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Biofilter Technology for NOx Control

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
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Research Division

BIOFILTER TECHNOLOGY FOR NO_X CONTROL

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Contents

EXECTUTIVE SUMMARY

BIOFILTER TECHNOLOGY FOR NOx CONTROL

Little attention has been given to the transformation of nitrogen compounds in vapor phase biofilters. Both production and removal of oxides of nitrogen (NOx) have been demonstrated in laboratory experiments in the Center for Environmental and Water Resources Engineering at the University of California, Davis. Thus there is a potential that under certain operating conditions NOx may be emitted from biofilters designed to remove volatile organic compounds from contaminated air. Additionally it appears possible to design and operate biofilters for the purpose of removing NOx from contaminated air. The number of new companies offering biofilters as economical air pollution control devices for treatment of air contaminated with volatile organic compounds is rapidly growing. Many companies are seeking to apply biofilters to relatively high concentrations, several hundred to the thousand-ppm$_v$ range. Locally anaerobic conditions in which nitrous oxide (N_2O) and nitric oxide (NO) are produced and released to the atmosphere can occur. On the other hand, it appears possible to design biofilters for the aerobic oxidation of N_2O and NO to NO_3^- or the anaerobic reduction of N_2O and NO to N_2. The potential of biological processes for NOx control appears to be considerable.

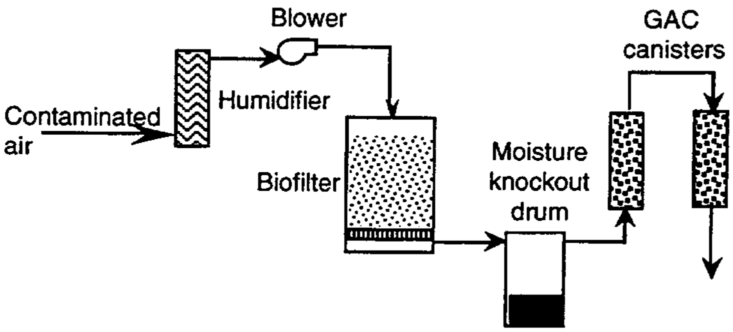
The specific objectives of this project were:

1. To determine whether significant emission of nitrogen-containing compounds such as NH_3, N_2O, NO or NO_2 occur during normal and/or "upset" biofilter operations.
2. To determine if oxidation of N_2O and NO to NO_3^- can be carried out in biofilters using microbial nitrification.
3. To develop operating parameters for promoting control of NO_X using local anaerobic denitrification and contaminated air feed stock.

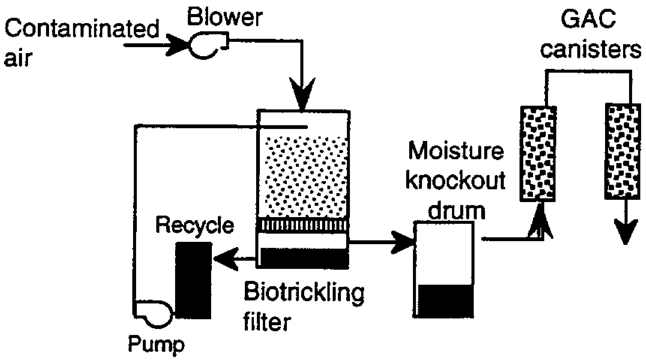
Biofiltration of Contaminated Air

Biofiltration is a control technology, which is increasingly utilized to remove biodegradable pollutants from air streams. Biofiltration systems consist of packed bed reactors and the necessary blowers, controls and humidification devices to bring contaminated air into contact with packing material and to provide the appropriate environment for a microbial community growing on the packing. Two general types of biofilter system are in use; conventional biofilters and biotrickling filters (see Figure 1). Conventional biofilters commonly utilize packing materials such as compost - bulking agent mixtures and are maintained at a moisture content of 50 to 60 percent by weight by humidification of the inlet air and periodic water addition. Biotrickling filters usually incorporate more rigid packing materials such as porous rock (e.g. pumice or lava rock), extruded plastic rings or saddles, and extruded diatomaceous earth pellets. A buffered, liquid stream containing required nutrients is continuously recycled over the packing in biotrickling filters. Loading rates used with biofilters and biotrickling filters are similar.

Air fluxes and empty bed contact times are typically in the 1.5 to 4.5 ft^3/ft^2-min range and 0.5 to 1.5 minutes, respectively. Contaminant concentrations of up to several 1000 ppm$_v$ are acceptable, although clogging due to excessive microbial growth may become a problem at higher mass loading rates. Outlet concentrations of less than 50 ppb$_v$ are generally possible with inlet concentrations in the range of 1 ppm$_v$ to 1000 ppm$_v$. Complex organic mixtures, such as gasoline, are good candidates for treatment by biofiltration as well as easily degraded hydrophilic compounds such as alcohols and ketones.



a. Conventional biofilter



b. Biotrickling filter

Figure 1.
Typical flow sequence of vapor phase biofilter and biotrickling filter systems. The granular activated carbon canisters are for polishing purposes only.

Experimental Program

Two parallel investigations were conducted, laboratory studies to investigate the biological oxidation of nitric oxide, NO, in biofilters and field studies to determine if significant NOx production could be observed in operating biofilters.

Biological Oxidation of NOx: Biological oxidation of NOx is carried out by obligate chemoautotrophic bacteria that also carry out the second step in the conversion of ammonia to nitrate, a process called nitrification which is characterized by the reactions below. Note that N_2O and NO are more reduced than NO_2^-, the normal energy source for the *Nitro* bacteria. Actual reaction mechanisms have not been identified at this time but the process is commonly observed in soil.

$$NH_4^+ + \frac{3}{4}O_2 \xrightarrow{\textit{Nitroso}\text{ bacteria}} NO_2^- + 2H^- + H_2O$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{\textit{Nitro}\text{ bacteria}} NO_3^-$$

In the laboratory studies cultures of NO_2^- oxidizing bacteria were grown in the biofilter by spraying a nutrient solution containing 75 mg/L of nitrogen as $NaNO_2$ over the packing for several weeks. When a visible biofilm the experimental program with NO was started. Two types of experiments were conducted, short term NO loading and continuous NO loading. The short term experiments were conducted because the available NO source at the beginning of the project was limited to tanked gas, which was very expensive. Application times for the short term experiments ranged between 40 minutes and 48 hours. Later in the project a NO generator was constructed and continuous loading experiments were conducted.

Laboratory Reactors: The initial experiments were conducted using a 100 mm diameter biofilter having a packing depth of 1100 mm and an overall depth of 1300 mm. The packing material was composed of 9 mm fritted glass Siran rings. Biofilm development was poor and after several attempts to increase microbial accumulation a decision was made to construct new biofilters using packing known to support bacterial cultures. The second set of reactors were designed to be operated as biotrickling filters because it was undesirable to pass the NO containing air through the nutrient solution nebulizers used in the first reactor. Two 150 mm diameter acrylic units were constructed with a packing depth of 380 mm. Packings used were extruded diatomaceous earth pellets and 5 mm graded pumice. Biofilm growth on the NO_2^- based nutrient solution was substantially better than for the Siran rings and essentially complete conversion of NO_2^- to NO_3^- was established in a matter of weeks. The initial experiments with the second reactors were conducted using bottled NO. Conversion to continuous NO feed was made on completion of the NO generator.

Field Studies: Six operating biofilters were sampled to determine if this control technology is a significant source of oxides of nitrogen. One unit was located at a soil vapor extraction site in Richmond, California, two were located at the Joint Water Pollution Control Plant in Carson, California, one was at a bathware manufacturing plant, and two were research units located at UC Riverside and UC Davis, respectively. The most heavily loaded biofilters were of most interest because these units have a potential to develop a thick biofilm with significant anaerobic activity.

Samples were taken from inlet and outlet flow of the units and stored in either stainless-steel canisters or Tedlar™ bags after condensing and removing the water vapor with an ice-bath "cold finger." Tedlar™ bags were stored in the dark to slow NO reactions. However, in the only case in which both containers were used, the stainless steel canister yielded a sample with a NO concentration near the detection limit, but the Tedlar™ bag sample did not provide a quantifiable peak. Therefore, there were probably significant loses of NO in the Tedlar™ bag samples. Samples were analyzed for NO within 3 days and for N_2O within 6 days.

NO samples were analyzed with a Sievers Instrument Model 270B Nitric Oxide Analyzer which uses gas phase chemiluminescence to detect NO concentrations larger than approximately 30 $\mu g/m^3$ (25 ppb_v). N_2O samples were analyzed with a Hewlett Packard gas chromatograph equipped with an electron capture detector to quantify N_2O concentrations larger than approximately 0.9 mg/m^3 (500 ppb_v).

Results

Laboratory NO Oxidation: Inlet NO concentration to the laboratory biofilters 100 ppm_v. Acclimation of the microbial population to the introduction of NO was very rapid. However, removal rates were low. In the initial set of experiments, using the Siran ring packing, up to 70 percent removal of the inlet NO was achieved but the empty bed contact times were 12 to 13 minutes. Outlet concentrations observed were linearly related to the inlet concentration. The sparse distribution of the biofilm on the packing was believed to be the principal reason for the low reaction rates and the decision to redesign the laboratory systems was made.

When the nitrate oxidizing culture had been established on the two biotrickling filters and the NO generator was fully functioning the continuous loading experiments were begun. The initial operating conditions were an inlet NO concentration of 100 ppmv and an empty bed contact time of one minute. Oxidation of NO began immediately but the removal was less than 20 percent. The nitrogen loading was 0.012 g NO-N per m3-min, less than five percent of the NO_2^--N loading used in growing the culture. Because the culture was well established, complete removal was expected. Mass transport limitations were hypothesized as the cause of the limited removal. This was verified in a set of experiments in which bed drying occurred and removals increased as water content decreased, as shown in Figure 2.

