

**Robin Gilb**

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**From:** Mike Cudahy [mikec@cmservnet.com]  
**Sent:** Tuesday, August 15, 2006 4:52 PM  
**To:** Robin Gilb; Dennis Beddard  
**Cc:** Richard W Church; Jeff Church  
**Subject:** PPFA - PEX document - Dr. Hoffman paper  
**Attachments:** CCC-Friedlander-Dr. Hoffman.pdf

Dennis & Robin,

I would like to call HCD's attention to a document previously submitted as a response to many of the accusations found in the Reid document. The Dr. Hoffman paper, already in the record, in combination with other more recent submittals from PPFA and Friedlander, should prove useful for California in adopting PEX pipe. Please consider it, and other submitted materials, in your process to allow all Californians the choice to use PEX pipe.

To locate this document in the BSC site, click here:

[http://www.bsc.ca.gov/prpsd\\_chngs/documents/monograph\\_reference/CCC-Friedlander-Dr.%20Hoffman/CCC-Friedlander-Dr.%20Hoffman.pdf](http://www.bsc.ca.gov/prpsd_chngs/documents/monograph_reference/CCC-Friedlander-Dr.%20Hoffman/CCC-Friedlander-Dr.%20Hoffman.pdf)

It is also attached to the email.

Thank you very much for your attention,

Mike

**Michael Cudahy**  
**Codes and Training Specialist**



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PEX.040



Robert Friedlander

August 8, 2005

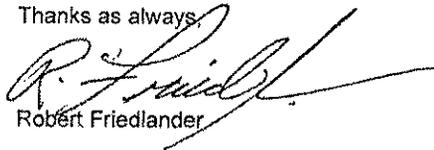
Stan Nishimura  
Executive Director  
California Building Standards Commission  
2525 Natomas Park Drive, Suite 130  
Sacramento, CA 95833

Dear Stan:

Now that I am finally back in my office after two fun weeks of travel (NOT) I have reviewed what was submitted by me during the public hearing on 8/1/05. It appears that I submitted the contents of my backup folder which did not include the copy of Dr. Hoffmann's report and CV. That was in the pile of items that I had been reading the night before. Please accept this copy which was listed on my letter as an attachment.

I am sorry if this caused the Commission any unrest, it was an oversight on my part.

Thanks as always,



Robert Friedlander

610 S. Sherman St., Suite 100 Richardson, Texas 75081  
(972) 960-2828 / Fax (972) 960-6911 / E-mail bob@friedlander.net

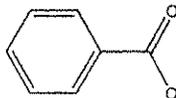
## Analysis of PEX and Drinking Water Supplies relative to the UPC of California

Prof. Michael R. Hoffmann, Ph.D.

*Michael R. Hoffmann*Caltech, 1200 E. California Blvd.  
Pasadena, CA 91125**Forward:**

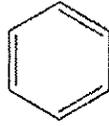
The following analysis and discussion has been prepared in response to a letter dated 23 July 2001 from Mr. Thomas Reid to Mr. Daniel Cardozo, which had the subtitle, "Environmental Effects of California Adoption of PEX for Potable Water," and which raised a number of questions regarding the possible use of PEX pipes in California.

Based on a careful and comprehensive review of the published scientific literature and subsequent analysis, it is clear the use of PEX pipes for drinking water supplies poses little, if any, risk to human health and environmental safety especially when compared to plastic drinking water bottles and related plastic materials that are commonly used as packaging materials for a wide range of food products intended for human consumption. In addition, any long-term environmental consequences are insignificant especially in light of the massive quantities of similar plastic materials that are ultimately contained within sanitary and industrial landfills or otherwise introduced into the environment. The opponents to the use of PEX pipes for household drinking water supplies in California raise the issue of compounds such as MTBE and benzeno-related compounds being released to the water within the pipes. In this regard, it should be noted that only one type of PEX piping (i.e., PEX-A, *vide infra*) has the potential to release MTBE as a breakdown product of the cross-linking agent used to create the sturdy piping material known as PEX from conventional high-density polyethylene. Other commercially-available PEX pipes (e.g., PEX-B and PEX-C) do not release detectable traces of MTBE because they are prepared without the chemical ingredient, t-butyl peroxide that serves to initiate the cross-linking polymerization that results in a more rigid and durable product. Furthermore, the benzeno-containing compounds, as mentioned by Mr. Cardozo in subsequent communications, are breakdown products of other plastic additives, common to virtually all plastic products and commonly used in many household products (e.g., shampoo, laundry detergent, etc.). For example, sodium benzoate is a "benzene-compound" that is the sodium salt of "benzoic acid," which is an FDA-approved benzeno-related compound that has been used by food manufacturers for over 80 years to inhibit microbial growth under low pH conditions. Sodium benzoate (with benzene at its chemical core and an added carboxylate constituent) is widely used as a chemical preservative in soft drinks, packaged beverages, fruit preserves and jellies, concentrated orange juice, margarine, and fast-food burgers as primary examples.



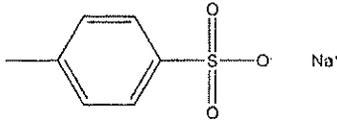
The chemical structure of sodium benzoate (a "benzene compound") used as a FDA approved food preservative (*vide supra*). Chemical formula:  $C_7H_5NaO_2$ ; Molecular Weight: 144.11 amu.

The structure of sodium benzoate can be compared to its core component, benzene as follows:



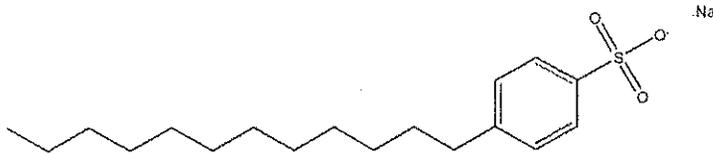
*The chemical structure of benzene. Chemical formula:  $C_6H_6$ ; Molecular Weight: 78.11 amu.*

Furthermore, most laundry detergents that are used in large quantities daily in California and around the world have a benzene ring as their core structure (e.g., linear alkyl benzene sulfonates). Some examples of specific laundry-detergent additives in common usage are sodium *p*-toluene sulfonate, sodium *p*-xylene sulfonate, and sodium cumene sulfonate.



*Structure of sodium *p*-toluene sulfonate, Chemical Formula:  $C_7H_7NaO_3S$ ; MW = 194.18.*

An example of a widely-used "benzene compound", laundry detergent is sodium dodecylbenzene sulfonate, which is shown below.



*Chemical structure of sodium dodecylbenzene sulfonate:  $C_{18}H_{29}NaO_3S$ ; MW = 348.47 amu*

The real questions regarding the stated opposition to PEX piping as a potential source of toxic chemicals to drinking water and to the environment must be posed in terms of actual concentrations of specific compounds relative to their known toxic thresholds. For example, sodium benzoate when used as a food preservative has a threshold limit in products of 0.1% by weight before it poses a risk to human health. In addition, the people of California are exposed on a daily basis to the "benzene compounds" or related compounds of concern via many different pathways such as personal care products, drinking water supplied in plastic bottles, household cleaning products, etc.

The following analysis will establish that much is already known about the specific chemical properties and potential consequences of its widespread use in order to make a decision on its suitability as a household plumbing product in California.

**Introduction:**

In the following sections, Mr. Thomas Reid's statements, which were made without any scientific reference or documentation, are systematically analyzed.

*Opening Statement by Mr. Thomas R. Reid on 23/07/01 (vide infra TRR):*

*"The state of California is considering adopting a portion of the Uniform Plumbing Code (UPC) which would allow the use of plastic pipe manufactured from cross linked polyethylene (PEX) for potable water use inside dwellings. The installation and use of PEX could result in direct and indirect impacts on the physical environment. If approved, PEX plastic pipe could be installed in thousands of homes in California; because of the potential scope of usage of PEX, these impacts may be cumulatively considerable."*

**Response by Professor Michael R. Hoffmann (vide infra MRH):**

The assertion by Mr. Reid that there may be considerable, cumulative environmental damage due to the use of PEX pipes for potable water use is both a misrepresentation and an alarmist assertion that is not supported by any known evidence within the European Union (EU), where PEX pipes for potable water supplies have been for sometime and are now are in widespread usage, and by ongoing studies in the scientific and engineering literature. The points raised by Mr. Reid in his letter need to be addressed on the basis of a careful reading and interpretation of the current scientific literature, on the basis of years of practical experience gained throughout the EU, and after a quantitative extrapolation to realistic water flow conditions under a wide-range of operational parameters; and not on the basis of unsupported assertions. For example, the EU has established maximum exposure levels for additives used in all types of plastic packaging material for food and beverages including mineral water, milk products, and purified drinking water. None of the laboratory experiments performed to date on the wide range of plastic products including PEX indicates that under extreme testing conditions that identifiable contaminant levels approach maximum allowed exposure levels. Maximum contaminant levels for an array of chemical compounds can be found at the European Union's Joint Research Facility's website (<http://cpl.jrc.it/smi/>).

Closely related plastic materials (e.g., high-density polyethylene, HDPE and medium-density polyethylene, MDPE), which are produced with the same cross-linking agents, anti-oxidants, and colorants as PEX that are speculated by Mr. Reid to be major environmental contaminants, are already used extensively in commercial applications (e.g., plastic food wraps, bottles, storage tanks and vessels, etc.) and environmental applications (e.g., geomembranes for landfill containment and geo-structural devices for slope stability, etc.). For example, the same chemical compounds that may be released from PEX pipes at extremely low levels are also released from PET plastic bottles, which are routinely used for high-priced bottled water (e.g., Evian, Volvic, Vittel, etc.) and from polycarbonate bottles used to carry water by backpackers and for baby bottles. Thus, there are many modes of exposure to synthetic chemical compounds by humans or the environment than through water flowing in PEX water pipes. In addition, on a mass basis

alone the quantity of disposable plastic bottles (PET and polycarbonate) far exceeds any quantity the quantity of PEX piping that would ultimately retained or stored in the ambient environment.

Numerous scientific studies (*vide infra*) on PEX and related plastic materials show that chemical releases are far below maximum contaminant levels established by the EU and the USEPA. Releases of various chemical components from PEX to water are lower or of the same magnitude as those obtained by releases from plastic bottles such as those used for drinking water or as baby bottles. Similar scare tactics as those employed by Mr. Reid concerning PEX have been used to raise alarms about polycarbonate baby bottles. However, those assertions have been rejected as being totally false when it came to threshold health and safety standards (i.e., releases at the part per trillion to part per billion levels under microwave heating conditions).

