

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230753632>

UV/H₂O₂ Treatment of Methyl tert-Butyl Ether in Contaminated Waters

ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · FEBRUARY 2000

Impact Factor: 5.33 · DOI: 10.1021/es9905750

CITATIONS

147

READS

224

4 AUTHORS, INCLUDING:



James R Bolton

University of Alberta

315 PUBLICATIONS **10,080** CITATIONS

SEE PROFILE



Safarzadeh-Amiri Ali

Trojan Technologies

46 PUBLICATIONS **939** CITATIONS

SEE PROFILE

UV/H₂O₂ Treatment of Methyl tert-Butyl Ether in Contaminated Waters

STEPHEN R. CATER,^{*,‡}
 MIHAELA I. STEFAN,^{#,§}
 JAMES R. BOLTON,^{‡,‡,§} AND
 ALI SAFARZADEH-AMIRI^{‡,†}

Calgon Carbon Corporation, 130 Royal Crest Court,
 Markham, Ontario, Canada, L3R 0A1, and The University of
 Western Ontario, 1400 Western Road, London,
 Ontario, Canada N6G 2V4

Methyl *tert*-butyl ether (MTBE) is a pollutant often found in groundwaters contaminated by gasoline spills or from leaking underground storage tanks. The common techniques often used for the remediation of contaminated water are not very effective for MTBE. This study examines the UV/H₂O₂ advanced oxidation technology to determine its effectiveness in the treatment of MTBE. The degradation of MTBE was found to follow *pseudo*-first-order kinetics, and hence the figure-of-merit *electrical energy per order* (E_{EO}) is appropriate for estimating the electrical energy efficiency. The E_{EO} values were found to depend on the concentrations of MTBE, H₂O₂, and other components, such as benzene, toluene, and xylenes (BTX). This study shows that MTBE can be treated easily and effectively with the UV/H₂O₂ process with E_{EO} values between 0.2 and 7.5 kWh/m³/order, depending on the initial concentrations of MTBE and H₂O₂. The treatment efficiency of 10 mg L⁻¹ MTBE is not adversely affected by the presence of low concentrations of BTX (<2 mg L⁻¹). However, the degradation efficiency is significantly decreased at BTX levels greater than 2 mg L⁻¹. A kinetic model, based on the initial rates of degradation, provides good predictions of the E_{EO} values for a variety of conditions.

Introduction

The addition of MTBE to gasoline poses a significant problem for the remediation of wastewater and water contaminated with gasoline because of the accidental spill and leakage from underground storage tanks and transfer pipelines.

MTBE has low odor (45 µg L⁻¹) and taste (39 µg L⁻¹) detection thresholds (1) and a high solubility in water [about 50 g L⁻¹ (2)]. In the case of reformulated-gasoline soil contamination, MTBE penetrates readily into the aquifer and also increases the solubility of other petroleum derivatives, such as BTEX, by a cosolvent effect (1, 3).

MTBE biodegrades very slowly in soils and groundwater (4–6). Recent laboratory research (7, 8) has demonstrated that pure bacterial strains or natural isolates can be effective in the oxidative biotreatment of MTBE, but the aquifers

generally do not contain the nutrients needed for biodegradation (2). Consequently, bioremediation appears to be difficult to apply to large volumes of MTBE-contaminated water at µg L⁻¹ to mg L⁻¹ MTBE levels.

Air-stripping is a traditional and reliable technology for the removal of VOCs from groundwater but is not easily applicable to the treatment of MTBE, which has a low Henry's Law constant [$H/RT = 0.0216$ at 25 °C (9)] and partitions substantially into water. By this process, up to 99% of the MTBE can be stripped from contaminated groundwater, but large air-to-water ratios (100:1 and higher) and multiple air strippers in series are required. Water heating combined with aeration improves the removal yield of any volatile organic strongly partitioned into water. Both high airflow and water heating significantly increase the capital and operating costs of this technology. Moreover, the process achieves only a mass transfer from one phase to another, without solving the remediation problem.