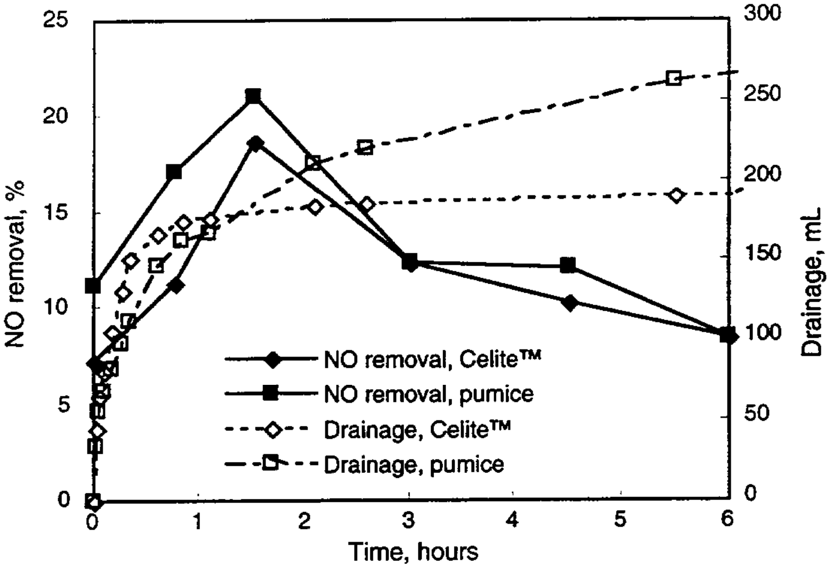


Figure 2.
Effect of column water content on NO removal in biofilters with Celite™ and pumice packings.

Field Studies: Hydrocarbon loadings to the field biofilters varied from 3000 g/m^3-d at the Soil vapor extraction site to less than 10 g/m^3-d at the Joint Water Pollution Control Plant's headworks. Outlet NO concentrations were higher than inlet in all cases. However, the outlet concentrations and the mass emission rates were low enough to be considered insignificant in each instance. The N_2O emissions were more difficult to characterize because the quantification limit was 500 ppb$_v$. Only the biofilter at the bathware plant produced detectable N_2O concentrations. However, the production in this case was low enough to be insignificant

Conclusions

The principal conclusions from this project were:

1. Laboratory biofilters operated at a one minute empty bed contact time and an inlet NO concentration of 100 ppm$_v$ were able to remove 25 ppm$_v$.

2. Mass transfer from the gas to the liquid phase appears to be the rate-limiting factor in removal of NO in biofilters.

3. Field studies at four sites provide no evidence that biofilters installed to treat relatively high hydrocarbon loadings produce significant quantities of NOx.

INTRODUCTION

Recent work with nitrogen limitations in biofilters at the Center for Environmental and Water Resources Engineering at the University of California, Davis resulted in the concern that these systems may leak nitrogen compounds into the atmosphere under certain conditions and the belief that biofilters could be designed and operated in a manner that could remove oxides of nitrogen (NOx) from gas streams [Morgenroth et al., 1995a,b, DuPlessis et al., 1996, 1998]. There are major implications of these findings for the use of biofilters as air pollution control devices. The number of new companies offering biofilters as economical air pollution control devices is rapidly growing. Many companies are seeking to apply biofilters to relatively high concentrations, several hundred to the thousand ppm_v range. Under such conditions thick biofilms can develop that may inadvertently be sources of nitrous oxide (N_2O) and nitric oxide (NO) release to the atmosphere (release of these compounds to the atmospheres from soil is well known). Thus biofilters, just as more conventional physico-chemical control technologies, can have the potential to produce by-product streams that are detrimental to the environment. On the other hand, release of these pollutants can be avoided and microorganisms can actually take up these compounds under the proper conditions, thus offering potential for an economical NO_x control technology that should be exploited.

Locally anaerobic conditions in the bed can result in both generation of N_2O and NO and reduction of N_2O and NO to N_2. Both processes have been observed in laboratory units and a biofilter has been operated with an air (17 percent O_2) feed stream that has removed up to 58 ppm_v of NO ($C_{NOi} = 80$ ppm_v, $C_{NOo} = 22$ ppm_v) using an empty bed contact time of 4 minutes. However, the bulk of the removal was accomplished in the first quarter of the bed, suggesting that the same performance might be achieved in a residence time of about one to two minutes.

Oxidation of ammonia to nitrite by bacteria of the *Nitroso* genera and oxidation of nitrite to nitrate by bacteria of the*Nitro* genera are ubiquitous reactions in soil and natural waters. The intermediates, N_2O and NO, are potentially oxidizable by bacteria of the members of these groups. Thus, two approaches to removing NO_x from stationary sources using biofilter technology are promising: reduction to nitrogen gas or oxidation to nitrate. As noted above, the potential exists that commercial biofilters can be sources of NO_x emissions if operated incorrectly. The research conducted in this project addressed all three of these issues.

Objectives

The specific objectives of this project were:

1. To determine whether significant emission of nitrogen-containing compounds such as NH_3, N_2O, NO or NO_2 occur during normal and/or "upset" biofilter operations.
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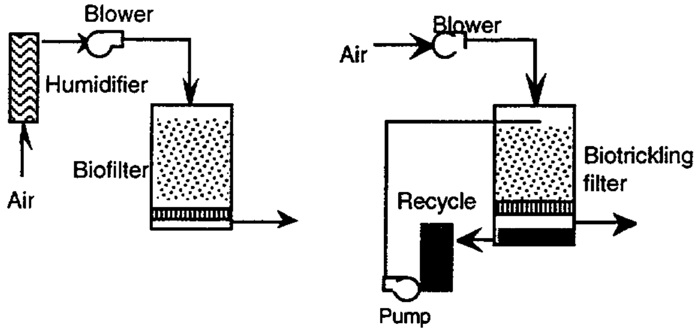
Biofiltration of Contaminated Air

Biofiltration is a control technology which is increasingly utilized to remove biodegradable pollutants from air streams. Biofiltration systems consist of packed bed reactors and the necessary blowers, controls and humidification devices to bring contaminated air into contact with packing material and to provide the appropriate environment for a microbial community growing on the packing. Two general types of biofilter system are in use; conventional biofilters and biotrickling filters. These differ in the mode of moisture and nutrient addition and pH control. In conventional biofilters, the contaminated air stream is passed through a humidification chamber, nutrients are added periodically, and pH is controlled by adding a solid buffer material such as crushed limestone to the packing mixture. In a biotrickling filter, moisture and nutrients are added and pH is controlled through use of a recycle stream. Both configurations make use of a liquid film because bacteria obtain all of their nutrients from the liquid phase. However, conventional biofilters have very thin liquid films and biotrickling filters have relatively thick liquid films. Schematic diagrams of a typical conventional biofilter and biotrickling filter systems are shown in Figure 1.



a. Conventional biofilter b. Biotrickling filter

Figure 1.
Typical flow sequence of vapor phase biofilter and biotrickling filter systems. The granular activated carbon canisters are for polishing purposes only.

The most common application of biofiltration is for the removal of odors, most of which result from H_2S and organic sulfides. However, biofilters are increasingly being used for removal of a wide range of volatile organic compounds, including petroleum hydrocarbons, solvents, and alcohols [Baltzis and Wojdyla, 1995; Evans, 1995; Ergas et al., 1995b, Devinny et al., 1995; Deshusses, 1995].

Biological transformations in microbial reactors are usually oriented toward reproduction of the microorganisms. In the simplest case the reactions can be conceptualized as a chemical reaction process, as indicated in Equation 1.

$$\text{Organic Compound} + O_2 + \text{(nutrients)} \rightarrow \text{Microbial Cells} + CO_2 + H_2O + \text{(other products)} \qquad (1)$$

The organic compound serves as a source of energy and of carbon for the production of new cells. Many organic compounds contain elements necessary for growth, such as nitrogen, phosphorus or iron, but in most cases an additional source of these *nutrients* must be provided. Molecular oxygen is the most commonly used terminal electron acceptor in microbial respiration. Electrons stripped from the energy source (organic compound in most cases) are added to the oxygen and the resulting reduced product is water. As stated above, the fundamental purpose of the transformation process is microbial growth and new cells are a major product of the reaction. Some of the organic compound is oxidized to the lowest possible energy state, carbon dioxide. Usually some portion of the organic compound is only partially transformed and incompletely oxidized organic materials are also a product. Equation 1 provides a very simple picture of what actually occurs in a biodegradation process. In almost all cases a number of microbial species are present and the degradation process results from interactions of this community or consortium. Several trophic levels may exist, including predators and scavengers that consume the partially degraded materials left by the primary degraders.

NITROGEN METABOLISM

Microbial transformations of nitrogen are of five types: (1) respiration or denitrification, the use of nitrogen compounds or ions as terminal electron acceptors analogous to the use of oxygen, (2) nitrification, the use of nitrogen compounds as energy sources, (3) assimilation, the incorporation of nitrogen compounds or ions into new cell tissue, (4) fixation, the conversion of molecular nitrogen to ammonia, and (5) production of ammonia through deamination of amines. Nitrogen is the nutrient required for growth in the largest amounts and is, on a dry mass basis, the third most common element in tissue. Living cells are approximately 14 percent nitrogen. Most bacterial species are capable of assimilating nitrogen in a range of oxidation states, with the most common being the -3 (NH_3, NH_4^+) and +5 (NO_3^-). Nitrogen incorporated into cell compounds such as proteins and nucleic acids is always at the -3 oxidation state. If the available nitrogen is at an oxidation state above -3, it is reduced through enzyme-catalyzed reactions. In nature most nitrogen is found in either the -3 or +5 oxidation states, and most of the literature on nitrogen metabolism reflects this situation. An overall picture of nitrogen metabolism showing points where nitrification and denitrification may be linked is provided in Figure 2.