#### 1a. Scientific Report and Analysis

Mr. Reid claims that nothing is known about the chemical consequences of using PEX pipes. This is not true at all. Much is already known. For example, Skjevrak et al.<sup>1</sup> report on the diffusive release of several identifiable chemical components from HDPE and PEX such as 2,4-di-*tert*-butyl-phenol (2,4-DTBP) and 4-methyl-2,6-di-*tert*-butylphenol (BHT -- alternative name - 3,5-di-*tert*-butyl-4-hydroxytoluene) after 72 hours of exposure to pure water with a surface area to volume ratio of 4 (which they note is unusually high compared to practical applications. Both DTBH and BHT have been previously reported degradation product from antioxidants (e.g., Irgafos 168), which are used to extended the lifetime of plastic pipes. After 72 hours of exposure of HDPE pipes to water under quiescent conditions, the total organic carbon (TOC) loading in the water increased from non-detectable to the range of 1.3 to 1.9  $\mu\text{g L}^{-1}$  or 1.3 - 1.9 ppb (parts per billion by mass) for 7 different brands of HDPE pipes. In the case of PEX pipes of the same dimensions, Skjevrak and co-workers, reported higher TOC levels (e.g., 1.3 to 2.5  $\text{mg L}^{-1}$  or 1.3 - 2.5 ppm) for two brands of PEX-A. Nonetheless, these they noted that these TOC levels were below maximum contaminant levels, MCL's ( <http://www.epa.gov/safewater/mcl.html> ). The TOC was dominated by MTBE which is a breakdown product of t-butyl peroxide, which is the chemical source of free radicals used to promote the chemical cross-linking of PEX-A. PEX-B and PEX-C, it should be noted, are not cross-linked with t-butyl peroxide. Substantially smaller amounts of t-butanol, p-butoxyphenol, and 5-methyl-2-hexanone were identified as specific components of the measured TOC released to water after 72 hours of leaching at room temperature. For three consecutive 72 hours leaching periods with pure water at time zero, concentrations of TOC for the 7 brands of HDPE ranged from 20  $\text{ng L}^{-1}$  (ppt) to 2.5  $\mu\text{g L}^{-1}$  (ppb). It should be pointed out that these tests represent organic compound accumulations in water in non-flowing systems. The amounts released during continuous or intermittent flow conditions would be substantially less and most likely below detection limits. Thus, these tests and others which will be discussed below represent worst-case scenarios which are very unlikely to be encounter during normal usage. In regard to extensive environmental damage, it should be noted that one of the identified compounds BHT is widely used as a food preservative in massive quantities. Thus, extensive environmental contamination due to the use of PEX pipes for home water distribution as claimed by Mr. Reid is a highly misleading exaggeration relative to all of the other sources of the identified compounds to the environment (e.g., through HDPE food packaging and bottling materials). For example, BHT is a well-known antioxidant that is used as common food preservative which is approved by the FDA for use in food, oils and fats. In the

majority of samples tested. TOC levels release to water after 72 hours of quiescent leaching (i.e., non-flowing conditions) were in the ppt to ppb range (i.e., nanogram or microgram per liter range).

#### 1b. Practical Implications and Interpretation

It is clear from a careful reading of the scientific and engineering literature that detectable but minimal amounts of some chemical compounds can be leached or released from plastic materials into clean water. This is true for plastic water bottles, plastic baby bottles and for PEX and HDPE pipes. As noted above, typical release rates for prolonged exposures are most often in the range of ppt to ppb levels. On the other hand, there are no MCL's established for above identified leachates. In the specific case of TOC, there is no MCL. However, there is an EPA requirement to remove 38% of TOC during drinking water treatment. For example, for the Longmont, Colorado<sup>5</sup> drinking water the source water had TOC levels ranging from 2.8 to 6.0 ppm (mg L<sup>-1</sup>) and after conventional water treatment the TOC levels were reduced to 1.4 to 1.9 ppm. The State of California's Department of Health Services<sup>6</sup> has set a MCL for MTBE of 13 ppb or health and safety and a level of 5 ppb for taste and odor concerns.

<sup>5</sup> ([http://www.ci.longmont.co.us/water\\_waste/lab/tap\\_water.htm](http://www.ci.longmont.co.us/water_waste/lab/tap_water.htm))

<sup>6</sup> (<http://www.dhs.ca.gov/ps/ddwem/chemicals/MTBE/mtbeindex.htm>)

The research paper by Skjevrak et al. notes that ppb (parts per billion) levels of total organic carbon (TOC) are released from new PEX and HDPE pipes to quiescent water after 3 consecutive days of exposure. In this regard, it should be noted that many urban and rural drinking waters contain ppm (parts per million) levels of TOC even after treatment (*vide supra* – Longmont, CO), and in some cases, they contain TOC levels that are 100 to 1000 times more concentrated than found in the experiments described above. Skjevrak et al. used highly purified laboratory water that was pre-treated by reverse osmosis and UV irradiation as a starting point in their PEX leaching experiments. In addition, the research results reported by Skjevrak et al. also pertains to the concerns raised by Dr. Michael Fox ([www.chemmax.com/polytube1.htm](http://www.chemmax.com/polytube1.htm)) about the probable appearance of MTBE (methyl tertiary butyl ether) and t-butanol as breakdown products of the free-radical initiator t-butylperoxide (i.e., the inducer of chemical cross-linking in PE to produced PEX-A). The bottom-line message from the above study and those mentioned by Dr. Fox, are that a home-owner with any type of piping should run the water for several minutes each day for the first 3 to 6 months or longer before usage or consumption to minimize exposure to unwanted chemicals. This is a wise approach and commonly practiced approach taken by most homeowners regardless of the pipe material in use. It should also be noted that there are already many organic chemicals in domestic drinking water at the ppb or ppt levels; however, at these levels the compounds are below the maximum contaminant levels (MCL) which are established and regulated by local, state, and federal environmental agencies. This includes drinking water that may be carried through PEX pipes. It is also well known that PEX meets NSF 61 water quality standards for pipes that carry potable water. In other cases, existing code-approved plumbing materials have not met the chemical standards in terms of an extensive list of chemical leachates as identified by the NSF in their report to Health Canada about materials that failed to meet NSF 61 standards ([http://www.hc-sc.gc.ca/hccs-sesc/water/pdf/nsf61\\_dvsc/components.pdf](http://www.hc-sc.gc.ca/hccs-sesc/water/pdf/nsf61_dvsc/components.pdf)). However, as noted PEX pipes meet those standards.

It also needs to be noted that similar chemical compounds have been observed in water stored in polycarbonate bottles (e.g., water storage bottles and plastic baby bottles) and from PET (polyethyleneterephthalate) bottles, which are commonly used for commercial drinking water storage and distribution (e.g., Evian, Vittel, Volvic, Crystal Geysir, etc.). For example, Nerin et al.<sup>2</sup> report that typical polycarbonate bottles (Nalgene) released monomers, oligomers, UV stabilizers, antioxidants, degradation products, and other additives. Specific compounds released to water include phenol, bisphenol A, 2, 4-di-tert-butylphenol, cyasorb UV5411, bis(2-ethylhexylphthalate), Irganox 1076, and Irgafos 168. In the case of PET bottles<sup>3</sup>, bisphenol A<sup>4,5</sup> is the compound that is of the greatest concern. In addition to bisphenol A, acetaldehyde and formaldehyde are leached from the PET plastics into the water. However, none of the leached levels of chemicals approached regulated MCL limits or achieved dangerous levels for unregulated chemical compounds.

In a study of leaching from HDPE plastic milk containers and bottles into milk, Casajuana and Lacorte<sup>6</sup> measured the concentrations of nonylphenol; di-*n*-butyl phthalate; butylbenzyl phthalate, bisphenol A; bisphenol A diglycidyl ether; bis-(2-ethylhexyl)phthalate, diethyl phthalate; dimethyl phthalate; 4-*n*-nonylphenol ranging from 0.06 to 0.36  $\mu\text{g}/\text{kg}$  (ppb levels). None of the above compounds or the sum of total of all compounds, achieved the maximum leached level allowed by law in the European Union. Casajuana and Lacorte also noted that the encountered levels cannot be considered to be a health risk. In another study, Brede et al.<sup>5</sup> found a mean level of bisphenol A 0.23  $\mu\text{g L}^{-1}$  in 12 different brands of polycarbonate baby bottles exposed to hot water at 100 °C for 1 h. They also noted that none of the 12 bottles released bisphenol A at levels that exceed the recently established provisional tolerable daily intake (0.01  $\text{mg kg}^{-1}$  of body weight per day) in the European Union.

*Second Paragraph of TRR's Opening Statement and Request for a Detailed Impact Analysis:*

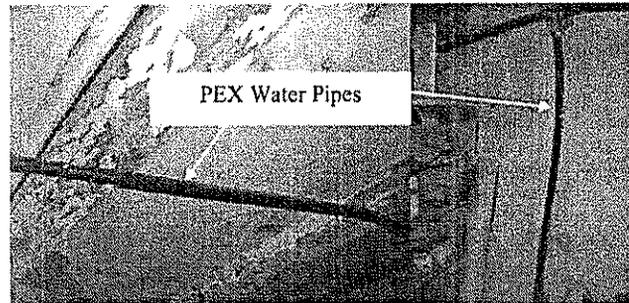
*"For these reasons, the Department of Housing and Community Development (HCD) needs to comply with the California Environmental Quality Act (CEQA) so that it is adequately informed about the environmental consequences of the proposed approval of PEX. In this letter I outline some of the areas of potential environmental impact. Because PEX is not widely used in the United States, information is not readily available from external sources. Clearly, the present record lacks sufficient information to allow the state to dismiss the potential for environmental impact. Thus HCD should use the CEQA process to gather the necessary information to determine whether or not the impact potential would be realized."*

**Response by MRH:**

Based on our reading of the scientific and engineering literature and also based on the extensive experience gained throughout the European Union, sufficient information and data has been gathered to provide a realistic assessment of potential environmental and health impacts due to the use of PEX especially when compared to metal pipes and their associated fittings (i.e., copper and lead contamination derived from water pipes can be considerable). For example, in

Germany older houses are being routinely re-plumbed with PEX tubing. Shown below is a recent photograph taken in the cellar of a 300-year old German farm house that has been re-plumbed in PEX.