MTBE has a moderate affinity for granulated activated carbon (GAC), and for concentrations in the range of 10–100 µg/L, GAC is an effective remediation technology.

For concentrations above 100 µg/L, MTBE can be treated at best with only moderate effectiveness by conventional remediation processes. Therefore, there is a need for an alternative process for the remediation of MTBE-contaminated groundwater and wastewater in relatively high concentrations between 0.1 and 80 mg/L. Advanced oxidation technologies (AOTs) provide a promising treatment option for MTBE in these ranges. As is well-known, the UV-driven AOTs combine the use of UV light in conjunction with an oxidizer, such as H₂O₂ and/or ozone, to generate hydroxyl radicals (•OH), which attack almost non-selectively any organic compound with very high reaction rate constants ($k \sim 10^6$ – 10^9 M⁻¹ s⁻¹).

The UV/H₂O₂ process involves the photolysis of hydrogen peroxide to generate hydroxyl radicals (•OH), which are very effective in the oxidation and mineralization of most organic pollutants (10, 11). This process has been used routinely worldwide for groundwater and drinking water remediation. Its main advantage over ozone-based processes is that it does not form bromate ion (a suspected carcinogen) from bromide (12, 13). Also with ozone-based treatments, there may be a need to treat the off-gas and VOCs may be stripped.

Very few UV/H₂O₂ studies have been directed specifically toward the destruction of MTBE in gasoline-contaminated wastewater and groundwater. Wagler and Malley (14) studied the UV/H₂O₂ treatment of MTBE in a model groundwater using a low-pressure mercury lamp. They observed only a minor pH effect in the low-alkalinity water and increasing rates of destruction as the hydrogen peroxide concentration was increased.

The present investigation was undertaken to obtain an understanding of the treatment efficiency of the degradation of MTBE in groundwater by the UV/H₂O₂ process as a function of the concentrations of various components. The companion paper by Stefan et al. (15) presents a thorough study of the intermediates and mechanism of the UV/H₂O₂ degradation of MTBE.

Experimental Section and Methods

Materials. MTBE was obtained from Aldrich (97%), and hydrogen peroxide (35%) was purchased from Canada Colors (Toronto, ON, Canada) and used as received.

General Procedure. All experiments were conducted using Toronto municipal drinking water. The contaminated water was treated in a standard Rayox 1 kW batch reactor. The unit

* Corresponding author phone: (905)477-9242, ext. 331; fax: (905)477-4511; e-mail: cater@calgcarb.com.

‡ Calgon Carbon Corporation.

§ The University of Western Ontario.

§ Current address: Bolton Photosciences Inc., Siebens Drake Research Institute, Room 230, 1400 Western Rd., London, ON N6G 2V4.

† Current address: Hydroxyl Systems Inc., 9800 McDonald Park Rd., P.O. Box 2278, Sidney, BC, Canada V8L 3S8.

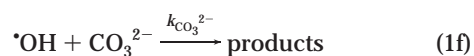
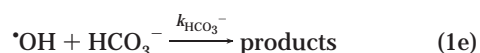
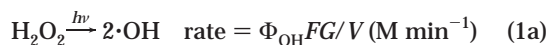
consists of a 40 L cylindrical (35.6 cm OD) stainless steel reactor equipped with a 1 kW Rayox medium pressure lamp mounted vertically in the reactor and separated from the water by a 6.35 cm OD quartz sleeve. The horizontal path length is 14 cm. A pneumatically activated transmittance controller automatically wipes the quartz sleeve at regular intervals to ensure that the quartz remains clean throughout the entire run. A mixer in the reactor ensures complete mixing of the sample during the tests. The unit is also equipped with a steel shutter which, when closed, blocks the transmittance of the UV light into the sample solution. The solution can also be cooled (if needed) during a run by passing cooling water through a cooling coil placed in the reactor. The solution was spiked with MTBE and H₂O₂, and a time of 5 min was allowed for dissolution and mixing before an initial sample was taken prior to opening the shutter. Samples were taken at regular intervals for the determination of the concentration of MTBE as a function of UV dose.