Denitrification

Denitrification, unlike assimilative nitrogen reduction, is carried out by a limited number of bacterial species. In concept the process is very similar to the use of oxygen, and the oxidized nitrogen compound takes the place of oxygen in Equation 1. The reactions involved in denitrification are still not completely understood, but NO_2^-, N_2O and NO have been identified as intermediates (Shapleigh et al., 1985; Firestone et al., 1979; Ye et al., 1994; Tiedje et al., 1988). The reduction steps appear to be as shown in Equation 2.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (2)$$

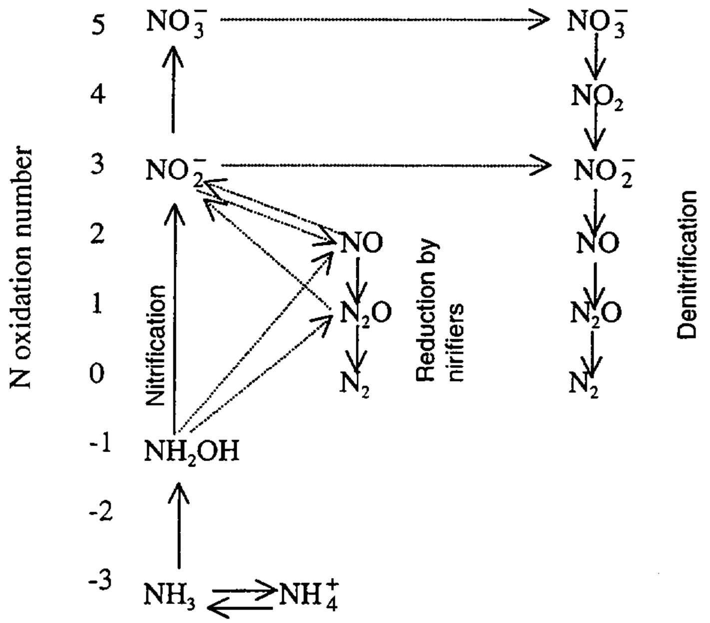


Figure 2.
Pathways of microbial nitrogen metabolism. Nitrification is carried out by obligate chemoautotrophic organisms. Denitrification is carried out by many genera of heterotrophic bacteria.

The oxidation state of nitrogen goes from +5 to +3 to +2 to + 1 to 0 in the four steps. Each of the intermediates may be released under some circumstances. For example NO_2^- often accumulates in the initial days of operation of denitrification processes but gradually disappears as the reactions become balanced. NO and N_2O may be released as a result of a variety of environmental conditions such as low pH and sudden fluctuations in temperature.

Use of NO_3^- as an electron acceptor produces less energy being available for growth than oxygen. As a result, oxygen is the preferred electron acceptor and oxidized nitrogen compounds are not used in significant quantities when oxygen is available. Conditions of intermittent low oxygen concentration or lack of oxygen result in a competitive advantage for bacterial species capable of using oxidized nitrogen as an electron acceptor. Under such conditions denitrifying bacteria synthesize the necessary enzymes to carry out the reduction process.

Nitrification

A group of bacteria are capable of using reduced nitrogen compounds (e.g., NH_3, NO_2^-) as energy sources, and CO_2 as a carbon source, in a two stage process known as nitrification. The first stage, oxidation of ammonia to nitrite ion, is carried out by four genera of bacteria all having the term *Nitroso* as part of their names (e.g., *Nitrosomonas europea, Nitrosococcus mobilis*), while the second stage is carried out by three genera having the term *Nitro* as part of their names (e.g., *Nitrobacter, Nitrospira*) as shown in Equation 3.

$$NH_3 + CO_2 + O_2 + (\text{nutrients}) \rightarrow \text{New Cells} + NO_2^- + H_2O + H^+ \tag{3a}$$

$$NO_2^- + CO_2 + O_2 + (\text{nutrients}) \rightarrow \text{New Cells} + NO_3^- + H_2O + H^+ \tag{3b}$$

The stoichiometry of the transformations in Equations 2a and 2b is not given because of variation with environmental conditions. However, the cell production is always small in both reactions and excellent approximations are given by Equations 4a and 4b.

$$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 2H^+ \tag{4a}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{4b}$$

Nitrification occurs under aerobic conditions, with optimal activity at mesophilic temperatures and neutral to alkaline pH values, with no growth or activity at acidic pH values (Prosser, 1989). Under oxygen-starved conditions, nitrifying bacteria have been observed to carry out denitrification reactions involving NO and N_2O in soil [Baumgartner and Conrad, 1992].

NO_x Production and Removal in Biofilters

Nitric oxide is produced and consumed primarily by the microbially mediated processes of nitrification and denitrification. Other biological reactions and chemical reactions may be of importance under certain circumstances. The literature review presented below is focused on production and consumption mechanisms of nitric oxide by denitrifying heterotrophic and nitrifying autotrophic bacteria. Most investigations of nitric oxide production and consumption mechanisms are performed in natural soil environments, and separation of the activity of nitrifying and denitrifying bacteria is often difficult. Potentially, biofilters can be both a source of NH_3 and NO_X and a method of NO_X removal from gas streams, as indicated in Figure 2. Production of the intermediates NO and N_2O in denitrification has been observed for over 40 years. Observations of the production of these compounds by nitrifiers, under aerobic conditions, has been more recent [Baumgartner and Conrad, 1992; Skiba et al., 1993]. Microbial nitrification, NO_X respiration, and assimilation all have promise as methods of removing NO_X from air streams in biofilters.

Several researchers have reported success controlling NO emissions by promoting microbial denitrification in a biofilter (Shanmugasundrum *et al.*, 1993; Apel *et al.*, 1995; du Plessis *et al.*, 1996). As noted above, microbial denitrification is a step-wise conversion of nitrate (NO_3^-) to diatomic nitrogen (N_2). However, the process does not necessarily proceed from start to finish. There are at least three intermediates in the denitrification process ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Presumably nitrogen may enter or leave the pathway at any step of the conversion. To achieve significant conversion of NO through denitrification, oxygen must either be eliminated from the gas stream or the biofilm must be thick enough to ensure anaerobic sites exist (du Plessis et al., 1996). Apel et al. (1995) found that oxygen concentrations as low as 5 percent significantly depressed denitrification. However, du Plessis et al. (1996, 1998) utilized a porous packing medium (Celite™ R-635) that provided anaerobic zones deep in the pores. Complete elimination of oxygen from gas streams may not be practical having high initial concentrations. However, exhausts from combustion processes may have low enough oxygen concentrations to make NOx control by denitrification practical.

Nitric Oxide Production in Soil

Nitric oxide production by denitrification is often difficult to measure in a soil environment due to high re-utilization rates and slow release of NO at high water contents. A study performed with high density denitrifying bacterial cultures in soil indicated that NO was not a major by-product of denitrification (Anderson *et al.*, 1986). However, experiments with low density cell suspensions have shown that NO was the dominant product of denitrification (Zafiriou *et al.*, 1989). Depending on the population of denitrifiers, the rate of re-utilization of NO could be high in soil environments, resulting in minimal NO accumulation (Firestone *et al.*, 1989). Another factor influencing the bulk NO production rate is the water content of the soil. High water content increases the diffusion time of NO to the bulk atmosphere, providing additional time for further reduction to N_2O or N_2 (Firestone *et al.*, 1989).

According to Conrad [1996] it is impossible to predict how much NO a typical soil denitrifier will produce. The production rates depend not only on microbial species but also on physiological conditions [Anderson et al., 1986, Remde et al., 1991]. The difference in enzyme regulation between different denitrifiers is probably responsible for the difference in NO production rates [Conrad, 1996].

NO production in soil may be dominated by denitrifiers or nitrifiers depending on substrate availability, soil pH, moisture content, nitrogen content and bacterial speciation (Baumgartner, 1992).

Experiments indicate that NO production rates in soil under anaerobic conditions were 35 to 140 times higher than for the soil incubated in air (Remde *et al.*, 1989). These experiments suggest that NO production is stimulated when conditions are favorable for an anaerobic process such as denitrification (Remde *et al.*, 1989). The maximum production rates observed in these soil experiments was 200 ng NO-N/g soil-hr (200 ng N in the NO form/g soil-hr) at a flow rate of 1.5 L N_2/min through approximately 100 g of soil sample.

The concentration of NO will determine whether a soil environment is a net sink or source for NO (Remde *et al.*, 1989, 1991 a). Experiments indicate that the NO production rate is independent of NO concentration, but the NO consumption rate is proportional to NO concentration (Remde *et al.*, 1989, 1991 a). Remde *et al.* (1989) developed a reactor to simulate a soil environment, the NO concentration was slowly increased in the reactor until a critical concentration was reached at which production and consumption were equal. Above the critical concentration, NO uptake dominates NO production. The critical concentration measured under aerobic conditions was approximately 600 ppb_v and 70 ppb_v for acidic and alkaline loam respectively (Remde et al., 1989). For anaerobic conditions the production rate of NO was always higher than the consumption rate, even under high NO concentrations (2000 ppb_v).

Under an anaerobic incubation condition, the soil released NO at rates up to 14.6 nmol/g-soil hr [Remde et al., 1991 a]. At NO mixing ratios higher than 500 ppmb, the NO release rate decreased hyperbolically [Remde et al., 1991 a]. In a pure culture of denitrifying bacteria the maximum production rate of NO measured was slightly higher than 200 fmol/cell hr for *P. stutzeri* when gas flow rate was adjusted to approximately 100 ml N_2/min [Remde et al., 1991 a]. Although it was shown that denitrifying bacteria in soil and pure culture are capable of both production and consumption of nitric oxide, the NO production rate was always higher than the NO consumption rate [Remde et al., 1991 a].

Nitric Oxide Consumption in Soil

Nitric oxide consumption by microorganisms is not well characterized (Baumgartner *et al.*, 1995). Since NO is an intermediate in the sequential reduction of NO_3^- to N_2, denitrifiers probably utilize NO as an electron acceptor (Conrad, 1996). Reduction of NO to N_2O is catalyzed by NO reductase and is coupled with electron transport phosphorylation (Ye et al., 1994) which supports the role of NO as an electron acceptor. NO consumption occurs in anoxic microniches within generally oxic soil (Baumgartner *et al.*, 1995). NO consumption is sometimes stimulated by anoxic incubation conditions and/or by addition of nitrate and glucose (Baumgartner *et al.*, 1995, Schuster *et al.*, 1992). Positive stimulation by anoxic conditions and additions of nitrate also suggest denitrifying activity.

