰值多出现在午夜至凌晨。峰谷常出现在午后(图 1)。通过观察没有发现其与稻田甲烷的排放速率的日变化形式有任何关系。从而可以初步得出结论，该地区上空的甲烷背景值的日变化主要受甲烷的光化学汇的控制，其他因素的影响与之相比居次要地位。

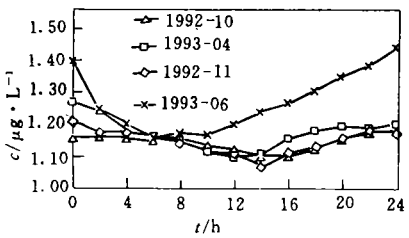

图 1　甲烷浓度的日变化

2.3　水稻种植期稻田上空甲烷浓度和水稻甲烷排放速率的季节变化关系

根据有关文献报道[4]，稻田甲烷的排放有明显的季节性，排放高峰多出现在水稻的分蘖期和扬花期。针对这种情况，在 1992-7 至 1992-8 间水稻生长的旺盛期，进行了加密观测。结果发现当地上空甲烷浓度的变化受水稻甲烷排放速率的影响很大，在同期观测中[4]，水稻甲烷在分蘖期和扬花期的 2 个排放高峰都可以在当地上空的甲烷背景值的变化中体现出来。特别是 7 月初和 8 月中的排放高峰期间 2 者的相关性相当好，相关系数可达 0.85 以上(图 2)。从而说明，稻田甲烷的季节性排放特征在周围相当大的区域中带有普遍性；当地上空甲烷背景值的变化受稻田源强度变化的影响较大，而甲烷是这个地区这段时期内最主要的排放源之一。

2.4　甲烷浓度的年际变化动态分析

2 a 的年平均值分别为 1.160，1.170 μg/L。如果将 2 a 的月平均值做线性关系进行回归，就可以发现其总的变化趋势是一条斜率为0.00231

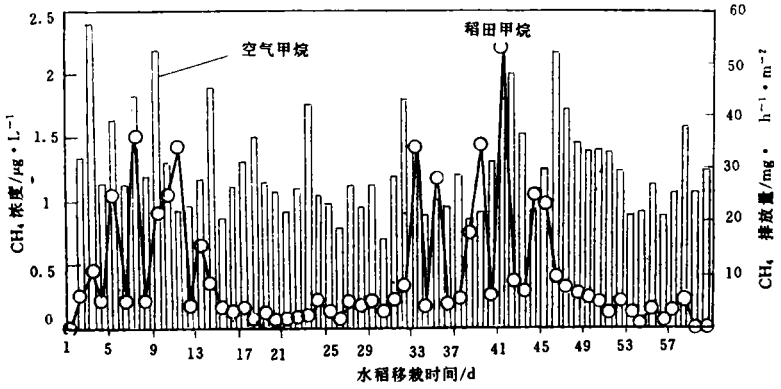

图 2 稻田上空甲烷浓度变化和水稻排放通量的关系

的直线。如果用 2 a 的月平均值作动态平均分析就可以得到甲烷浓度的年际变化趋势(表 2)。动态平均分析的年变化率为 0.00198。这个变化率比 Rasmussen 在 Cape Meares 和我国西北民勤地区以及世界其他地区观察到的近年来大气中甲烷的年际变化率都要小得多[5]。造成这种现象的主要原因还不清楚，估计这和该地区本身的背景值就比较高，又与人为的排放源比较接近有关。但是近来有研究表明大气中甲烷的浓度变化在 1%的速率持续增加了 200 a 之后有放慢并降低的势头[6]。由于本研究受实验点的地理位置和观测的时间尺度以及实验手段等诸多因素的限制，还不能断定所观测到的变化趋势和全球的总趋势有关。但从观测结果中可以发现，甲烷在大气中的浓度增长速率在某些地区之间并不完全相同，其年度内的变化规律受当地源与汇的变化影响很大。

表 2 甲烷年际变化动态

动态年	1	2	3	4	5	6	7	8	9	10	11	12	13
甲烷浓度(μg/L)	1.160	1.158	1.157	1.159	1.157	1.160	1.163	1.162	1.166	1.168	1.172	1.173	1.170

3 结论

(1) 本地区大气甲烷浓度在一年中有比较明显的季节变化特征，即“冬春低夏秋高”，夏季浓度的变化幅度比较大，冬季较小。这种变化特征和本地区甲烷的源与汇的变化有关。

(2) 本地区大气甲烷的日变化没有固定的形式。水稻种植期间所排放的甲烷是本地区大气中甲烷的主要来源之一。水稻生长期间大气中甲烷浓度和水稻甲烷的排放速率有密切的关系。

(3) 本地区大气中甲烷的年平均浓度为 1.16 μg/L，平均浓度年际增长率约为 0.2%。

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Study on the Catalytically Hydrogenated Conversion of CO_2 Using Ru/Al_2O_3 Catalyst. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 23—25

In this paper the catalytically hydrogenated conversion of CO_2 was studied using Ru/Al_2O_3 catalyst, the influence of different reaction conditions, such as reaction temperature (260—520℃, 5000—10000 h^{-1}) and CO_2/H_2 ratio in inlet gas, on CO_2 conversion efficiency and CH_4 formation were reported. At reaction temperature higher than 350℃ the CO_2 conversion efficiency was over 95%. and CH_4 formation rate was about 45%—79%. There was no significant influence on CO_2 conversion efficiency and H_2O formation when the space velocity from 5000 h^{-1} to 10000 h^{-1}. However, for the CH_4 formation efficiency there was a trough at the space velocity of 7000—9000 h^{-1}. The CO formation changed a little at space velocity of 5000—9000 h^{-1}, but it increased a lot at 10000 h^{-1}. The higher CH_4 formation efficiency was obtained when there existed excess of H_2. The highest CH_4 formation efficiency obtained was 98%.