The light source was 1 kW medium pressure Hg UV lamp specifically manufactured for Calgon Carbon Corporation (CCC). The lamp's emission characteristics were reported previously (16). The photon flow G (einstein min⁻¹) was obtained from the known 200–300 nm power efficiency (25%) of the Rayox 1 kW lamp used and a weighted average wavelength (weighted over the spectral photon flux output of the lamp) of 258 nm. Eighty-eight percent of the lamp output was estimated to enter the reactor.

F was determined by dividing the 200–300 nm absorption region into 10 nm bands, within which the Beer–Lambert Law is assumed to hold.

Analytical Methods. The concentration of MTBE was measured by gas chromatography using either a Varian Model 3300 GC alone (DB-Wax column) or coupled to a Tekmar 3000 purge and trap concentrator (for measuring low MTBE concentrations in the $\mu\text{g/L}$ range). Some analyses were carried out on a Hewlett-Packard Model 6890 gas chromatograph with an autosampler and an HP-Wax column, as described in the companion paper (15).

Kinetic Model. A simple kinetic model, based on the initial rates of destruction, has been developed. Consider the following kinetic scheme for the simultaneous decay of three pollutants (A, B, and C) in tap water where HCO₃⁻ and CO₃²⁻ are potential scavengers of •OH radicals



where Φ_{OH} is the quantum yield for production of hydroxyl radicals in reaction 1a, G is the absolute photon flow from the UV lamp in the 200–300 nm region, F is the fraction of G that is absorbed in the reactor by H₂O₂, and V is the volume (L) of contaminated water in the reactor. The rate constants can be obtained from a large compilation (17).

From a steady-state kinetic analysis, the initial rates of decay of A, B, and C are

$$-\frac{d[A]}{dt}\bigg|_{t=0} = \{k_A[A]_0(\Phi_{\text{OH}} FG/V)\} / \{k_A[A]_0 + k_B[B]_0 + k_C[C]_0 + k_{\text{HCO}_3^-}[\text{HCO}_3^-]_0 + k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]_0 + k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + \sum_i k_{\text{S}_i}[\text{S}_i]_0\} \quad (2a)$$

$$-\frac{d[B]}{dt}\bigg|_{t=0} = \{k_B[B]_0(\Phi_{\text{OH}} FG/V)\} / \{k_A[A]_0 + k_B[B]_0 + k_C[C]_0 + k_{\text{HCO}_3^-}[\text{HCO}_3^-]_0 + k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]_0 + k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + \sum_i k_{\text{S}_i}[\text{S}_i]_0\} \quad (2b)$$

$$-\frac{d[C]}{dt}\bigg|_{t=0} = \{k_C[C]_0(\Phi_{\text{OH}} FG/V)\} / \{k_A[A]_0 + k_B[B]_0 + k_C[C]_0 + k_{\text{HCO}_3^-}[\text{HCO}_3^-]_0 + k_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]_0 + k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 + \sum_i k_{\text{S}_i}[\text{S}_i]_0\} \quad (2c)$$

where the subscript “o” indicates initial concentrations and the S_i represent various unspecified scavengers (e.g., natural organic matter).

If $k_A[A]_0$ is negligible compared to the sum of the other terms in the denominator of eqs 2a, the kinetics for the decay of A will be *pseudo*-first-order. Similar reasoning is valid for B and C. In practical applications, the level of hydrogen peroxide used is such that the term $k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]$ is always dominant in the denominator of eqs 2 and does not change very much during the reaction run. The *pseudo*-first-order rate constant k_1' (min⁻¹) then is the initial rate (M min⁻¹) divided by the initial concentration. The model can easily be extended to any number of pollutants and additional hydroxyl radical scavengers, such as chloride, bromide, etc. A spreadsheet has been developed in which a variety of factors (chloride level, alkalinity, nitrate level, pH, water absorbance spectrum, etc.) can be accounted for.