NO consumption in soils is often modeled using Michaelis-Menton kinetics (Remde *et al.*, 1991 b, Schuster *et al.*, 1992).

$$r_{NO} = r_{NO_{max}} \left(\frac{C_{NO}}{K_M + C_{NO}} \right) \tag{5}$$

Where r_{NO} = rate of NO uptake, ng N/g soil-hr
$r_{NO_{max}}$ = maximum rate of NO uptake, ng N/g soil-hr
C_{NO} = concentration of NO-N in the gas phase, ppb_v
K_m = affinity coefficient, ppb_v

Note that the affinity coefficient, K_m, inversely impacts the rate. Higher K_m values result in lower the reaction rates. Affinity coefficients of denitrifiers for NO are very low. Both pure cultures of denitrifiers and bulk soil samples exhibited NO consumption kinetics with affinity coefficient (K_m) values below 8 nM (Remde *et al.*, 1991 b, Baumgartner *et al.*, 1992, Schuster *et al.*, 1992). The fact that under anaerobic conditions the NO production rates were always greater than the NO consumption rates was explained by low $r_{NO_{max}}$ and K_m values, which for soil were 11-12 nmol/g-hr and 980 ppb_v, and for pure bacterial cultures range between 1-109 nmol/g hr and 320-3250 ppbv, respectively (Remde *et al.*, 1991 a). The K_m values determined from soil experiments by Schuster *et al.* (1992) were even lower with a range between 1-5 ppm_v, equivalent to 2-10 nM of NO in the soil water phase.

Two species of heterotrophic denitrifiers, *Paracoccus denitrificans* and *Pseudomonas denitrificans*, grown in suspended mineral media solution were capable of consuming NO (Shanmugasundram *et al.*, 1993). Nitric oxide was used as an electron acceptor; succinate, yeast extract, and heat/alkali pretreated sewage were used as carbon and energy sources; ammonium ion was used as a source of reduced nitrogen. The feed gas consisted of 0.5% NO, 5% CO_2 and balance N_2. NO consumption capability is likely a common feature of all denitrifying bacteria.

Soil experiments indicate that the rate of anaerobic consumption of NO from the gas phase was not significantly affected by water content (Schuster *et al.*, 1992). This result suggested that diffusion of NO into the soil particles was not limiting the NO consumption process. Schuster *et al.* (1992) suggested that most of the consumption was taking place on the outside of soil particles; and denitrifiers, bacteria with high affinity for NO, were responsible for NO consumption.

Biofiltration of Nitric Oxide by Denitrification

Biofiltration of nitric oxide by denitrification from contaminated air streams has been explored (Apel *et al.*, 1995; du Plessis *et al.*, 1996a; 1996b). Apel *et al.* (1995) used denitrifying bacteria grown on wood compost to remove NO under anoxic conditions. They achieved removals of over 90% in the biofilter unit which was supplied with molasses as a carbon source. However, addition of 5% oxygen into the feed gas stream decreased the NO removal to only 39%.

Denitrification activity under batch and flow-through conditions was observed in a superficially aerobic (gas phase oxygen concentration greater than 17%) synthetic media biofilter treating toluene (du Plessis *et al.*, 1996 b). The presence of a thick biofilm, which filled the media pores, allowed for formation of anaerobic zones where denitrification likely took place. Nitric oxide concentrations were reduced from 60 ppmv to 15 ppmv (75% reduction) at a flow rate of 3 L/min (empty bed contact time of 6 minutes).

Biofiltration of Nitric Oxide by Nitrification

In soil research, nitrification has been shown to be responsible for both production and consumption of nitric oxide. Engineering applications using the nitrification process for control/consumption of nitric oxide have not previously been described in the literature.

Nitric Oxide Production

Nitric oxide production by nitrifying bacteria is poorly understood (Firestone *et al.*, 1989). It has been observed that *Nitroso* bacteria can produce significant amounts of nitric oxide (Anderson *et al.*, 1986). The intermediates of +1 (N_2O) and +2 (NO) oxidation states in chemoautotrophic nitrification are not known with certainty (Hooper, 1984). Nitric oxide could be produced by nitrifiers via oxidation of hydroxylamine (NH_2OH) to NO_2^- or reduction of NO_2^- to NH_2OH (Firestone *et al.*, 1989, du Plessis *et al.*, 1996 b). Recent studies of ammonia oxidizing bacteria in aerobic soil provide evidence for NO production via reduction of NO_2^- (Firestone *et al.*, 1989). Reduction reactions are usually associated with activity of denitrifying bacteria. However, there are some indications in the literature that under conditions of low partial pressure of oxygen, nitrifiers are capable of carrying out reduction reactions (Skiba *et al.*, 1993, du Plessis *et al.*, 1996 b). However the evidence is conflicting, and there are also indications that production of nitric oxide by nitrifiers is unaffected by partial pressure of oxygen (Anderson *et al.*, 1986).

Nitrification is responsible for the production of nitric as well as nitrous oxide under certain conditions in soils (Schuster *et al.*, 1992). The production of nitric oxide in these experiments was not influenced by soil-moisture content or by addition of glucose, as long as the soil was incubated under air. Initially the rates of production were low but, fertilization with NH_4^+ increased the production rates of nitric oxide, confirming that the production was due to nitrification activity (Schuster *et al.*, 1992). Nitrification may produce significant amounts of nitric oxide, but the rates of NO production in aerobic soil (nitrifying conditions) were generally much lower (by a factor of 35 to 140) than the rates under anaerobic incubation (denitrifying conditions) (Remde *et al.*, 1989).

Nitric Oxide Consumption

Nitric oxide consumption is positively correlated with the number of NO_2^- oxidizers present (Baumgartner *et al.*, 1992). Therefore, bacteria of genus *Nitrobacter* probably contribute significantly to nitric oxide consumption. This conclusion agrees with the research of Freitag *et al.* (1990) who demonstrated that nitric oxide is an efficient substrate for NADPH generation in *Nitrobacter.*

Nitric oxide consumption by soil microorganisms indicated that under anaerobic conditions production rates were faster than uptake, while under aerobic conditions the opposite was true (Remde *et al.*, 1989). Remde et al. (1989) also demonstrated that nitric oxide consumption was linearly dependent on the nitric oxide concentration (up to 600 ppb_v), indicating that a first order kinetics equation describes nitric oxide uptake by aerobic microorganisms.

Schuster *et al.* (1992) also showed that microbial nitric oxide consumption in soil followed first order kinetics and was not saturated up to 14 ppm_v NO. The nitric oxide consumption was negatively correlated with the water content of the soil; the best consumption rate was observed for air-dried soil. "This result suggests that processes in the interior of the soil crumbs may contribute to the NO consumption, and that diffusion of NO into the soil crumbs may have been limiting." Inhibition by acetylene abolished nitric oxide consumption by the soil microorganisms, proving that nitrifying bacteria were responsible for nitric oxide removal [Schuster et al., 1992].

Summary of Transformations of NO

Consumption of NO is much more rapid under aerobic conditions (Remde *et al.*, 1989). The consumption rate is linear with respect to the inlet concentration and is not saturated for concentrations greater than 14 ppmv NO (Remde *et al.*, 1989; Schuster *et al.*, 1992). Nitrifying bacteria, nitrite oxidizers such as *Nitrobacter*, contribute to nitric oxide consumption (Baumgartner *et al.*, 1992; Remde *et al.*, 1989; Schuster *et al.*, 1992; Freitag *et al.*, 1990).

EXPERIMENTAL DESIGN AND METHODOLOGY

Several experimental set-ups were used in an attempt to promote conversion of NO and improve performance.

Reactor 1 consisted of a schedule 40 polyvinyl chloride column with an inner diameter of 10.16 cm and an overall height of approximately 130 cm, as shown in Figure 3. The unit was located in a constant temperature room maintained at 23°C. The column had inlet, outlet and two intermediate gas sampling ports. A stainless steel screen supported approximately 110 cm of packing. The empty bed volume of the column including plenum space was 10.5 L.

Mineral medium was supplied to the biofilter by means of a HEART® nebulizer (Vortran Medical Technology, Inc.) which generated a fine aerosol of inorganic mineral medium-containing droplets, approximately 10 to 25 µm in diameter (Kinney et al., 1996). The medium was fed to the nebulizer by a metering pump (Fluid Metering, Inc.) at approximately 25 ml/hr.

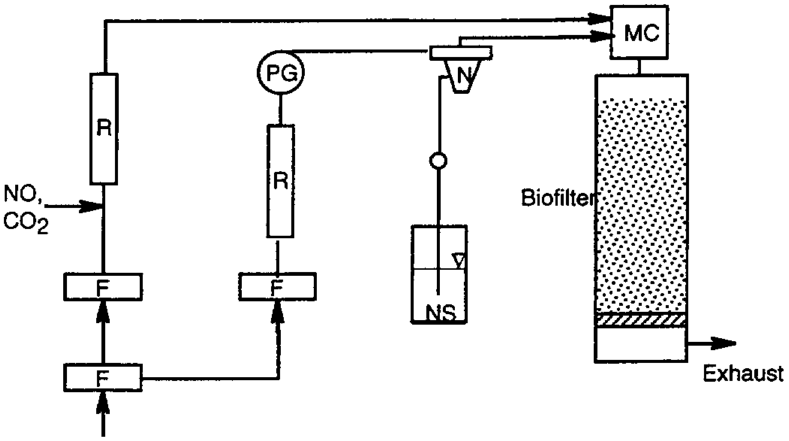


Figure 3.
Schematic diagram of Reactor 1 used in NO oxidation experiments. (F - filter, R - regulator, PG - pressure gage, N - nebulizer, NS - nutrient solution, MC - mixing chamber)

Compressed air from the laboratory was filtered through three Speedaire microfiber filters (Dayton Electric Manufacturing Co.) that removed particulate matter from the air and reduced the gas pressure to 1 and 30 psig, respectively. The air stream exiting the filter at 1 psig was used to dilute the nitric oxide before it entered the mixing chamber. The nitric oxide was supplied from the gas tank (Puritan Bennett) attached to a two-stage regulator (Tescom) and low flow controller. The 30 psig air stream supplied the nebulizer. Aerosol generated in the nebulizer was delivered to the mixing chamber as well. During carbon dioxide experiments an additional gas line was connected from the carbon dioxide tank (Liquid Carbonic) with a two-stage regulator (C.A. Norgren Co.) to the mixing chamber. Upon exiting the mixing chamber the air mixture was delivered to the inlet of the biofilter. All air streams were controlled by rotameters (Aalborg Instruments) that were located in the air lines ahead of the mixing chamber. The air stream to the nebulizer was monitored with a pressure gauge (Ashcroft, Inc.). Upon exiting the biofilter the excess moisture in the exhaust stream was collected in the leachate reservoir (see Figure 3) and the air stream exited the constant temperature room via an exhaust line.