Key words: carbon dioxide, catalyst, catalytically hydrogenated, methane.

Monitoring on The Concentration of Atmospheric Methane of A Rice Cropping Region in Beijing Area. Cui Ping et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 26—28

Monitoring on methane concentration in the atmosphere in the rice cropping region was carried out between Oct. 1991 and Nov. 1993. Results indicated that the average concentration of methane of the two testing years in the local region were 1.16 and 1.17 μg/L respectively. The variation of methane concentrations showed a strong seasonal pattern. The concentration and concentration deviation were high in summer and low in winter. During rice vegetation period, the methane concentrations were closely related with the variation of methane emission rates from rice paddies indicating rice paddies is one of the most important methane sources of the region. Running analysis showed that the average increasing rate of atmospheric methane in the region was 0.2%, much lower than some previous reports.

Key words: methane, rice, monitoring, Beijing area.

A simulation Study on the Accumulation of Added Rare Earth Elements in Aquatic Ecosystem. Chen Zhaoxi et al. (Dept. of Chem. Eng., East China Institute of Metallurgy, Maanshan 243002): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 29—31

The accumulation and distribution coefficients of added rare earth elements (RE) in various parts of simulated aquatic ecosystem were investigated. The results showed that concentrations of added RE in bottom mud and water bodies varied smoothly and in *Lemna minor* and *Cyprinus carpio* varied extremely with the time in the period of experiment. Distribution coefficients of added RE in bottom mud were higher than 96%, in *Lemna minnor*, were range of 0.26—1.61%, in water, were range of 0.54%—0.91%; and in carp were less than 0.035%, but almost on linear increment in the period of experiment. Bioconcentration of added RE in carp was also discussed.

Key words: aquatic ecosystem, accumulation, rare earth elements, bioconcentation.

The Quantum Chemistry Studies of the biradical Mechanism of Destroying Ozone in the Atmosphere. Sun Huabin et al. (Institute of Military Medicine, Jinan Command, Jinan 250014): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 32—34

The reaction mechanisms of the singlet biradicals NH, CH_2, CCl_2 with ozone in the atmosphere have been studied using RHF method of quantum chemistry. The geometries of the reactants, intermediates and products of the above reactions are optimized with the gradient technique at the 3-21G level, their energies have been calculated at the 6-31G or 6-21G level. The structure data of all species have been obtained. The calculated results show that there are two stages in the above reactions, the reactions of the biradicals with ozone take place first to form the stable intermediates, then the intermediates are decomposed by illuminating to the stable molecules HNO, H_2CO and Cl_2CO etc., respectively. In terms of dynamics two reactions in two stages belong to the types $[\pi_{4s}+W_{2s}]$ and $[\pi_{2s}+\pi_{2s}]$, respectively, and they are permited thermodynamically. In this study, a method to investigate complicated reaction based on the combining thermodynamics with Woodward-Hoffmann approach without calculation of transition state was attempted to provide by authors.

Key words: biradical, loss of ozone, reaction mechanism.

The Structure and Toxicity Relationship Study for Nitroaromatics to *Scenedesmus obliquus*. Lu Guanghua et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 35—36

E_{LUMO}, E_{HOMO}, $\Delta(\Delta H_f)$, μ and $Q_{\cdot NO_2}$ of 18 nitroaromatic compounds were calculated using the quantum chemical method MNDO. The quantitative structure-activity relationships (QSAR) were developed using the five quantum chemical descriptors for the acute toxicity of nitroaromatics to *Scenedesmus obliquus*. Through step-wise regression analysis, one best equation contained three variables was obtained: $-\log EC_{50}=2.92-0.077\Delta(\Delta H_f)+0.08\mu+0.28E_{HOMO}$, $n=18$, $r=0.961$, $S=0.173$. The equaiton was used to estimate the toxicity of the studied compounds, and the toxic effect was discussed.

Key words: structure, toxicity, nitroaromatics, *Scenedesmus obliquus*.

Effects of Rare-Earth Elements on Growth and Reproduction of *Chlorella pyrenoides*. Hu Qinhai et al. (Dept. of Environ. Sci., Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 37—38

It was studied that effects of rare-earth elements (La, Ce, Pr, Nd and their mixture) on growth and reproduction of *Chlorella pyrenoides*. The results showed that effects of rare-earth elements on growth and reproduction of *Chlorella pyrenoides* were not apparent under lower concentration (2 mg/L), but it was inhibited as the concen-