Electrical Energy per Order (E_{EO}). The Photochemistry Commission of the International Union of Pure and Applied Chemistry recently proposed figures-of-merit for AOTs (18). In the case of low pollutant concentrations (which applies here), the appropriate figure-of-merit is the *electrical energy per order* (E_{EO}), defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m³ of contaminated water. The E_{EO} (kWh/m³/order) can be calculated from the following equations for a batch type reactor

$$E_{\text{EO}} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \quad (3a)$$

$$E_{\text{EO}} = \frac{38.4 \times P}{V \times k_1'} \quad (3b)$$

where P is the power input (kW) from the wall to drive the UV lamp(s), t is the irradiation time (min), V is the volume (L) of the water in the reactor, C_i and C_f are the initial and final pollutant concentrations, and k_1' is the *pseudo*-first-order rate constant (min⁻¹) for the decay of the pollutant concentration. The factor 38.4 in eq 3b is the conversion factor $1000 \times \ln(10)/60$.

Results and Discussion

This study was focused on the photodegradation of MTBE in spiked tap water. The Toronto tap water used for these

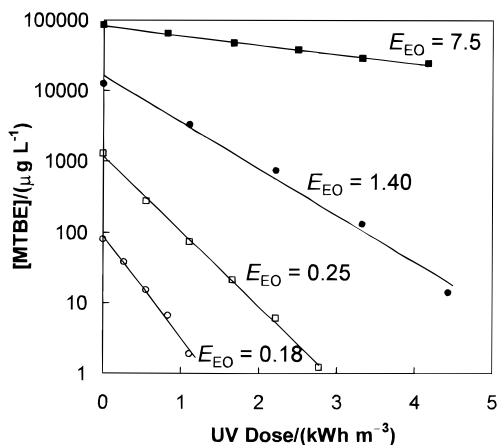


FIGURE 1. Concentration of MTBE versus UV dose (kWh/m^3) on a semilog scale. The E_{EO} values are obtained from the negative inverse slopes of the least-squares fit lines. The concentration of H_2O_2 was 30 mg L^{-1} for each run.

TABLE 1. Reaction Rate Constant and the E_{EO} for Photooxidation of MTBE

[MTBE]/ mg L^{-1}	k_1'/min^{-1}	$E_{EO}/(\text{kWh}/\text{m}^3/\text{order})$	
		exptl	model
0.08	7.1	0.18	0.30
1.3	5.1	0.25	0.37
12	0.98	1.4	1.04
85	0.18	7.5	5.56

^a $[\text{H}_2\text{O}_2] = 30 \text{ mg L}^{-1}$ for all runs.

tests had a chemical oxygen demand (COD) of about 5 mg L^{-1} and an alkalinity of about 80 mg L^{-1} . The pH of the tap water was about 6.8–7.0 and absorbed slightly in the UV (below 220 nm).

Effect of MTBE and H_2O_2 Concentrations. The rate of destruction of MTBE is influenced by the initial concentrations of both hydrogen peroxide and MTBE. Figure 1 shows the treatment of MTBE at four different initial concentrations (the concentration of H_2O_2 was 30 ppm for all runs); in all cases the decay of MTBE was found to follow first-order reaction kinetics with a *pseudo*-first-order rate constant k_1' . Thus, it is appropriate to analyze the data in terms of the *electrical energy per order* (E_{EO}) figure-of-merit. The E_{EO} may be obtained from the negative inverse of the slope of a plot of $\log(\text{concentration})$ vs energy dose (kWh/m^3) (see Figure 1). The reaction rate constants and the E_{EO} s are presented in Table 1. Note that k_1' increases (E_{EO} decreases) as the concentration of MTBE decreases. At higher concentrations of MTBE, higher concentrations of intermediates are formed. These intermediates are also highly reactive toward hydroxyl radicals. Thus, MTBE and its intermediates compete more effectively for $\cdot\text{OH}$ radicals, reducing the treatment efficiency of MTBE. Increasing the MTBE concentration from about 100 ppb to 100 000 ppb increases the electrical energy per order by a factor of about 40.