Column packing consisted of 9 mm diameter sintered glass Siran rings (Jaegar Biotech). Sintered glass is made by combining soda-lime glass powder with salt and heating the mixture to 700°C. The glass powder melts, forming the matrix of the ring. The rings are then washed, removing the salt from the matrix, and leaving open pores. Pore diameter sizes vary from 60 to 300 µm. Physical properties of the artificial media are summarized in Table 1:

Table 1.
Physical properties of Siran rings (* provided by manufacturer)

Characteristic	Measurement
Ring Diameter *	9 mm
Surface to Volume Ratio *	46 m^2/L
Rings per Liter *	1100
Mass per Ring	0.33 g
Specific Surface Area	0.126 m2/g
Pore Volume *	55-60%
Pore Diameter *	60 - 300 µm

The inorganic mineral medium solution was prepared by dissolving 0.38 g of NH_4Cl (100 mg NH_4Cl-N), 4.3 g of Na_2HPO_4, and 1.7 g KH_2PO_4 in a 1 L of tap water. Ammonium chloride was used as a nitrogen source to support the population of nitrifying bacteria in the biofilter. Na_2HPO_4 and KH_2PO_4 were used as a phosphorus source as well as for buffering capacity of the medium, designed to maintain the pH of the system at 7.4. During the fourth set of the experiments (see Results and Discussion section) $KHCO_3$ (100 mg/L $KHCO_3$) was added to mineral medium as a supplemental source of inorganic carbon. For the fifth set of the experiments NH_4Cl in the mineral medium was substituted with $NaNO_2$ (100 mg/L $NaNO_2$-N).

To prepare the original microbial seed, 2 L of activated sludge from the City of Fairfield nitrifying waste water treatment plant were added to 3 L of mineral medium. The artificial packing for the biofilter was soaked for 4 days in this microbial seed solution. The biofilter packing was drained before placement into the biofilter.

The column was re-inoculated with activated sludge from the City of Fairfield wastewater treatment plant in the second and third month of biofilter operation. The reinoculations were performed by flushing activated sludge through the column manually 5 to 7 times in an attempt to increase bacterial count of the nitrifiers.

Due to the high cost of nitric oxide gas, it was only supplied to the biofilter during the analysis periods. The minimum analysis period lasted for 40 minutes to allow for establishment of gas/liquid equilibrium. The maximum analysis period lasted 48 hours to observe change in removal rate over time. The nitric oxide analysis was accomplished using a Nitrogen Oxide Analyzer (Lear Sigler Co.). The air flow through the nebulizer was turned off during nitric oxide measurements to reduce the total flow rate through the column and to prevent the entry of aerosol droplets into the nitric oxide analyzer. The pH was measured using a pH meter (Hach Co.) following the calibration procedure described in the Hach manual. The air flow rates were measured using a dry gas meter (Rockwell Co.) and soap-film meters (Accuflow, SKC-West Inc.).

As will be explained below, NO oxidation rates were very low in the experiments using Reactor 1. Reactors 2 and 3 (schematic diagram shown in Figure 4) were constructed to eliminate the difficulties associated with the first set of experiments. These reactors consisted of acrylic columns with an inner diameter of 15.24 cm. Five liters of medium were added to each column, producing a medium depth of approximately 38 cm.

The glass packing medium used in the first set of experiments was believed to have limited the development of a healthy biofilm and thus limited the elimination capacity of the biofilter. Therefore, different media were used in the second set of reactors. One filter was packed with R635™ extruded Celite (diatomaceous earth pellets) and the other with pumice (1/4 inch aggregates). Another reason for comparing these two media was to find a low cost alternative, pumice, for the relatively expensive Celite used in laboratory scale projects.

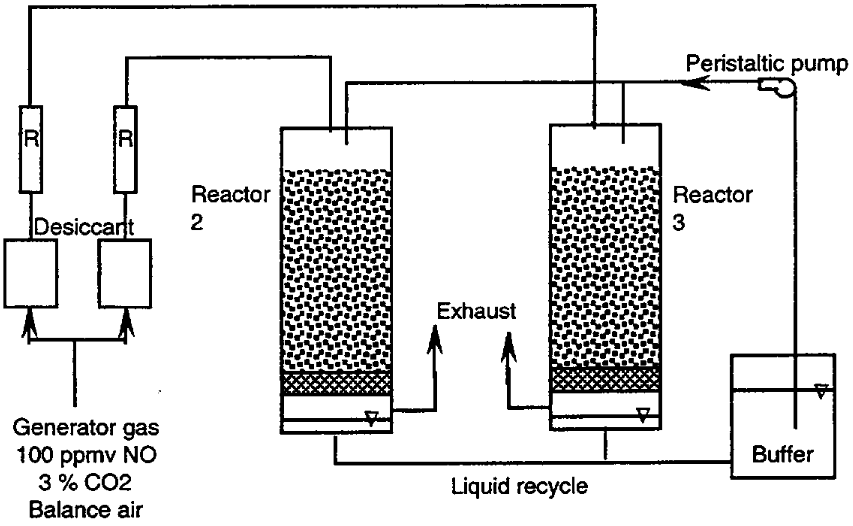


Figure 4.
Schematic diagram of experimental configuration used for reactors 2 and 3. Reactors 2 and 3 were identical other than the packing. Celite™ R-635 was used in Reactor 2 and graded (0.25 inch) pumice was used in Reactor 3. (R - rotometer)

The reactors were seeded with a mixture of 3 L of activated sludge from the City of Vacaville nitrifying wastewater treatment plant and 5 L of a 50 mg-N/l nitrite solution. Air was bubbled through the mixture until the production of nitrate was detected. Both media were then placed in the filters and drained. The limited removal efficiency of Reactor 1 was attributed partly to minimal microbial growth. Therefore, a mineral solution containing 75 mg-N/l as $NaNO_2$ and 1 mg-P/l as KH_2PO_4 and UC Davis tap water was sprayed over the media for an extended period of time. A substantial NO_2^- oxidizing population was produced during this period.

Another problem with Reactor 1 was that NO could only be supplied to the column intermittently due to the high cost of tank NO. Therefore, a generator was constructed for the second phase of experiments to provide the reactors with a constant supply of NO. Nitric oxide was produced by a natural gas or propane flame inside a black steel burner. However, the NO concentration was lower than the desired operating concentration (<25 ppmv). Ammonia, which is relatively inexpensive compared to pure NO, was bled into the flame to increase the NO production to approximately 100 ppmv. Combustion gas produced was cooled by a water cooling coil which removed acidic moisture. The cooled gas was then passed through a bed of desiccant and the flow was split to the two columns. Development of this generator not only allowed for continuous NO flow to the filters, but also provided an accurate simulation of combustion off-gases for which this technology would be ultimately useful.

The moisture delivery system for these reactors also had to be changed. Nebulizers could no longer be used because the air flow through these units dilutes the contaminated gas. Therefore, the units were operated as biotrickling filters with a buffer solution flow of approximately 82 $L\ m^{-2}\ h^{-1}$. The buffer solution consisted of 4.3 g of Na_2HPO_4, and 1.7 g KH_2PO_4 in a 1 L of tap water. The tap water provided any trace nutrients that might have been required by the microorganisms and the buffer capacity of the solution maintained the pH of the leachate between 6.5 and 7.5.

A third unit, Reactor 3a, was a modified form of Reactor 3 which was packed with pumice. The two previous reactors were operated as biotrickling filters. The high liquid loading on the filters reduced the conversion of NO due to diffusion limitations. For this reason, the pumice reactor was reconfigured with an ultrasonic nebulizer to provide a lower moisture loading rate (Figure 6). The ultrasonic nebulizer produces a fine aerosol of distilled water, which is drawn up the right column by flow from the NO generator and across into the biofilter. Since the aerosol does not contain any type of buffer, buffer is added periodically with a spray nozzle over the biofilter bed.

RESULTS AND DISCUSSION OF NITRIFICATION EXPERIMENTS

NO Oxidation in Reactor 1 Experiments

The first nitric oxide removal test was performed on the tenth day after inoculation of the Reactor 1 (Figure 3). Nitric oxide was delivered to the column at a flow rate of approximately 3.3 L/min and at concentration of 50 ppmv. Removal of 5 ppmv was observed at the outlet of the column one hour after test initiation. The reduction in concentration remained constant for 24 hours as was demonstrated by subsequent measurements.

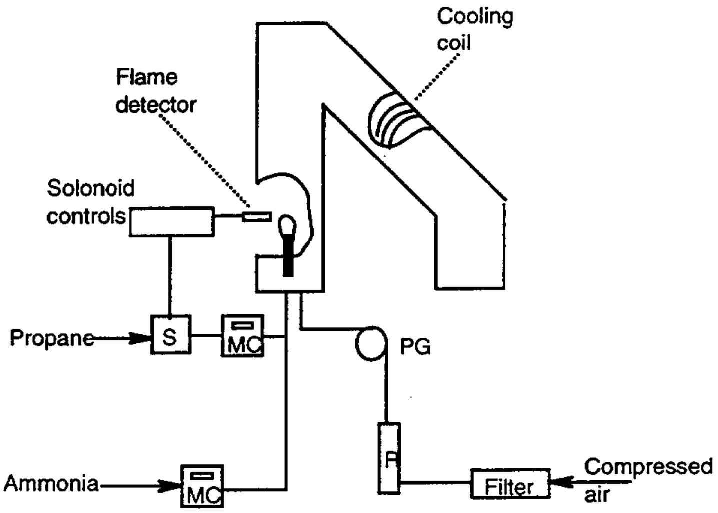


Figure 5.
Schematic diagram of NO generator. (S - solenoid valve, MC - mass flow controller, PG - pressure gage, R - rotometer)

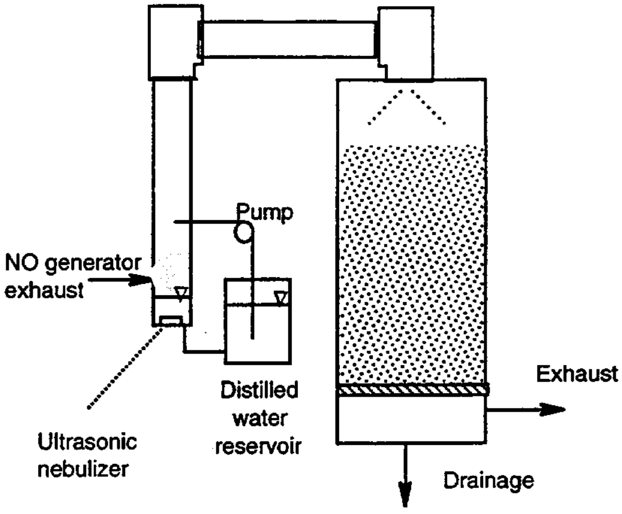


Figure 6.
Schematic diagram of reactor 3a.