Figure 1. PEX Pipes under a German Farm House



The body of scientific evidence already presented in the open literature about the potential impacts of the use of PEX pipes will be presented and discussed in subsequent sections (*vide infra*).

*Statement by TRR:*

*"For polyethylene to serve hot water use, the individual polymer chains must be cross-linked together with supplemental chemical bonds. The three commercial methods of cross linking give rise to three classes of PEX: PEX-A, the so-called Engel method where the polyethylene resin and a chemical additive are heated to produce cross linking; PEX-B, the silane method which produces silicon-oxygen cross link bonds; and PEX-C, where cross linking is initiated by gamma or electron beam radiation. All types of PEX would be permitted under the proposed code as long as they met the requirements of relevant ASTM or NSF testing. The different manufacturing processes produce slightly different products with different chemical and mechanical characteristics. Historically, the push to allow plastic pipe in California has come from one manufacturer seeking to expand its market. For PEX, the manufacturer pushing for approval represents only one of the three manufacturing methods and has supplied information of limited scope. For HCD to adequately consider the environmental impact of the code adoption, HCD needs to define the "project" under CEQA completely and obtain information about all three commercial forms of PEX."*

**MRH Response:**

At this point in time, enough is known about all three types to make a decision about household usage in California. A complete discussion will be provided herein.

Statement by TRR:

*"The cross linking of polyethylene produces the chemical structure necessary to resist softening at elevated temperatures. The cross linking does not change the fundamental chemistry of polyolefin polymers, and hence PEX is susceptible to the same chemical attack from oxidants or ultraviolet light as are other polyolefins. For this reason, PEX resin used to manufacture pipe for plumbing has chemical additives such as antioxidants, ultraviolet blockers, fillers and pigments. HCD will need to obtain information on all of these additives as well as the underlying manufacturing process and the chemicals that uses. The information is essential for HCD to be able to appraise the potential for chemical leaching and to evaluate factors that may affect mechanical stability and performance of the plumbing system."*

**MRH Response:**

At the present time, the additives are quite well-known and documented. They can be traced through SciFinder Scholar, the comprehensive American Chemical Society database, via the patents on the various PEX preparations and production methods, and through Web of Science and Web of Knowledge searches.

Statement by TRR:

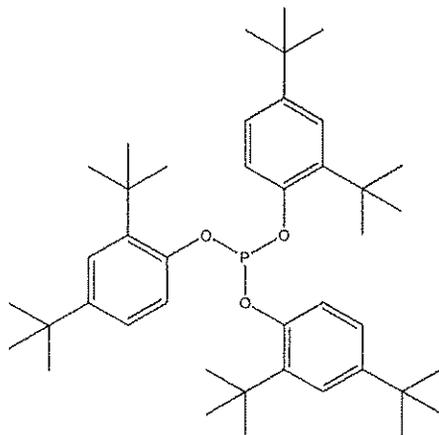
*"PEX manufacturers obviously seek to distance themselves from the PB pipe fiasco. HCD should insist, however, that PEX manufacturers provide full information about the antioxidant system used for PEX to show that the failures from PB could not happen with PEX. If the same antioxidant system is being used for PEX as was used for PB, then there needs to be an explanation. The state is being offered the same story with PEX as with PB: "this plastic pipe is used everywhere but California with no problems", but something in the environmental conditions in the arid lands from Southern California and Arizona to Texas caused failures that had not been experienced elsewhere."*

**MRH Response:**

There is a large database of knowledge any possible antioxidants which are in use. For example, the Irga-labeled (*vide supra*) family of antioxidants are widely used in various HDPE products. In some cases, Vitamin E is used as the primary antioxidant in plastic formulations.

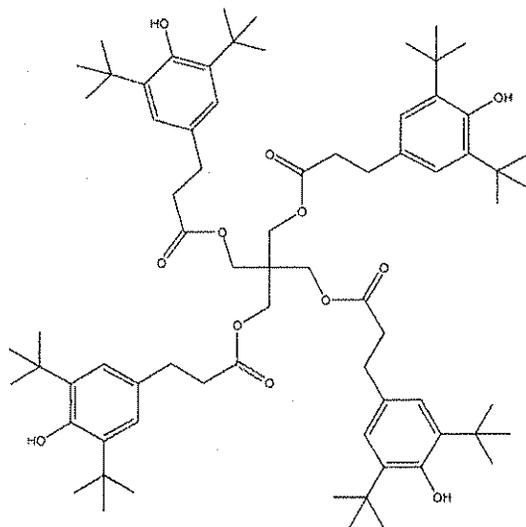
The most commonly used antioxidants are:

**Irgafos 168:** phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1) - C<sub>42</sub>H<sub>63</sub>O<sub>3</sub>P



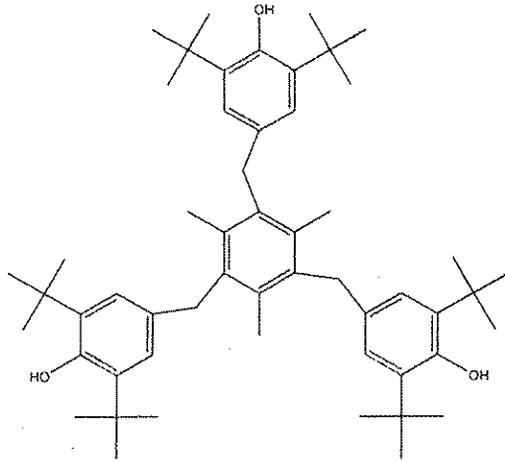
**Chemical Structure of Irgafos 168**

**Irganox 1010:** Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl ester  
 $C_{77}H_{108}O_{12}$



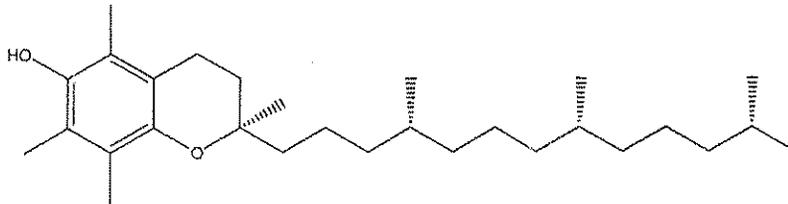
**Chemical Structure of Irganox 1010**

**Irganox 1330:** Phenol, 4,4',4''-[(2,4,6-trimethyl-1,3,5- benzenetriyl)tris(methyleno)] tris[2,6-bis(1,1-dimethylethyl)- C<sub>5</sub>H<sub>7</sub>O]<sub>3</sub>



**Chemical Structure of Irganox 1330**

**Vitamin E** [CAS # 59-02-9] 2H-1-Benzopyran-6-ol, 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-, [2R-[2R\*(4R\*,8R\*)]]-; 5,7,8-trimethyltolcol



**Chemical Structure of the Anti-oxidant Vitamin E**

*TRR Statements on Environmental & Health Related Issues:*

*"Several environmental issues are readily identifiable that are relevant to plastic pipe and specifically to PEX. Foremost among these is the concern for public health which includes chemical leaching from the pipe and permeation of the pipe by contaminants in the environment. Based on the PB experience, there is a real concern for consumer protection and reliability of the pipe system. There are also potential issues for fire safety, solid waste management, and air and water quality. Chemical leaching is a complex problem to assess. Obviously, HCD would need to begin with a complete disclosure of the composition of all forms of PEX which*

*may be used in California. This means PEX classes A, B, and C, as described above. HCD would need to identify the potential health risk associated with these chemicals and then assess their potential to be leached into the potable water carried by a PEX pipe. Chemical leaching would also need to take into account breakdown products from antioxidants and other substances that may be formed in the pipe by reaction with chlorine in the water supply."*

**MRH Response:**

Over the last five years a number of fundamental studies on the durability, chemical consequences, and biochemical impact of PEX and HDPE plastic materials have been carried out. It is known that virtually all plastic materials leach chemical components and *in situ* breakdown products to water, milk, and other food items. As mentioned above, PET, HDPE, PEX, and polycarbonate materials all leach chemical components into water and have measure solid-phase diffusion properties for the permeation of other chemical compounds. However, at the present time, with perhaps a few exceptions, none of the reported levels in the open scientific literature reach what would normally be considered dangerous levels to human health or present an environmental safety issue.

The European Union has established maximum exposure levels for plastic additives used in package material (e.g., plastic milk and drinking water bottles, plastic food wrappings). None of the laboratory experiments indicate any levels obtained upon extreme testing conditions that approach the maximum allowed exposure levels. As mentioned above this data can be found at <http://epf.jrc.it/Spain>.

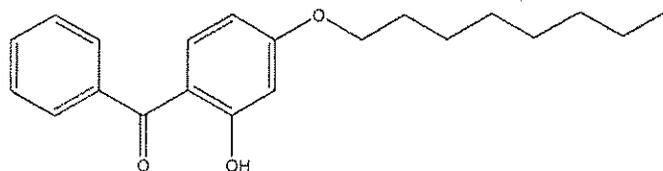
For example, Gill et al.<sup>7</sup> investigated the degradation of cross-linked polyethylene tubing that was subjected to high-temperatures (90 – 120 °C), high pressures, and chlorinated water (0 – 5 ppm reactive chlorine) in flow-through systems (e.g., home plumbing applications) in order to estimate service lifetimes. They examined the combined effects of free chlorine, pH, and metal ion content and determined that the time to failure correlated better with the oxidation-reduction potential than with the free chlorine concentration. They determined the relative rate of consumption of the embedded antioxidant using the oxidation induction time as a function of fraction of the time to failure in their tests. For example, at 115 °C the antioxidant was consumed in less than half the time to failure at 115 °C. However, there was no observed degradation of the plastic until the antioxidant was completely consumed.

Dear and Mason<sup>8</sup> reported that the lifetime of polyethylene products depends on retention of the antioxidant in the plastic. In dry air, the life-span of the material can be many decades. However, when the same material is immersed in water the loss of the antioxidant from PE can be accelerated. Dear and Mason measured the depletion rate of antioxidants in polyethylene when exposed to water containing different chlorine concentrations. They noted that when the working and environmental stresses remain within defined limits, that the life-span of PE products can be many decades.