Table 1 also gives E_{EO} values estimated from the kinetic model. The model correctly predicts the trend of the E_{EO} s, in that the higher the concentration of MTBE, the larger the E_{EO} , but there are significant differences between the experimental and model E_{EO} s. Part of these differences can be explained in the fact that the model expresses the effectiveness of the UV/ H_2O_2 process only in terms of the initial concentrations. However, the experimental E_{EO} s are determined from the whole experimental curve and thus accounts indirectly for the partial treatment of the generated

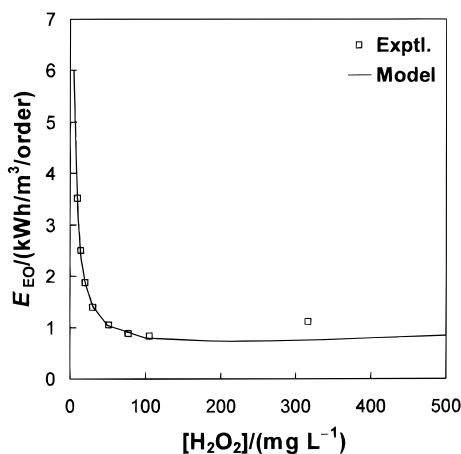


FIGURE 2. Electrical Energy per Order versus the initial concentration of H_2O_2 . The open squares are the experimental values, whereas the solid line represents the predictions of the kinetic model. The initial concentration of MTBE was 8–10 mg L^{-1} .

intermediates. This factor explains why the model underestimates the E_{EO} at the higher concentrations of MTBE.

The smaller experimental E_{EO} values at low MTBE concentrations may arise from $\cdot\text{OH}$ generation sources not accounted for in the model. For example, water typically contains low levels of iron, which can decrease the E_{EO} values. Photolysis of Fe(III) generates $\cdot\text{OH}$ radicals. In addition Fe(II), a product of this reaction, can generate more $\cdot\text{OH}$ radicals via the Fenton reaction with hydrogen peroxide. These processes are not accounted for in the kinetic model.

Figure 2 shows the destruction of MTBE as a function of the H_2O_2 concentration. As is evident, the rate of destruction and thus the electrical efficiency increases with increasing concentrations of hydrogen peroxide up to about 100 ppm H_2O_2 , above which, both decrease. The reason for this is that at higher concentrations of hydrogen peroxide, more UV is absorbed by hydrogen peroxide and the rate of generation of hydroxyl radicals is higher, which leads to a higher rate of oxidation of MTBE. However, above 100 ppm H_2O_2 , the H_2O_2 itself becomes a significant competitor for the hydroxyl radicals. As seen in Figure 2, the kinetic model provides a very close correlation of calculated and experimental E_{EO} values.

Effect of Added BTX Concentrations. Sometimes a groundwater contaminated with MTBE is also contaminated with benzene, toluene, and xylenes, because of their presence in gasoline. Therefore, the effect of BTX concentrations on the degradation of MTBE has been investigated. The E_{EO} for the treatment of MTBE as a function of BTX concentration is shown in Figure 3. As can be seen, photooxidation of 10 mg L^{-1} MTBE is not affected greatly for BTX concentrations of less than about 2 mg L^{-1} . At higher concentrations, however, the effect is dramatic. The solid line is obtained from the kinetic model, in which specific account is taken of the increase in the absorption spectrum arising from added amounts of BTX. Again the agreement is quite satisfactory. At lower MTBE concentrations, lower levels of BTX will affect the E_{EO} for MTBE at corresponding ratios of BTX to MTBE.

There are a number of reasons for the increase in E_{EO} with the concentration of BTX. First, the BTX components are highly reactive toward hydroxyl radicals and compete effectively with MTBE for the capture of these radicals. Second, BTX are relatively strong absorbers in the UV region. In addition, as the treatment progresses, phenolic intermediates are generated, which are stronger absorbers of the UV light than their parent compounds. Finally, the phenolic intermediates are also highly reactive toward hydroxyl radicals, further slowing the treatment of MTBE.