For a two month period following the initial NO test of biofilter performance the system was operated with the NH_4Cl feed to increase the population of nitrifying bacteria in the biofilter. Removal of nitric oxide was monitored approximately weekly. At the end of the two month period the nitric oxide removal had increased to 72 percent at flow rate of 0.65 L/min, which corresponds to 13.5 minutes residence time.

A second set of experiments was performed to determine if the flow rate of the nitric oxide gas would have a significant influence on the removal rate. Data from these experiments are shown in Figure 7 for flow rates of 0.5 L/min and 0.8 L/min. Note that a change in the flow rate of the gas from 0.8 L/min (residence time 10.9 minutes) to 0.5 L/min (residence time 17.5 minutes) resulted in an increase in removal from 52% to 69%. Such behavior of the biofilter column agrees with the soil microbiology work of Schuster et al. [1992], who observed that nitric oxide consumption by nitrifying bacteria in soil can be limited by diffusion of the gas into the liquid film.

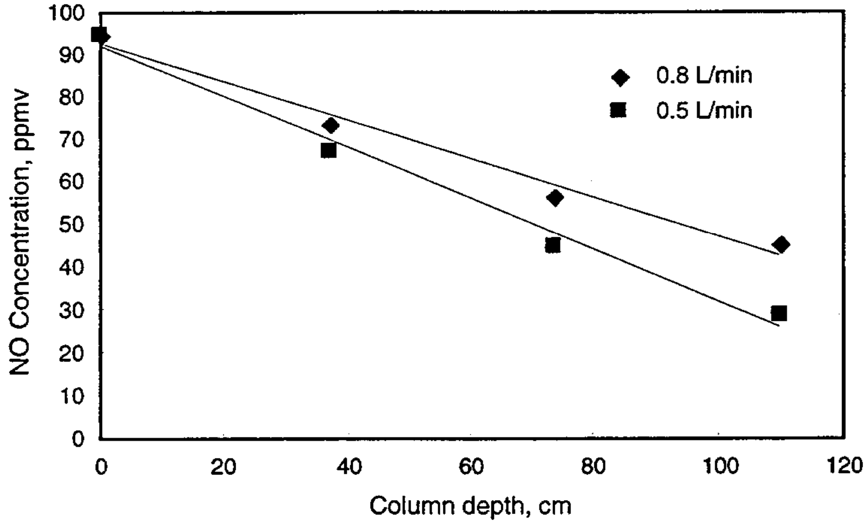


Figure 7.
Dependence of NO removal on gas flow rate. Note that the mass removal rate at 0.8 L/min is somewhat greater than at 0.5 L/min although the fractional removal is less.

A third set of experiments was designed to observe the response of the biofilter to a range of nitric oxide concentrations. Results of these experiments are summarized in Figure 8. Nitric oxide was varied between 20 and 140 ppm_v while the flow rate was kept constant at 0.5 L/min by varying the flow rate of the dilution gas (residence time =17.5 minutes). From Figure 8 it can be seen that nitric oxide removal increases linearly with inlet concentration, which suggests that bacterial enzymes do not reach saturation at the maximum concentration of 140 ppmv of nitric oxide tested. Again, this observation agrees with soil microbiology research that showed a linear relationship for nitric oxide consumption up to 14 ppm_v [Schuster et al., 1992; Remde et al., 1988].

A fourth set of the experiments was designed to increase the population of nitrifiers in the biofilter in the attempt to improve removal. Because carbon dioxide is the only source of carbon for nitrifying bacteria, the relatively low atmospheric carbon dioxide concentration could be a limiting factor for growth of nitrifiers in the presence of high concentrations of ammonium ion. The previous sets of experiments had been performed with ambient CO_2 in the laboratory compressed air. During this set of experiments the concentration of carbon dioxide was increased to 3 percent. The CO_2 was delivered continuously to the biofilter for one week by mixing it with the nebulizer air stream. System pH decreased as a result of carbon dioxide addition, with the leachate ph decreasing from 6.8 to 5.9. Fractional NO removal versus column length before and after carbon dioxide addition is shown in Figure 9. All sections of the biofilter experienced a decrease in performance, indicating that as buffer capacity was exhausted the consumption of the nitric oxide dropped. Nitrifying bacteria are known to be most active at pH values above 6.5. To alleviate the problem of of pH decrease from increased gas phase CO_2, potassium biocarbonate ($KHCO_3$) was added to the mineral medium at a concentration of 100 mg/L. However, this addition of inorganic carbon source did not change the performance of the biofilter and the conclusion was drawn that carbon was not limiting.

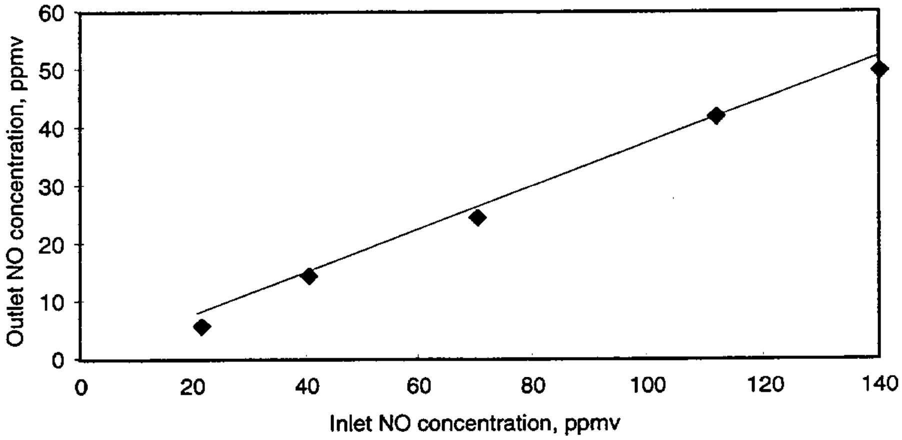


Figure 8.
NO removal as a function of inlet NO concentration.

The soil microbiology work of Baumgärtner et al. [1992] suggested that *Nitrobacter* is the organism responsible for the removal of nitric oxide. To test this hypothesis, sodium nitrite ($NaNO_2$) was substituted for ammonia chloride (NH_4Cl) in the nutrient medium solution. Bacteria of the genus *Nitrobacter* carry out the second step in the nitrification process: oxidation of nitrite (+3) to nitrate (+5). The first step, oxidation of ammonia (-3) to nitrite (+3), is carried out by *Nitroso* bacteria. Thus the switch to sodium nitrite in the mineral medium would support the growth of the nitrite oxidizing (characterized by *Nitrobacter)* population, but not of the ammonia oxidizing *Nitroso* bacteria. The change from ammonia to sodium nitrite did not immediately result in a change in the rate of consumption of nitric oxide. After 4 weeks of operation the removal of nitric oxide improved slightly from 60 percent to 65 percent at the inlet feed of 85 ppmv and flow rate of 0.5 L/min. Thus it was demonstrated that presence of *Nitrosomonas* is not necessary for nitric oxide consumption, and that *Nitrobacter* is responsible for nitric oxide removal. It should be noted that in nitric oxide, nitrogen is in a +2 oxidation state, not normally associated with *Nitrobacter* activity (+3 for nitrite to +5 for nitrate). Thus it is possible that under certain conditions *Nitrobacter* can be involved earlier in the nitrification process than nitrite (+3) oxidation. It is also possible that in natural soil and water systems, *Nitrobacter* is responsible for consumption of nitric oxide produced by ammonia oxidizing bacteria during the denitrification process that was described by Baumgartner et al. (1992) and Skiba et al. (1993).

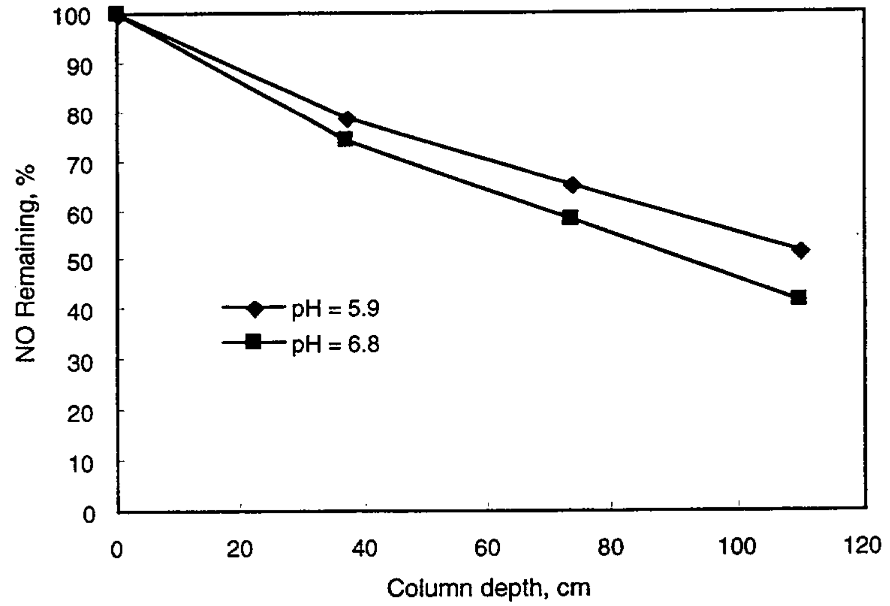


Figure 9.
The effect of pH on removal of NO in the biofilter.

NO Oxidation in Reactor 2 & 3 Experiments

Minimal biomass growth may have limited NO consumption in the first set of experiments (Reactor 1 experiments). Visual inspection of the media confirmed that the microbial density was very low. Therefore, the objective of the second set of experiments was to increase growth and hopefully removal. The filter media was also considered a possible growth limiting factor. Two alternative mediums were used, Celite™ R-635 and pumice, as noted above. As was explained above under Experimental Design and Methodology, the culture was grown on a solution containing 75 mg-N/l as $NaNO_2$ and 1 mg-P/l as KH_2PO_4. Effectively complete oxidation of the NO_2^- was established in both columns within a few weeks and the introduction of NO from the generator (Figure 5) began as soon as construction of the unit was completed.