Hassanpour and Khoylou<sup>9</sup> noted that plastic pipes are being used in greater numbers for hot water installations due to their flexibility, greater lengths, easier handling and an absence of

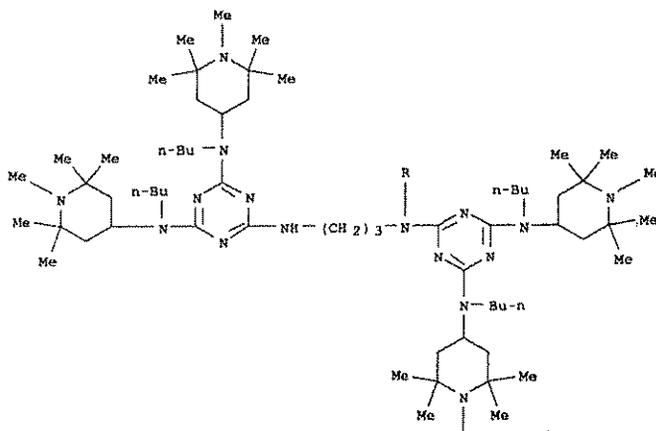
corrosion. The useful lifetime of unstabilized polyethylene is predicted to vary from a few months in hot water (30 - 40 °C) to almost two years in cool water (0 - 10 °C). In their research, Hassanpour and Khoylou prepared polyethylene with different types of stabilizers, in order to increase durability. The samples were irradiated with electron beams at 100-150 kGy to produce PEX-C. Samples were immersed in hot water for 1000 h and their thermostability was measured by the induction time technique using differential scanning calorimetry as a function of time. They examined the impact of Flame Retardant 116, Tinuvin 328, Tinuvin 622, Chimassorb 119, Chimassorb 944, and Irganox 1010 on the stability and lifetime of PEX-C. Examples of the chemical composition of these additives are presented below. The Chimassorb family of compounds provided the greatest stability (i.e., longest projected lifetimes) of PEX-C. Under normal circumstances, Chimassorb products are used as UV stabilizers. However, Hassanpour and Khoylou concluded that the UV stabilizers gave the strongest and longest lived (projected) PEX products.

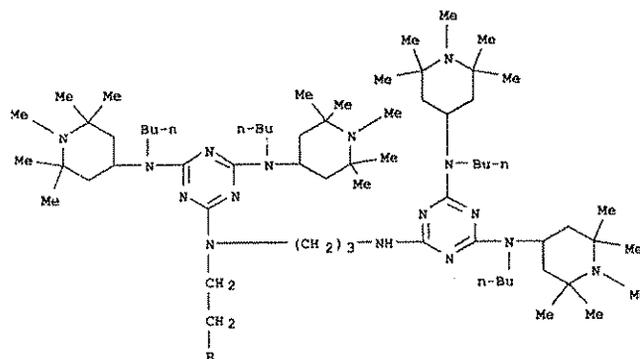
**Chimassorb 81:** 2-Hydroxy-4-n-octoxybenzophenone,  $C_{21}H_{26}O_3$



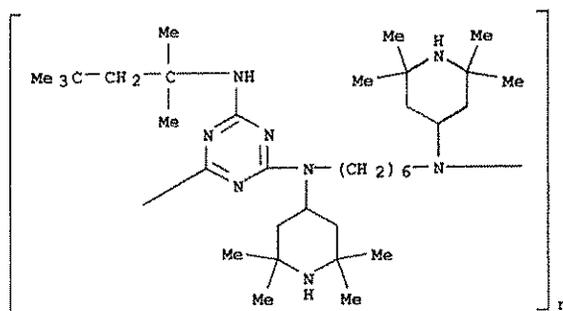
**Chimassorb 119:** 1,3,5-Triazine-2,4,6-triamine, N,N''-1,2-ethanediylbis[N-(3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidiny)amino]-1,3,5-triazin-2-yl]amino]propyl]-N',N''-dibutyl-N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidiny)-  $C_{132}H_{250}N_{32}$

PAGE 1-A

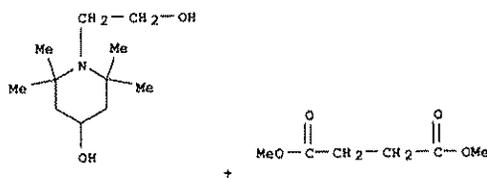




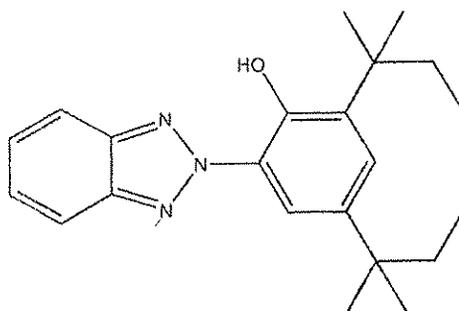
**Chimassorb 944:** Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidyl)imino]] - (C<sub>35</sub>H<sub>66</sub>N<sub>8</sub>)<sub>n</sub>



**Tinuvin 622:** Butanedioic acid, dimethyl ester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoethanol - (C<sub>11</sub>H<sub>23</sub>NO<sub>2</sub>·C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>)<sub>x</sub>

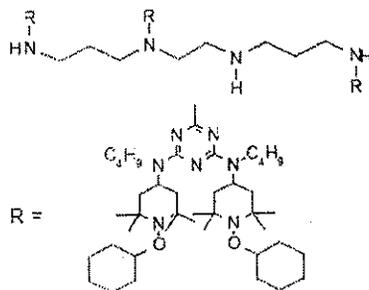


**Tinuvin 328:** 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol - C<sub>22</sub>H<sub>29</sub>N<sub>3</sub>O - MW = 352



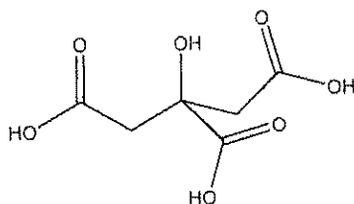
**Flame Retardant 116:** Polymeric product of N, N'-ethane -1,2-diylbis (1,3-propanediamine), cyclohexane, peroxidized 4-butylamino-2,2,6,6-tetramethylpiperidine and 2,4,6-trichloro-1,3,5-triazine - Molecular Weight - 2261 g mol<sup>-1</sup>.

FLAMESTAB NOR 116



Ali and Lcgocka<sup>10</sup> studied the effects of Irganox 1010 and citric acid as antioxidants and modifiers of the network structure and mechanical and thermal properties of low-density polyethylene (LDPE) during electron-beam cross-linking. Their results showed that the addition of the stabilizers had a retarding effect on the gel fraction of LDPE within the investigated range of electron-beam-irradiation doses. Tensile testing measurements showed that the addition of both stabilizers caused a slight reduction in the stress at break and an increase in the strain at break. They also showed that the thermal properties of the LDPE samples that were cross-linked with electron-beam irradiation (i.e., PEX material) were greatly improved due to the presence of the stabilizers. Their results indicated that the common chemical food additive, citric acid, was more effective as a stabilizing agent against thermal decomposition than Irganox 1010 and that PEX was a much more stable product than non-irradiated HDPE.

**Citric Acid:** 2-Hydroxy-1,2,3-propanetricarboxylic acid - C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>



Thus, the ideal formulation for PEX from an environmental and health perspective based on literature studies suggests that PEX products be made with any number of common and harmless anti-oxidants, which will provide greater stability than HDPE.

## 2a. Additional Scientific Reports and Analysis

Hassinen et al.<sup>11</sup> exposed chemically-stabilized, high-density polyethylene (HDPE) pipes to chlorinated water (3 ppm) at elevated temperatures (105 to 190 °C). Based on the measurement of oxidation induction times, they showed that the embedded stabilizers were rapidly consumed by the action of chlorinated water. Size exclusion chromatography and differential scanning calorimetry showed that extensive polymer degradation was strictly confined to the immediate surface of the unprotected inner walls and to the amorphous phase of the semi-crystalline polymer. Hassinen et al. studied HDPE pipes that had an external diameter of 12 mm and a wall thickness of 2.7 mm. The HDPE was stabilized with 0.1 wt-% Irganox 1010 and 0.2 wt-% Irgafos 168. The molar mass distribution of the HDPE, (PE 100) MW = 5600 g mol<sup>-1</sup> and 283000 g mol<sup>-1</sup>. The crystallinity of HDPE in the pipe wall was determined by differential scanning calorimetry to be 66% uniformly through cross-section except at the outer wall where the crystallinity was 58%. Micrometer thick degradation zones were observed on the exposed surfaces after 200 to 1000 h of exposure. The thickness of the porous layer, which was assessed by optical microscopy, increased at a constant rate after an initial incubation period. The activation energy for layer growth obtained was 100 kJ mol<sup>-1</sup>. Size exclusion chromatography was used to show that the molar mass decreased from the unexposed values, 5600 and 283000 g mol<sup>-1</sup>, to 2600 and 8300 g mol<sup>-1</sup> in the surface damaged zone. Since PEX products will be more stable and resistant to degradation, we can conclude that the development of a similar affected porous surface layer should be substantially less than that observed for HDPE.

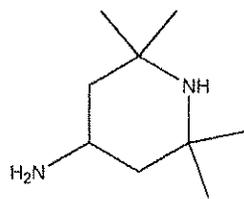
Haider and Karlsson<sup>12-15</sup> investigated the loss rates of various stabilizing agents from PE materials relevant to the fate of plastic materials in sanitary landfills. In the first paper in this series, they<sup>13</sup> followed the loss of Chimassorb 944 from low-density polyethylene films (LDPE) exposed to simulated landfill environments (e.g., aqueous media at pH 5 to 7, temperatures of 25, 50, 80 and 105 °C and solid-to-liquid ratios of 1:10 and 1.5). They determined the relative migration of the stabilizer, including diffusion and desorption from the films, along with the degradation of the polymeric matrix. They reported that release rate of Chimassorb 944 from the LDPE films increased at higher temperatures, longer exposure times, lower pH, and higher solid-to-liquid ratio. They concluded that the typical leachate concentrations of the antioxidants in the landfill will not reach a dangerous concentration for the aqueous environment based on the

known toxicity of Irganox 1010 and Irgafos 168. Furthermore, they note that these compounds will be degraded over time by microbial action.