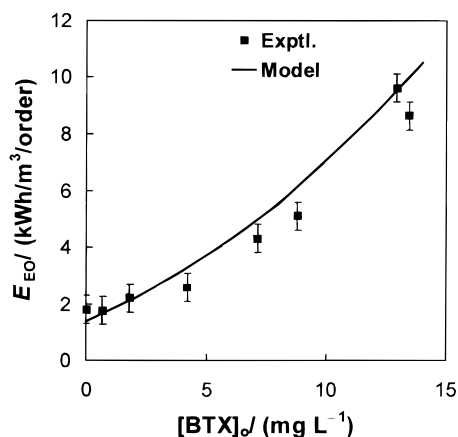


FIGURE 3. Electrical Energy per Order versus the initial concentration of benzene, toluene, and xylenes (BTX) (equal concentrations by mass). The initial concentration of MTBE was 8–10 mg L⁻¹ and that of H₂O₂ was 30 mg L⁻¹. The solid line represents the predictions of the kinetic model in which specific account is taken of the initial absorption spectrum of the solution.

Finally, it is useful to relate the E_{EO} s found in this study to treatment costs. If one takes the [MTBE] = 12 mg/L case, the E_{EO} is 1.4 kWh/m³/order. If the treatment objective is 10 µg/L, this means a log reduction of 3.08, and hence the total electrical energy required per m³ is 4.3 kWh. If the cost of electricity is \$0.06 per kWh, the contribution to the treatment cost from electrical energy will be \$0.26 per m³ or \$0.98 per 1000 U.S. gallons. In addition there will be smaller cost factors for the hydrogen peroxide used and for lamp replacement.

Acknowledgments

We wish to thank Mr. Keith Bircher, P. Eng., and Dr. Bertrand Dussert of Calgon Carbon Corporation for their helpful comments.

Literature Cited

- (1) Davidson, J. M.; Parsons, R. In *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference*, Nov. 13–15, 1996, Ground Water Publishing Company: Houston, TX, 1996; pp 15–29.
- (2) Squillace, P. J.; Pankow, J. F.; Korte, N. E.; Zogorski, J. S. *Environ. Toxicol. Chem.* **1997**, *16*, 1836.
- (3) Schirmer, M.; Barker, J. *Ground Water Monit. Rem.* **1998**, *18*, 113.
- (4) Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. *Appl. Environ. Microbiol.* **1994**, *60*, 2593.
- (5) Horan, C. M.; Brown, E. J. In *Proceedings of the 10th Annual Conference on Hazardous Waste Research*, May 23–25; Kansas State University, Manhattan, KS, 1995; pp 11–19.
- (6) Suflita, J. M.; Mormile, M. *Environ. Sci. Technol.* **1993**, *27*, 976.
- (7) Salanitro, J. P. U.S. Patent No. 5750364A, 1995.
- (8) Steffan, R. J.; McClay, K.; Vainberg, S.; Condee, C. W.; Zhang, D. *Appl. Environ. Microbiol.* **1997**, *63*, 4216.
- (9) Robbins, G. A.; Wang, S.; Stuart, J. D. *Anal. Chem.* **1993**, *65*, 3113.
- (10) Bolton, J. R.; Cater, S. R. In *Surface and Aquatic Photochemistry*; Helz, G., Zepp, R. G., Crosby, D., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 467–490.
- (11) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, *93*, 671.
- (12) Symons, J. M.; Zheng, C. H. *J. AWWA* **1997**, *89*, 106.
- (13) Von Gunten, U.; Hoigné, J. *Environ. Sci. Technol.* **1994**, *28*, 1234.
- (14) Wagler, J. L.; Malley, J. P., Jr. *J. NEWWA* September **1994**, 236.
- (15) Stefan, M. I.; Mack, J.; Bolton, J. R. *Environ. Sci. Technol.* **2000**, *34*, 650–658.
- (16) Safarzadeh-Amiri, A.; Bolton, J. R.; Cater, S. R. *Water Res.* **1997**, *31*, 787.
- (17) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- (18) Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. J. *Adv. Oxid. Technol.* **1996**, *1*, 13.

Received for review May 24, 1999. Revised manuscript received September 10, 1999. Accepted December 1, 1999.

ES9905750