When the NO generator was operating, the spray solution was changed from a buffered solution of $NaNO_2$ to a buffer solution without $NaNO_2$. The initial operating condition was an inlet NO concentration of 100 ppm_v and an empty bed contact time of one minute. Oxidation of NO began immediately but the removal was less than 20 percent. During growth on NO_2^-, the biofilters were loaded with about 0.375 g $N\text{-}NO_2^-$ m^{-3} min^{-1}, but once the biofilter was switched to NO feed, the loading decreased to 0.01227 g N-NO m^{-3} min^{-1}. Because the culture was well established, complete NO removal was expected, although a decrease might have been expected over time due to decreases in activity associated with the lower loading rate. NO is a more energy rich substrate than NO_2^-, but this does not explain a 15-fold drop in nitrogen consumption. The microbial population density was not limiting efficiency, but removal was very low.

Because reaction capacity was known to be high, it was hypothesized that mass transport limitations were controlling NO removal. Nitric oxide is slightly more soluble than oxygen. The dimensionless Henry's constants of NO and O_2 at 20°C are 20 and 30, respectively (Perry, 1963). However, the relative gas phase concentrations are very different (210,000 ppm_v for oxygen in air and 100 ppm_v for NO in the biofilter feed). Thus the driving force for NO removal was very low. The most important results of these experiments are shown in Figure 10 for a period following cessation of the buffer spray. The steady state removal with the buffer spray is given by the data points at time 0, the point when buffer spray ended (7 percent for the Celite™ reactor and 11 percent for the pumice reactor). During the following hours drainage from the column resulted in increasingly thin liquid films. As can be seen the fractional NO removals increased with increased cumulative drainage for two hours with maximum values of approximately 20 percent removal. As drainage continued, the columns dried and removal efficiency decreased.

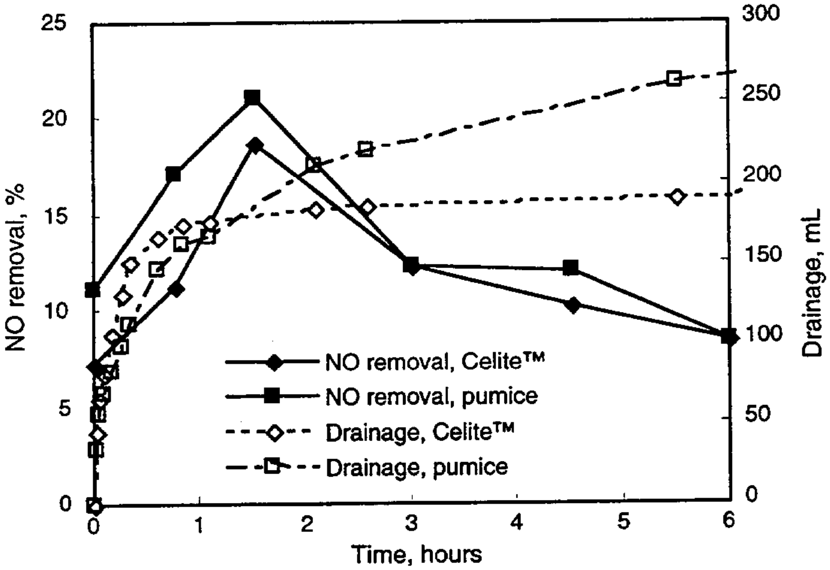


Figure 10.
Effect of column water content on NO removal in biofilters with Celite™ and pumice packings.

NO Oxidation in Reactor 3a Experiments

Because the liquid loading rate was limiting the consumption of NO, the pumice biofilter was reconfigured with an ultra-sonic nebulizer. This set-up allowed greater control of the liquid loading rate. The biofilter was operated for a period of 24 hours, during which there was minimal leachate production, but the highest removal observed was only 25 percent at an inlet NO concentration of 100 ppm_v.

Conclusions From NO Oxidation Experiments

NO removals of up to 70 percent were achieved, but contact times of 12 to 13 minutes were required. Nitrite oxidizers are responsible for the observed nitric oxide consumption. The uptake of NO is linear with NO concentration and not saturated for concentrations up to 140 ppm_v NO. Diffusion inhibits NO consumption in biofilters heavily loaded with nutrient solution. However, even if the liquid loading rate is minimized, the NO conversion was still only 25 percent of 100 ppm_v NO at a one minute residence time. This process is likely inhibited by the low solubility of NO and the low affinity of the organisms for NO at such low concentrations.

Biofiltration of NO in combustion off-gases may be more suited to denitrifying organisms. As noted above, denitrification can be carried out at relatively high ambient oxygen concentrations if local anaerobic conditions can be produced. Woertz (1998) reported that a fungal biofilter operated at a one minute empty bed contact time and a toluene loading rate of 90 $g/m^3 \cdot hr$ reduced the inlet NO concentration from 250 ppm_v to less than 20 ppm_v. Denitrifying fungi can survive in relatively acidic and dry environments and under low oxygen conditions may live close to the surface of the biofilm, therefore decreasing diffusion limitations.

RELEASE OF OXIDES OF NITROGEN ($NO+N_2O$) FROM BIOFILTERS

Six operating biofilters were sampled to determine if this control technology is a significant source of oxides of nitrogen. One unit was located at a soil vapor extraction site in Richmond, California, two were located at the Joint Water Pollution Control Plant in Carson, California, one was at a bathware manufacturing plant, and two were research units located at UC Riverside and UC Davis, respectively. The most heavily loaded biofilters were of most interest because these units have a potential to develop a thick biofilm with significant anaerobic activity.

Site Descriptions

The unit located at a soil vapor extraction (SVE) site was treating air from contaminated soil around a leaking underground storage tank at a gasoline service station. The biofilter system was designed, constructed and operated by Environmental Resolutions Inc. (ERI). It consisted of three compost biofilters, each one meter deep and one meter in diameter, configured such that the SVE gas was fed to two of the units and the combined flow was then passed through the third unit, as shown in Figure 11. Nutrients, including nitrate, are provided by time release pellets and moisture is provided by a humidification chamber.

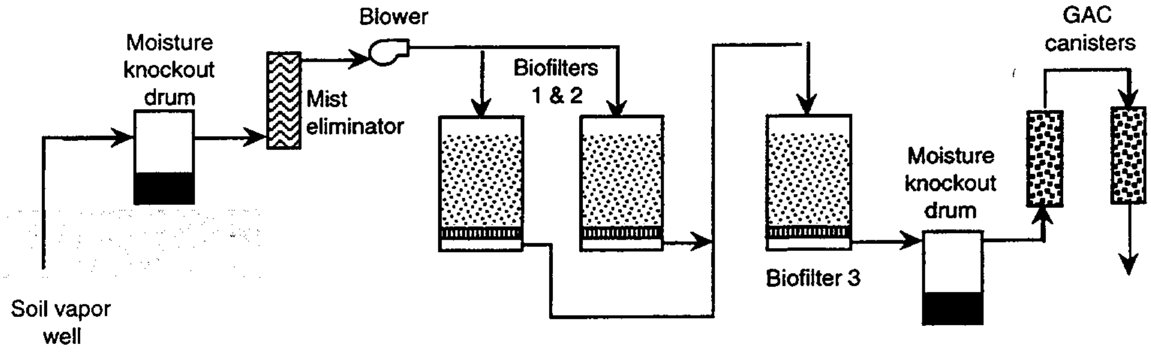


Figure 11.
Schematic diagram of ERI compost biofilter system at Richmond, CA, soil vapor extraction site.

The JWPCP (Joint Water Pollution Control Plant) in Carson, CA has several biofilters treating the off-gases from the headworks and secondary treatment sections of the plant. At the headworks, there is a compost biofilter (HBF) and a biotrickling filter (HBTF). The JWPCP HBF is a compost biofilter located at the headworks that has been superseded by the HBTF with lava rock. The HBTF has a lava rock media and the primary function is to remove hydrogen sulfide from the gases released at the headworks. Over a waste-activated sludge (WAS) channel in the secondary treatment section of the plant there is second compost biofilter (SBF) which treats very low levels of organic pollutants, primarily MTBE, which volatilize from the treated water. The biofilters draw in air from above the water surface and are not provided with additional moisture as the air is already saturated. The biotrickling filter draws water from the headworks channel and discharges to the same channel.

A biotrickling filter at the Lasco bathware facility is operated by the University of California, Riverside under the direction of Professor Marc Deshusses. The filter is 1.5 meters in diameter and approximately 2.26 meters deep. Total filter volume is 4 m^3 with an empty bed residence time of approximately 40 seconds. The packing was 2.5" diameter plastic sphere media. Exhaust from the bathware facility contains high levels of styrene (approximately 140 ppmv) and has a relatively cool temperature (61°C).

The two research units were examined at the Universities of California at Riverside (UCR) and Davis (UCD). Both were treating toluene at a concentration of approximately 100 ppmv and 260 ppmv for the UCD and UCR units respectively. The filter beds were approximately one meter deep. The UCR biotrickling filter (UCR BTF) was packed with a PVC pall ring media. The UCD biofilter (UCD BF) was packed with Celite™R-635 pellets. Both were supplemented with a nutrient solution containing NO_3^-.

Sampling Procedures

Two grab samples were obtained from each inlet and outlet flow stream (except the UCR biofilter, for which only one set was obtained). Samples were stored either in stainless-steel canisters (ERI, HBF, HBTF, Lasco and UCD) or Tedlar^{TM} bags (HBTF, SBF and UCR) after condensing and removing the water vapor with an ice-bath "cold finger." Tedlar^{TM} bags were stored in the dark to slow NO reactions. However, in the only case in which both containers were used, the stainless steel canister yielded a sample with a NO concentration near the detection limit, but the Tedlar^{TM} bag sample did not provide a quantifiable peak. Therefore, there were probably significant loses of NO in the Tedlar^{TM} bag samples. Samples were analyzed for NO within 3 days and for N_2O within 6 days.