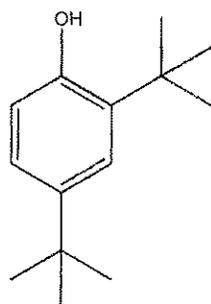
In their second paper, Haider and Karlsson<sup>14</sup> noted that plastics, which end up in soil or landfills will eventually be degraded. At the same time a slow migration of additives from the plastics will occur. The additives and the degradation products of these and the polymer are potential compounds can be altered further by microbial action. In this specific study, they measured the rate of the migration of antioxidants (Irganox 1010 and Irgafos 168) from medium density polyolefins films (MDPE) under the same conditions described above. They found that the release of both Irganox 1010 and Irgafos 168 increased at higher temperature, longer times, and lower pH. In addition, the loss Irgafos 168 occurred faster than Irganox 1010 at lower temperatures while at higher temperatures the opposite behavior was observed. Haider and Karlsson noted that no degradation of the polymeric matrix was detected over the timeframe of the tests that they carried out. Since MDPE is much less stable than PEX, it can be concluded the degradation of the PEX matrix under landfill conditions would be less than that observed for MDPE (i.e., PEX provides a more stable pipe material).

In a follow-up study, Haider and Karlsson<sup>15</sup> explored further the loss and transformation of Chimassorb 944 from LDPE films under similar conditions (*vide supra*). They observed that the progressive loss of the stabilizer was accompanied by structural changes of the polymeric matrix where the fastest loss rate of the stabilizer occurred in water via chemical hydrolysis. Some of the observed degradation products were (Z)-9-octadecenamide, 4-amino-2, 2, 6, 6-tetramethylpiperidine, 2, 4-di-*t*-butyl-6-nitro-phenol and 2-cyclohexene-1-dione-3,5-dimethyl-O-methylxime. One can conclude that the order of stability of the plastic materials would be LDPE < MDPE < HDPE << PEX.

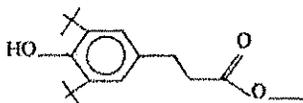
Haider and Karlsson<sup>12</sup> continued their examination of the loss Irganox 1010 and Irgafos 168 from MDPE films over a period of 4 years at 25 °C. They reported that the amount of antioxidant lost varied remarkably depending on the testing medium. The fastest loss of antioxidant was found on exposure to open air and sunlight while the slowest loss was observed in compost. GC-MS analysis showed that degradation of the polymeric matrix resulted in the formation of hydrocarbons and oxygen-containing compounds such as alcohols, carboxylic acids, aldehydes, and esters. The transformation products of the antioxidants formed as result of processing or exposure to the tested media were also identified. The transformation of the phenoxy radical of the Irganox 1010 produced the ester, acid, dealkylated cinnamate, and quinone products, whereas Irgafos 168 yielded oxidation products and 2,4-di-*tert*-butylphenol. An array of biochemical breakdown products were detected at various trace levels by Haider and Karlsson<sup>12</sup>. Based on their observations for MDPE films under composting conditions, it can be concluded that PEX due to its greater stability would undergo lower loss rates of matrix embedded anti-oxidants.



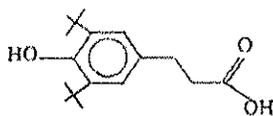
4-amino-2,2,6,6-tetramethylpiperidine



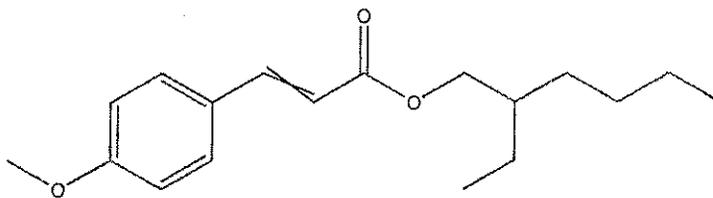
2,4-di-tert-butylphenol



methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate



3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid



2-ethylhexyl *p*-methoxycinnamate

*TRR Statement:*

*"Permeation is the phenomenon where relatively low molecular weight substances migrate through a seemingly solid polymer barrier. Permeation is a concern where the ground and groundwater are contaminated with petroleum compounds, with the gasoline additive MTBE, or with pesticides, particularly termiticides. Although most domestic plumbing will be within the structure itself, the approval considered by HCD includes external exposure from the water metered to the structure or under slab for slab on grade home construction. The latter is a particular concern because of the requirement for treating the sub-slab soil with termiticides in some geographic locations. HCD should request and review laboratory or field test data for PEX permeation. Note that the different types of PEX have different chemical cross-linking characteristics and would be expected to have different permeation behavior."*

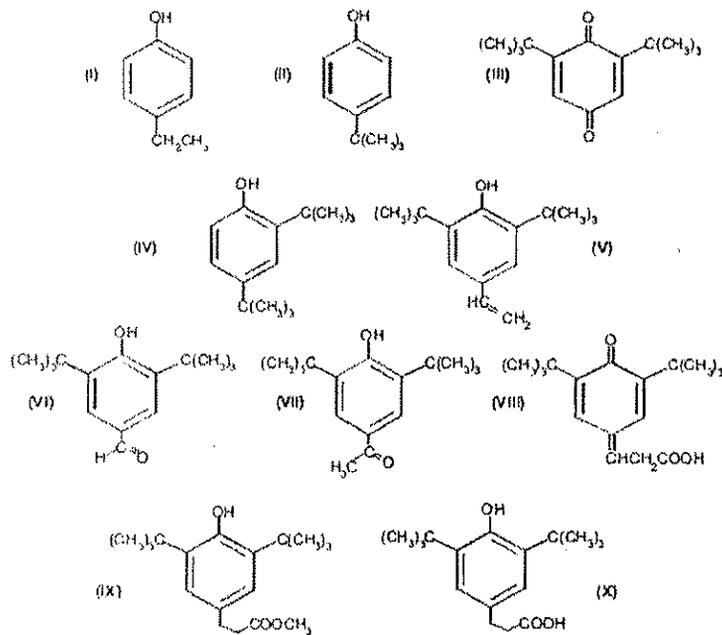
**MRH Response:**

Several scientific studies<sup>16-18</sup> have investigated the permeation rates of a variety of chemical compounds through HDPE barriers because this material is routinely used as geomembranes for landfill protection and for hazardous waste disposal sites. For example, Joo et al.<sup>16,17</sup> have determined the mass transfer rates of organic compounds into HDPE geomembrane material using batch immersion tests with dilute aqueous solutions. They found the partition coefficients of the organic compounds into HDPE (i.e.,  $\log K_{HDPE/W}$ ) were correlated on a log basis with the corresponding octanol-water partition coefficients (i.e.,  $\log K_{OW}$ ). The diffusion coefficients (D) of the organic compounds in HDPE were found to be in the range of  $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ . The measured D values decreased with the increase in their molecular diameters or size (thus, molecules of much higher molecular weight will diffuse slower through the solid material). The effects of the presence of other organic compounds, pH, ionic strength, temperature, and five-year aging of HDPE geomembranes on sorption were evaluated. All factors except temperature were found to be insignificant. Joo et al. presented a mathematical model, together with the experimentally determined mass transfer parameters, that can be used to predict the mass flux of organic compounds through HDPE geomembranes. In a follow-up study, Joo et al.<sup>17</sup> investigated the effects of aging and external tension of HDPE geomembranes on the mass transport of organic compounds. They determined that for HDPE geomembranes, which had served as a landfill liner for 5 years and was stretched by 8% of its initial length, the  $K_{HDPE/W}$  values for organic compounds increased by 5 to 58% while the D values for organic compounds increased by 10 to 86%. As a consequence, the breakthrough times were faster. However, it should be noted that the membrane liners are substantially thinner than the walls of PEX pipes. The percentage change in organic compound uptake as measured by the HDPE distribution coefficient or the octanol-water distribution coefficient may seem significant, however, with a  $\log K_{ow}$  of 7 (i.e.,  $K_{ow} = 10^7$ ) and 60% increase would correspond to a  $\log K_{ow}$  of 7.2, thus, in reality these changes are not significant. Even lesser changes would occur with PEX relative to HDPE that have been altered over time.

In an earlier study, Sangam and Rowe<sup>18</sup> measured the migration of the dilute aqueous organic contaminants through HDPE geomembranes. They employed semi-empirical methods to estimate partition and diffusion coefficients for organic contaminants in dilute aqueous solutions on a 2.0 mm thick HDPE geomembrane using three chlorinated hydrocarbons (dichloromethane, 1,2-dichloroethane and trichloroethylene) and four aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes). The results show that the partition coefficient,  $K_{HDPE/W}$ , can also be correlated directly to  $K_{OW}$ . Thus, the  $K_{OW}$  can also be used to predict partitioning of hydrophobic organic compounds to PEX.

Guillot et al.<sup>19</sup> investigated the interactions between water and cross-linked HDPE (PEX) pipes that are subject to regulatory control. They studied the impact of cross-linking HDPE with beta-irradiation at various cross-linking densities. These properties are supposed to have a significant effect on the migration potential of organic chemicals. With regard to the measurement of the migration potential, an organic solvent was used to accelerate the migration process and the quantity of migrating species was evaluated using gas chromatography. They point out that the measurement of the structural characteristics of PEX may provide a useful way to predict the potential migration of organic compounds. In this regard, they used measured the crystallinity of the PEX and evaluated the crosslink density through the gel fraction and through dynamic mechanical analysis in the rubbery state. Their results showed that irradiation increases the degree of cross-linking of PEX, which has the net effect of reducing the potential of migration of organic compounds. They concluded that cross-linking to produce PEX hinders the diffusion of organic compounds through the material.

Brocca et al.<sup>20</sup> investigated the diffusion of organic additives from four polyethylene (PE) materials into drinking water. The structures of the organic chemicals were identified in the water extracts by means of gas chromatography-mass spectrometry analysis. Most of them presented a basic common structure characterized by a phenolic ring typically substituted with hindered alkyl groups in positions 2 and 6 on the aromatic ring. The presence of some of the observed compounds was attributed to impurities or by-products that are typical of the phenolic additives used as antioxidants in pipeline production. Brocca et al. tested water samples from newly installed pipelines in a distribution system and identified three of the compounds in the exposed drinking water: 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde, 3,5-di-*tert*-butyl-4-hydroxy acetophenone, and cyclo-hexa-1,4 dien-1,5-bis (tert-butyl)-6-on-4-(2-carboxy-ethylidene). They identified the following chemical components leached into water from laboratory samples of PE:



- (I) 4-ethyl phenol (P)  
 (II) 4-*tert*-butyl phenol (P)  
 (III) 2,6-di-*tert*-butyl-p-benzoquinone (P)  
 (IV) 2,4-di-*tert*-butyl phenol (p)  
 (V) 3,5-di-*tert*-butyl-4-hydroxy styrene (T)  
 (VI) 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde (P)  
 (VII) 3,5-di-*tert*-butyl-4-hydroxy acetophenone (P)  
 (VIII) Cycle hexa 1,4 dien, 1,5-bis (tert-butyl), 6-on-4-(2-carboxyethylidene) (T)  
 (IX) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methyl propanoate (P)  
 (X) 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoic acid (P)

Since normal PE is a much less robust material than PEX, we can predict that the lease of related chemicals as shown above will be substantially less in high quality PEX products.

Gulec et al.<sup>21</sup> carried out a laboratory exposure study to assess the effects of acidic mine drainage (AMD) from metallic mine wastes on the bulk polymer properties of a 1.5-mm-thick HDPE geomembrane. Coupons of the geomembrane were immersed in tanks containing a synthetic AMD maintained at 20, 40 and 60 °C. Two other solutions (acidic water and deionized water at 20, 40, and 60 °C) were also used. Specimens were periodically removed from the tanks and tested to determine whether changes were occurring in the melt flow index (MFI), polymer structure (as determined by Fourier transform infrared spectroscopy, FTIR), and oxidation induction time (OIT). Only modest effects of AMD exposure were observed in the MFI and FTIR tests over the 22-month exposure period. The OIT changed appreciably during exposure,

and followed a first-order (exponential in time) degradation pattern. Greater depletion rates occurred at higher temperatures and in the chemical solutions. An Arrhenius model was used to estimate the antioxidant depletion time for HDPE geomembranes immersed in AMD. They made conservative estimates of the depletion time range from 46 years to 426 years depending on field temperature, initial OIT, and exposure conditions. Since PEX is more stable than conventional HDPE, the projected lifetime for PEX could be longer than the above estimate.

Bertoldo and co-workers<sup>22-24</sup> measured the diffusion coefficient of Irganox 1010 in an array of polymer blends. The diffusion experiments were carried using a stack of several polymer films of 60 - 70  $\mu\text{m}$  thickness under nitrogen atmosphere. The concentration profile of stabilizer in the film was monitored by UV absorbance at 282 nm. The diffusion of Irganox 1010 in each stack can be interpreted by using the Fick's second law. The best fit of the experimental data with Fick's Law allowed for the calculation of the diffusion coefficients D, for these polymers at 40, 70 and 80  $^{\circ}\text{C}$ . The diffusion coefficients<sup>23</sup> ranged from 0.7 to  $115 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  at 40  $^{\circ}\text{C}$  and from 61 to  $1690 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  at 80  $^{\circ}\text{C}$  with activation energies in the range of 105  $\text{kJ mol}^{-1}$ . These measured diffusion coefficients can be used to estimate the migration time of chemical compounds through various polymeric materials.

In their most recent study, Bertoldo et al.<sup>24</sup> investigated the extraction of Irganox 1010 from three polypropylene based polymeric films in water. They found no appreciable levels of Irganox 1010 in the extraction water at any time, however, its known degradation by-products were found by LC/MS analysis in the extraction water. The experimental extraction kinetics from the three polymers were compared with the theoretical curves based on the Fick's diffusion equations solved both for a semi-infinite (degradation reaction faster than extraction) and a finite system (no degradation reaction) and Irganox 1010 was demonstrated to be extracted by water from polypropylene based material faster than predictable only on the basis of the values of its coefficient of diffusion in the polymers and of partition between water and polymer. Since PEX is more stable than polypropylene the loss of Irganox 1010 anti-oxidant from PEX should be even less than observed for polypropylene.

Munier et al.<sup>25</sup> examined over 20 years of experimental data on the durability of cross-linked polyethylene (PEX) extruded pipes for hot water transport. The time to failure was determined against hoop stress and temperature (in the 20 - 120  $^{\circ}\text{C}$  range). The PEX samples (16 distinct materials) were compared to classical PE (6 distinct materials). It appears that cross-linking suppresses the ductile-brittle transition but does not modify significantly the behavior in ductile regions. It can be assumed that, for PEX, the ceiling conditions are determined by the oxidation embrittlement. Thus, PEX performs better than PE. Based on the cumulative studies, Munier et al. predicted lifetimes of greater than 50 years for PEX pipes at temperatures up to 80  $^{\circ}\text{C}$ .

Mueller and Jakob<sup>26</sup> collected data over 13 years on the oven aging in air and from water immersion tests for 6 years at 80  $^{\circ}\text{C}$  on various high-density polyethylene geomembranes (GM) used in landfill linings. The mechanical properties and oxidative induction times (OIT) of the samples were monitored during the long-term testing. Aging behavior in hot air is different from that in hot water. During oven aging a slow, exponential decrease of OIT is observed. Even after 13.6 years there is no indication of an oxidative degradation of the mechanical properties. During immersion in water a strong reduction in OIT occurs within the first year, after which time the

curve levels off. Oxidation starts when very low OIT-values are reached after about 5 years at which time the mechanical strength rapidly falls to values below the yield point. They concluded that the service life of HDPE GM's is essentially determined by the slow loss of stabilizers due to migration. The oxidation starts only after the depletion of antioxidants and then quickly leads to brittleness of the sample. However, no complete oxidative deterioration was observed up to the date of the study. They estimated that under normal ambient conditions many centuries will have to pass before the functional mechanical properties of state-of-the-art stabilized HDPE bulk material will be reduced below acceptable limits by oxidative degradation.

## 2b. Practical Implications and Interpretation

From data presented in the above research investigations, it is clear that organic chemical compounds can partition into HDPE and PEX. The ability to partition into these materials is correlated directly with the octanol-water partition coefficients of the individual organic chemicals. The octanol-water partition coefficient is a relative measure of the hydrophobic nature of the organic compounds. This means that the more hydrophobic a chemical compounds will partition more favorably than those compounds that are highly soluble in water. In spite of a measurable tendency to partition into plastic material, the ability of these compounds is retarded substantially given the low measured diffusion coefficients for selected chemicals.

We can estimate the characteristic time for diffusion of a chemical with a typical PEX diffusion coefficient of  $1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  through walls of a thickness of 5.0 mm ( $5 \times 10^{-3} \text{ m}$ ) as follows:

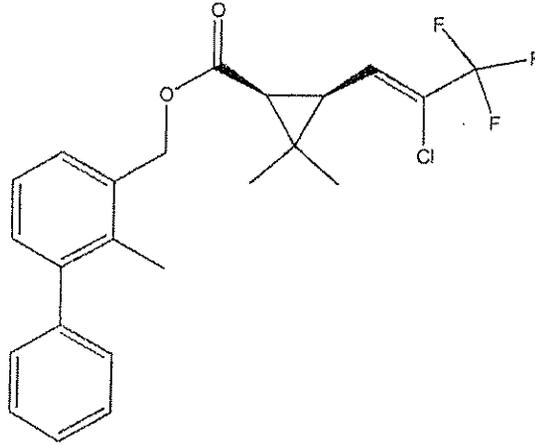
$$\text{Time to Permeate} = \frac{(\text{pipe wall thickness})^2}{\text{diffusion coefficient}}$$

$$t = \frac{X^2}{D} \left( \frac{\text{cm}^2}{\frac{\text{cm}^2}{\text{s}}} \right) = \text{time in seconds}$$

Thus, for a PEX pipe wall thickness of 0.5 cm (5 mm) and a typical diffusion coefficient for organic compound migration of  $1.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , the time to permeate through the walls would be  $2.5 \times 10^{11}$  seconds or approximately 8000 years. If the wall thickness were reduced to 2 mm, then the time to permeate completely through the pipe wall would be reduced to 1300 years. Characteristic times for diffusion through PEX pipes of variable wall thickness over a range of possible solid-phase diffusion coefficients are given in Table 1 below.

In Table 2, we list a representative group of termiticides that are used to control termites in soils along with some of their physicochemical properties. The group includes Bifenthrin Chlorpyrifos, Cypermethrin, Fenvalerate, Imidachoprid, and Permethrin. For example, Bifenthrin with a molecular weight of greater than 400 Daltons would be expected to diffuse through PEX with a diffusion coefficient in the range of  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ . With this estimate, we would predicted based on the range of conditions presented in Table 1, that the characteristic time for diffusion through a PEX pipe with a wall thickness of 0.2 mm would be greater than

2800 years, while the observed half-life for degradation of Bifenthrin in soil is 1328 days. Thus, the rate biodegradation in soils would clearly extend the rate of diffusive flux through solid PEX pipe walls, if these pipes were exposed to this particular termiticide or related compounds listed in Table 2.



Termiticide Trade Name: Bifenthrin,  $C_{23}H_{22}ClF_3O_2$  MW = 422.87

IUPAC Chemical Name: [1alpha,3alpha(Z)]-(+/-)-3-(2-Chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid (2-methyl[1,1'-biphenyl]-3-yl)methyl ester

**TRR Statement:**

*"Premature mechanical failure of plastic pipe is both a consumer protection and an environmental issue. It is difficult, disruptive, and expensive to replace a plumbing system that has failed. The failed pipe system leaves a homeowner without water, may physically damage the structure and furnishings, and may create conditions in the walls leading to mold which can produce indoor air quality health impacts. HCD needs to consider the mechanical reliability of the PEX systems that may be used in California. The different cross-linking mechanisms, PEX-A, B, and C, vary in the degree of cross-linking from 40 percent to 90 percent, with corresponding differences in mechanical stability. Although all of the pipe resins may pass ASTM when freshly manufactured, it is possible that different resin systems will react differently to antioxidant depletion and hence behave differently in actual use."*

**MRH Response:**

Gedde and co-workers<sup>11,27-40</sup> have spent more a decade researching the stability and properties of plastic pipes. Their cumulative data coupled with that provided by other researchers can be used to make quantitative estimates as to the stability of PEX and other plastic piping material.

*TRR Statement:*

*"The state cannot rely on the NSF certification process to assure the protection of public health because: 1) NSF disclaims responsibility and specifically disallows governmental reliance on its standards. 2) NSF does not release the results of tests on the materials it certifies. 3) NSF's testing protocols may not be adequate to determine the potential for chemical leaching."*

**MRII Response:**

Approval of an independent testing agency such as NSF, International that is consistent with the copious data available in the open scientific literature should allow a California State Agency to make a reliable assessment of suitability of a material for use in specific applications.

Virtually all plastic materials exude or leach various chemical components, constituents and breakdown products into standing water, food, milk, and other food products stored in plastic containers. In all known cases, the levels of chemical compounds released are far below threshold values for environmental and human health safety.