NO samples were analyzed with a Sievers Instrument Model 270B Nitric Oxide Analyzer which uses gas phase chemiluminescence to detect NO concentrations larger than approximately 30 $\mu g/m^3$ (25 ppb_v). N_2O samples were analyzed with a Hewlett Packard gas chromatograph equipped with an electron capture detector to quantify N_2O concentrations larger than approximately 0.9 mg/m^3 (500 ppb_v).

Sampling Results

NO average inlet and outlet concentrations had significant standard deviations (Figure 12). Only the ERI, Lasco, JWPCP HBF and UCD BF samples had quantifiable peaks. Several of these values were also close to the detection limit of the analysis. T-test analysis indicated that differences between the inlet and outlet values was not statistically relevant for a confidence level greater than 1%. The other samples (JWPCP HBTF and SBF and UCR BTF) had no quantifiable level of NO. The UCR BTF and JWPCP SBF samples were collected in Tedlar^{TM} bags. One set of samples from the JWPCP HBTF was taken using stainless-steel canisters. The samples collected in the stainless steel canisters showed low levels of NO, near the detection limit. But samples collected from the same BTF in Tedlar^{TM} bags were not quantifiable and likely corrupted by the reaction of NO. Therefore, any NO flux in these units may have been missed.

The inlet levels of NO at both the Lasco and ERI facilities are elevated, possibly due to automobile traffic in the area. These units also had the highest organic loading (Table 2). Both were provided with NO_3^- as a nutrient. The high organic loading may help explain the release of low levels of NO. The apparent production in other units is more difficult to determine. The NO levels in the JWPCP HBF and UCD BF are near the detection limit and the standard deviation among samples is of the same magnitude of the apparent production. The HBTF showed no NO activity at all. This may be due to the incompatibility of bacteria responsible for the NO production with the acidity developed in the BTF by the oxidation of H_2S to H_2SO_4.

The emission factors listed in Table 2, are all very low. The JWPCP HBF appears to produce significant amounts of NO based on the emission factor. But we believe this emission factor is over inflated by the low organic loading and due to uncertainty in the actual production. The emission rates are all very low. Keep in mind, however, that many of these units are pilot-scale (Lasco, JWPCP) or laboratory-scale (UCD BF) and may have a slightly higher production rate if expanded or less vigilantly maintained.

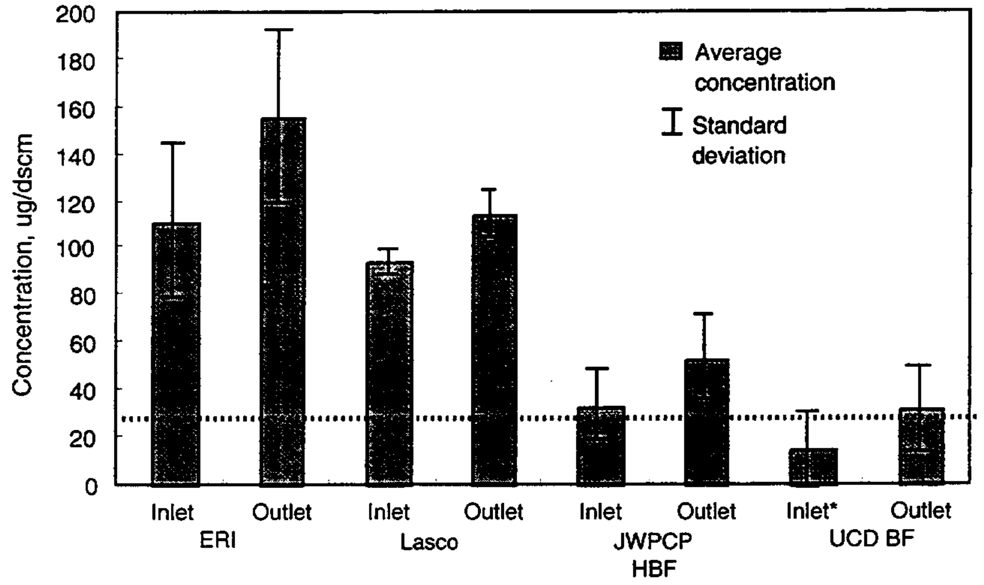


Figure 12.
NO production in biofilters and biotrickling filters. Detection limit = 30.7 µg/dscm (25 ppb_v)
(*sample not quantified, assigned a value of one-half the detection limit)

Table 2
Summary of HC loading rates, NO emission factors and NO emission rates for BF/BTF units.

Site	HC Loading	Emission Factor	Emission Rate	
	(g/m^3-day)	(g-NO/ton-HC)	(g-NO/day)	(kg-NO/year)
ERI	3,000	32	--	--
Lasco	1,400	110	0.83	0.31
JWPCP				
HBF	9.6	5700	4.9×10^{-3}	1.8×10^{-3}
SBF	N/A	N/A	BDL	BDL
UCD BF	540	45	8.0×10^{-4}	2.9×10^{-4}

(BDL below detection limit of analysis)

N_2O results were unfortunately much less revealing. Our analysis was only capable of quantifying concentrations > 500 ppbv. Therefore, minor N_2O fluxes in many of the units may have been missed. The only unit with detectable levels of N_2O was the Lasco unit. This unit may be producing N_2O. However, the actual magnitude of the source was difficult to determine. The inlet samples at the facility averaged 690 ppb_v N_2O with a standard deviation of 20%. However, the two outlet samples showed very different levels of N_2O

with an average of 2.3 ppm$_v$ N_2O and standard deviation of 88% (Figure 13). The N_2O level in the lower of the two outlet samples (550 ppb$_v$) was actually lower than the average N_2O level at the inlet (690 ppb$_v$). The samples were reanalyzed, but there is still a great discrepancy in the N_2O level in the two outlet samples. The difference in these samples cannot be explained, but for a possible sampling error. If there was production of N_2O in this BTF, the cause may be the high organic loading (providing substrate for denitrification) and the high liquid loading (slowing diffusion and providing time for further denitrification). If the results were reliable, the emission factor would be significantly higher than the NO emission factors (7,700 g-N_2O/ton-HC, 30 g-N_2O/day, 11 kg-N_2O/year) but still not significant. Another indication of diffusion limitation may be the removal efficiency of styrene. Only about 75 percent of the styrene was being removed in the biotrickling filter, although styrene degraded quite rapidly in the laboratory.

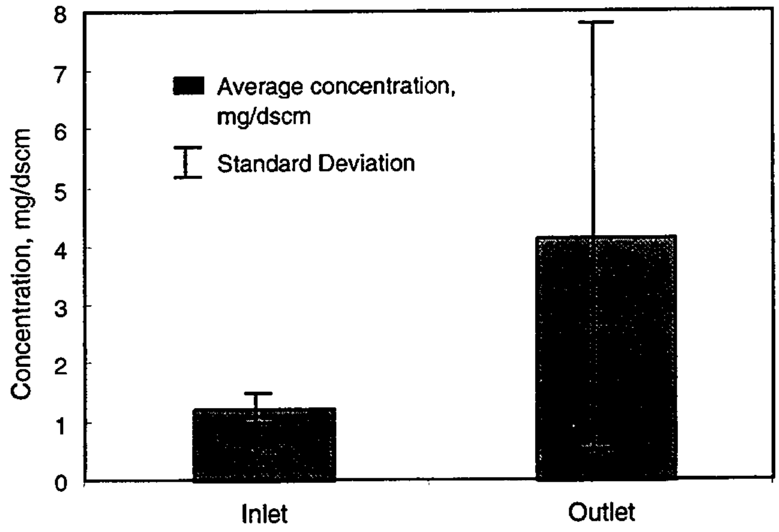


Figure 13.
N_2O production in the bathware manufacturing biotrickling filter Quantification limit = 0.9 mg/dscm (500 ppb$_v$)

Conclusions From Field Studies

The NO emissions from all units appear to be quite low with most of the NO emitted passing through the units from the inlet stream rather than being generated in the units themselves. However, outlet concentrations were higher than inlet concentrations in all cases and this suggests that some generation occurred in the biofilters. Outlet concentrations of NO are all below 200 µg/dscm. The higher emissions from some units may be due to higher organic loading or possibly operational factors such as liquid loading rate or nutrient (esp. NO_3^-) loading rate.

N_2O results were not conclusive, but the outlet concentrations appear to be less than 5 mg/dscm. The apparent production in this unit may be due both to high organic loading and the saturation of the media with the nutrient solution.

Whatever the net flux of oxides of nitrogen in BFs and BTFs, there does not seem to be any evidence that this flux should be of serious concern from an air pollution perspective.

COST OF NOx REMOVAL BY BIOFILTRATION

The principal components of biofiltration systems are the reactor, humidification system, piping, blower, and pad supporting the system. A large range of costs have been reported for biofiltration systems due largley to the inclusion of elaborate moisture control systems. However, the basic system with a manual moisture control system will cost approximately $10,000 per 100 cfm capacity using a one-minute empty bed contact time. (nominally a 100 ft^3 packing volume with the required ancillary components. The cost of packing is relativey minor, $0.50 to $1.50 per cubic foot for materials such as copost and lava rock, or 0.5 to 1.5 percent of the capital cost. .

Satisfactory NOx removals were not achieved in the laboratory systems operated in this project. Extrapolation of the best results to predict greater than 90 percent NOx removal would result in empty bed contact times of approximately six minutes. The fungal biofilter operated by Woertz (1998) produced nearly complete removal with empty bed contact times of one minute. Thus an optimistic capital cost estimate could be based on an empty bed contact time of one-minute and a conservative, but unguaranteed, estimate could be based on an empty bed contact time of six minutes. The range of capital costs would then be from $10,000 to $60,000 per 100 cfm of capacity. Economies of scale exist but the most likely use of biofilters for NOx control appears to be for small systems such as isolated diesel engines at well sights.

Operating costs for biofilters include electricity to operate blowers, minor system maintenance, and costs of personnel assigned to monitor and operate the systems. Power costs in Northern California for continually operated 100 cfm system (24 hours per day) are approximately $250 per month. Personnel costs will average about 2 hours per week, or possible $100 per month

Total cost of biofiltration, using an 8 percent annual interest rate and an amortization period of five years would fall in the range shown in Table 3:

Table 3
Estimated cost of removing NOx by biofiltration based on five year ammortization period and 8 percent interest rate.

EBCT Min	Capital Cost $	Operating Cost $/mth	Total Cost $/mth
1	10,000	350	550
6	60,000	350	1550

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