As mentioned above, conventional plastic water bottles made from PET (polyethyleneterephthalate) release an array of chemical compounds into water and other liquids upon long-term exposure. Therefore, we question the motivation of Mr. Reid concerning the possible use of PEX pipes in California when related plastic materials containing the very same chemical additives are in widespread usage to store drinking water that is routinely consumed by a large fraction of the California population.

In addition to chemical leaching from PET bottles, the leaching of chemical compounds from polycarbonate baby bottles has been investigated. For example, Peterson et al.<sup>41</sup> release of 2-butoxyethyl acetate (2-BEA) from polycarbonate baby bottles. They measured the leaching of 2-BEA into distilled water and 3% acetic acid at 40 °C for 10 days and they found actual migration of 2-BEA was found from eight of 12 bottles. However, migration above the EU health-safety threshold of 0.33 mg kg<sup>-1</sup> was not observed in the third sequential test from any of the 12 different brands of polycarbonate feeding bottles. A leaching level ranging from 0.05 to 0.26 mg kg<sup>-1</sup> from seven of 12 bottles was measured to 3% acetic acid in the third test, whereas no migration to distilled water was observed in the third test. The Danish Veterinary and Food Administration (DVFA) has assessed that a migration above 0.33 mg kg<sup>-1</sup> for 2-BEA from plastics articles used exclusively for infants is unacceptable. Thus, if polycarbonate bottles are considered to be safe, then high quality PEX should be given a similar consideration with respect to safety.

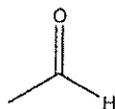
Loyo-Rosales et al.<sup>42</sup> noted that nonylphenol (NP) is used as an antioxidant and plasticizer in some plastic products. There is growing concern over potential human exposure to NP because of its endocrine-disrupting potential. The estimated the average daily intake of NP from food is 7.5 µg/day, excluding water. Loyo Rosales et al. measured NP, octylphenol (OP), and their respective ethoxylates in spring water bottled in three different types of plastic (HDPE, PET, and

PVC). NP was found in water from HDPE and PVC containers, at 180 and 300 ng/L (ppt levels), which represent 4.8% and 8% of the estimated daily input assuming a consumption of 2 L of water per day. OP was found in water from HDPE extracts in lower amounts, 12 ng/L, and neither the NP- nor the OP-ethoxylates were detected in any of the samples. The migration of NP from HDPE containers to milk surrogate is similar to that observed for bottled water. Since PEX is substantially more stable and chemically-resistant than HDPE and PET, we would expect to see ppt levels of leachates released to water stored under similar conditions.

Franz et al.<sup>43</sup> investigated the contamination and the frequency of misuse of poly(ethylene terephthalate) (PET) bottles. In order to establish average levels of contaminants in PET source materials for recycling, Franz et al. collected PET flakes from commercial washing plants (689 samples), reprocessed pellets (38) and super-clean pellets (217) obtained from 12 European countries between 1997 and 2001. They analyzed these materials by headspace gas chromatography and showed average and maximum levels in PCR PET of 18.6 and 86.0 mg kg<sup>-1</sup> for acetaldehyde and 2.9 and 20 mg kg<sup>-1</sup> for limonene, respectively. Acetaldehyde and limonene are typical compounds derived from PET itself and from prior PET bottle contents (flavouring components), respectively. Given the cleaning efficiency of super-clean processes as well as migration from the bottle wall into food, Franz et al. concluded 1) that consumers will be exposed to maximum to levels of contaminants of less than 50 ng day<sup>-1</sup> and 2) that recycled PET materials and articles produced by super-clean technologies can be considered to be safe in direct food applications in the same way as virgin food-grade PET. Once again, since PEX has greater overall stability than PET we anticipate that the daily exposure to contaminant levels will be in the rate of ng per day per person.

Freire et al.<sup>44</sup> investigated the fate of PET (polyethylene terephthalate) samples under severe heating conditions in order to estimate the flux of oligomers and volatile substances as potential migrants into foods. The treated samples were tested for migration into water, 3% acetic acid and 15% ethanol solutions for 1 hour at 95 °C. Overall migration and the specific migration of terephthalic acid, ethylene glycol, and diethylene glycol were found to be very low.

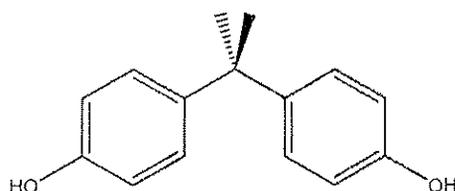
Bashir et al.<sup>45</sup> noted that acetaldehyde (AA), which is the principle metabolite of ethanol in humans and the primary source of the "hangover," is a primary degradation byproduct of PET when PET pellets are melted or extruded to form bottles. The maximum value of AA allowed in drinking water is 3 ppm (3 mg L<sup>-1</sup>). Bashir et al. found major differences in the performance of various commercial PET resins in terms of the potential release of AA to bottled water. Likewise, there may be a variation in the source material used to produce PEX pipe that may result in different leaching and degradation rates.



Acetaldehyde, C<sub>2</sub>H<sub>4</sub>O

The major concern with polycarbonate bottles appears to be that a compound known as bisphenol-A<sup>2,4-6,46-49</sup> or 2,2-bis(4-Hydroxyphenyl)propane is released from the plastic to water.

Brede et al.<sup>5</sup> subjected polycarbonate baby bottles to simulated use by dishwashing, boiling and brushing in order to determine the potential migration of bisphenol A. Their testing, which was performed with both new and used bottles, showed a significant increase in migration of bisphenol A due to continued use of the bottles. Brede et al. argued that bisphenol A was produced from the polycarbonate polymer degradation. They tested 12 different polycarbonate baby bottles by filling them with hot water (100 °C) for 1 h. The mean bisphenol A level in water from new bottles was 0.23 µg L<sup>-1</sup>, while the mean levels released from bottles subjected to simulated use were 8.4 µg L<sup>-1</sup> (they had been dishwashed 51 times) and 6.7 µg L<sup>-1</sup> (dishwashed 169 times), respectively. However, none of the bottles released bisphenol A at levels that exceed the established tolerable daily intake level (0.01 mg kg<sup>-1</sup> of body weight per day) in the European Union. Since polycarbonate bottles are widely accepted and used most often to feed the most sensitive group of individuals, there should be similar considerations given to PEX when produced properly.

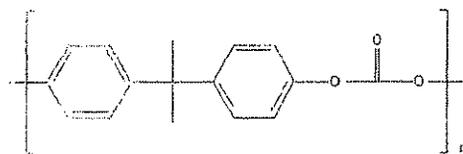


**Bisphenol A - C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>**

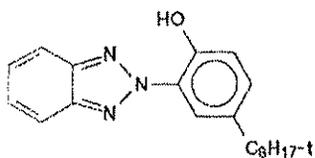
As noted earlier, Nerin et al.<sup>2</sup> identified phenol, bisphenol A, 2,4-di-tert-butylphenol, Cyasorb UV5411, bis(2-ethylhexylphthalate), Irganox 1076, and Irgafos 168 in leachates of polycarbonate bottles under a extreme and worst case scenario obtain by microwave heating with organic solvents. Nonetheless, their experiments indicate that well-accepted plastic materials such as polycarbonates and PET are potential sources for lower molecular weight organic compounds to water and to the environment. Even though compounds can be detected their actual levels are within acceptable ranges. PEX would give similar or better results.

Wong et al.<sup>48</sup> determined the residual bisphenol A (BPA) levels in 28 different brands of polycarbonate (PC) baby bottles that were available in the Singapore market. With a detection limit of 3 mg/kg, BPA residues were detected in 19 out of the 28 PC baby milk bottles at levels between 4 and 141 mg/kg, with a mean of 28.1 and a median of 17.2 mg/kg. The potential migration of BPA from each of the 28 PC milk bottles was also measured using food-simulating solvents and time conditions recommended by the US Food and Drug Administration (US FDA), but using temperatures more severe than actual use. The highest BPA migration levels were found to be 0.64 µg/in<sup>2</sup> in 10% ethanol at 70 °C and 0.43 µg/in<sup>2</sup> in corn oil at 100 °C were observed after incubating cut portions of the milk bottles for 240 h. With this migration data and using US FDA's procedure for estimation of dietary exposure, the worst-case dietary exposure assessment for the intake of BPA by infants between birth and three months of age was below the oral Reference Dose of 0.05 mg/kg of body weight per day established by the US EPA. Wong et al. showed that the dietary exposure to BPA from the actual use of PC milk bottles is unlikely to pose a health risk in infants.

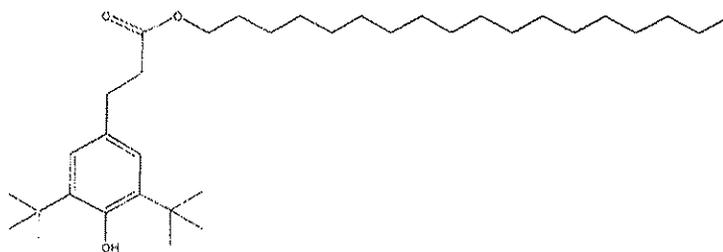
Polycarbonates are made from the reaction of bisphenol A and phosgene gas (COCl<sub>2</sub>). The bisphenol A that is released reflects the small percentage of unreacted monomer.



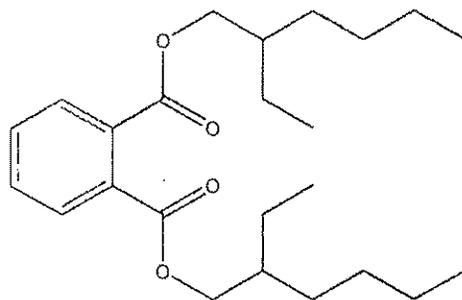
polycarbonate (bisphenol + phosgene)



Cyasorb UV5411, 2-(2'-hydroxy-5'-octylphenyl)-benzotriazole



Irganox 1076, octadecyl 3,5-di-(tert)-butyl-4-hydroxyhydrocinnamate



bis(2-ethylhexylphthalate) or di-sec-octyl phthalate,  $C_{24}H_{38}O_4$

**Conclusions (MRH Analysis):**

1. Under extreme conditions, plastic materials (i.e., HDPE, PET, PC, PEX, PVC, etc.) can release chemical compounds at detectable levels to various solvents including water. However, even at the maximum release rates observed for HDPE, PET, polycarbonate, and PEX plastics there is no evidence of any health or safety risks either to human health or to the health of the environment.
2. PEX and HDPE materials have projected lifetimes (i.e., retain their integrity) of 40 to 100 years or more under normal usage depending to some degree on their thickness. Their suitability for domestic water supplies is enhanced substantially when efficient but safe anti-oxidants are used in PEX formulations.
3. Any migration or diffusion of chemical contaminants found in soils through PEX pipes would require extremely long contact times based on measured diffusion coefficients or detectable penetration to occur into intact pipes, rendering any argument of diffusion of termiticides in soil through PEX pipes moot.
4. The quantity of PEX pipe in totality, now and in the future, will have a negligible long-term impact on the environment, especially in light of the wide variety of other plastic materials currently in production and in use in vastly larger quantities.

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Table 1. Predicted characteristic times for molecular diffusion through PEX Pipes with variable wall thickness from 0.2 to 0.5 cm and variable solid-phase diffusion coefficients that range from  $10^{-9}$  to  $10^{-15}$   $\text{cm}^2 \text{s}^{-1}$ .

D ( $\text{cm}^2 \text{s}^{-1}$ )	X (cm)	X <sup>2</sup>	secs	days	years
1.00E-15	0.5	0.25	2.50E+14	2893518519	7927448
1.00E-14	0.5	0.25	2.50E+13	289351852	792745
1.00E-13	0.5	0.25	2.50E+12	28935185	79274
1.00E-12	0.5	0.25	2.50E+11	2893519	7927
1.00E-11	0.5	0.25	2.50E+10	289352	793
1.00E-10	0.5	0.25	2.50E+09	28935	79
1.00E-09	0.5	0.25	2.50E+08	2894	8
1.00E-15	0.4	0.16	1.60E+14	1851851852	5073567
1.00E-14	0.4	0.16	1.60E+13	185185185	507357
1.00E-13	0.4	0.16	1.60E+12	18518519	50736
1.00E-12	0.4	0.16	1.60E+11	1851852	5074
1.00E-11	0.4	0.16	1.60E+10	185185	507
1.00E-10	0.4	0.16	1.60E+09	18519	51
1.00E-09	0.4	0.16	1.60E+08	1852	5
1.00E-15	0.3	0.09	9.00E+13	1041666667	2853881
1.00E-14	0.3	0.09	9.00E+12	104166667	285388
1.00E-13	0.3	0.09	9.00E+11	10416667	28539
1.00E-12	0.3	0.09	9.00E+10	1041667	2854
1.00E-11	0.3	0.09	9.00E+09	104167	285
1.00E-10	0.3	0.09	9.00E+08	10417	29
1.00E-09	0.3	0.09	9.00E+07	1042	3
1.00E-15	0.2	0.04	4.00E+13	462962963	1268392
1.00E-14	0.2	0.04	4.00E+12	46296296	126839
1.00E-13	0.2	0.04	4.00E+11	4629630	12684
1.00E-12	0.2	0.04	4.00E+10	462963	1268
1.00E-11	0.2	0.04	4.00E+09	46296	127
1.00E-10	0.2	0.04	4.00E+08	4630	13
1.00E-09	0.2	0.04	4.00E+07	463	1

Table 2. Representative soil termiticides and some of their physicochemical properties and degradation lifetimes in soil.

Termiticides	Solubility $\mu\text{g L}^{-1}$ (ppb)	Log K <sub>ow</sub>	k <sub>bio</sub> (day <sup>-1</sup> ) soils	Degradation Half-Life (days)
Bifenthrin	0.014	6.4	0.00052	1332
Chlorpyrifos	1120	5.0	0.0022	315
Cypermethrin	4.0	6.5	0.011	63
Fenvalerate	24	6.2	0.012	60
Imidachoprid	610,000	0.57	0.0007	990
Permethrin	5.5	6.1	0.033	21

Respectively submitted by Prof. Michael R. Hoffmann on 29 July 2005.

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- Lady Davis Distinguished Lecturer - Hebrew University - Jerusalem (1996)
- Fellow of the International Union of Pure and Applied Chemistry (2000)
- ACS Creative Advances in Environmental Science and Technology Award (2001)
- Davis Distinguished Lecturer – University of New Orleans (2001)
- Dodge Distinguished Lecturer – Yale University (2002)
- Johnston Distinguished Lecturer – UC – Berkeley (2003)
- Gordon Distinguished Lecturer – University of Toronto (2003)
- Jack E. McKee Award & Medal (2003)

### *Biosketch*

Michael Hoffmann was born in Fond du Lac, Wisconsin in 1946. He received a BA degree in chemistry in 1968 from Northwestern University, a PhD degree from Brown University in 1974, and post-doctoral training in Environmental Engineering at the California Institute of Technology from 1973 to 1975. Prof. Hoffmann has served as a Professor of Environmental Engineering and Environmental Chemistry since 1975. From 1975 to 1980, he was member of the faculty At the University of Minnesota and since 1980 a member of the faculty At Caltech (Engineering & Applied Science). Dr. Hoffmann has published more than 220 peer-reviewed professional papers and is the holder of 7 patents in the subject areas of applied chemical kinetics, aquatic chemistry, atmospheric chemistry, environmental chemistry, catalytic oxidation, heterogeneous photochemistry, sonochemistry, electrochemistry, and pulsed-plasma chemistry. Prof. Hoffmann has served as the Chairman of the Gordon Research Conference, Environmental Sciences: Water and as an Associate Editor of the Journal of Geophysical Research. He is currently on the Editorial Boards of Environmental Science and Technology and the Journal of Physical Chemistry. He also serves on the Scientific Advisory Board of the Max Planck Institute for Chemistry. In 1991, Prof. Hoffmann received the Alexander von Humboldt Prize for his research and teaching in environmental chemistry. In 1995, he was presented with the E. Gordon Young Award by the Chemical Society of Canada in recognition of his work in the field of environmental chemistry. In 2001, Prof. Hoffmann was presented with the American Chemical Society Award for Creative Advances in Environmental Science and Technology for "his fundamental and lasting contributions to the science of aquatic chemistry, to the development of aquatic remediation processes, and to understanding heterogeneous and multiphase processes in the atmospheric environment." Prof. Hoffmann has been honored recently As "Davis Memorial Lecturer" at the University of New Orleans, "Dodge Distinguished Lecturer" in Chemical Engineering at Yale University, the "Johnston Distinguished Lecturer in Chemistry at UC-Berkeley, and the "Gordon Distinguished Lecturer in Chemistry At the University of Toronto." He has also served as a Distinguished Lecturer at the Hebrew University (Jerusalem), the University of Sao Paulo (Brazil), and the University of Buenos Aires. In October 2003, Prof. Hoffmann received the Jack E. McKee Award Medal for his work in environmental remediation technology. Many of his former graduate students and post-doctoral fellows are now professorial faculty members at major universities around the USA and also abroad.

### *Administrative Experience – Short List*

Dean of Graduate Studies, 2002 -  
Executive Officer (i.e., Department Chair), 1996 – 2002  
Chair of *Ad Hoc* Committee on Parking, Caltech, 2001  
Graduate Option Representative, 1999 – 2001  
Commissioner (Faculty Chair), SCIAC Athletic Conference 1998-2000  
Graduate Admissions Officer, 1990 – 1998  
Faculty Chair of Undergraduate Admissions, 1986 - 1988

### *Representative Publications*

Prof. Hoffmann has published more than 230 scientific articles in the field of environmental chemistry and environmental technology. Professor Hoffmann has been recognized by ISI Web of Science & Citation Indices as one of the most Highly Cited Researchers in Engineering in the world (<http://isihighlycited.com/>).

#### ***Representative Publications in Environmental Photochemistry:***

Bahnemann D. W., Hoffmann M. R., Hong A. P., and Kormann C. (1987) Photocatalytic Formation of Hydrogen Peroxide. *ACS Symposium Series* **349**, 120-132.

Bahnemann D. W., Kormann C., and Hoffmann M. R. (1987) Preparation and Characterization of Quantum Size Zinc-Oxide - A Detailed Spectroscopic Study. *Journal of Physical Chemistry* **91**, 3789-3798.

Carraway E. R., Hoffman A. J., and Hoffmann M. R. (1994) Photocatalytic Oxidation of Organic-Acids on Quantum-Sized Semiconductor Colloids. *Environmental Science & Technology* **28**, 786-793.

Choi W. Y. and Hoffmann M. R. (1995) Photoreductive Mechanism of  $\text{CCl}_4$  Degradation on  $\text{TiO}_2$  Particles and Effects of Electron-Donors. *Environmental Science & Technology* **29**, 1646-1654.

Choi W. Y. and Hoffmann M. R. (1996) Kinetics and mechanism of  $\text{CCl}_4$  photoreductive degradation on  $\text{TiO}_2$ : The role of trichloromethyl radical and dichlorocarbene. *Journal of Physical Chemistry* **100**, 2161-2169.

Choi W. Y. and Hoffmann M. R. (1997) Novel photocatalytic mechanisms for  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ , and  $\text{CCl}_3\text{CO}_2^-$  degradation and the fate of photogenerated trihalomethyl radicals on  $\text{TiO}_2$ . *Environmental Science & Technology* **31**, 89-95.

Choi W. Y., Termin A., and Hoffmann M. R. (1994) Effects of Metal-Ion Dopants on the Photocatalytic Reactivity of Quantum-Sized TiO<sub>2</sub> Particles. *Angewandte Chemie-International Edition in English* **33**, 1091-1092.

Choi W. Y., Termin A., and Hoffmann M. R. (1994) The Role of Metal-Ion Dopants in Quantum-Sized TiO<sub>2</sub> - Correlation between Photoreactivity And Charge-Carrier Recombination Dynamics. *Journal of Physical Chemistry* **98**, 13669-13679.

Cornu C. J. G., Colussi A. J., and Hoffmann M. R. (2001) Quantum yields of the photocatalytic oxidation of formate in aqueous TiO<sub>2</sub> suspensions under continuous and periodic illumination. *Journal of Physical Chemistry B* **105**, 1351-1354.

Cornu C. J. G., Colussi A. J., and Hoffmann M. R. (2003) Time scales and pH dependences of the redox processes determining the photocatalytic efficiency of TiO<sub>2</sub> nanoparticles from periodic illumination experiments in the stochastic regime. *Journal of Physical Chemistry B* **107**, 3156-3160.

Faust B. C., Hoffmann M. R., and Bahnemann D. W. (1989) Photocatalytic Oxidation of Sulfur-Dioxide in Aqueous Suspensions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. *Journal of Physical Chemistry* **93**, 6371-6381.

Herrmann H., Martin S. T., and Hoffmann M. R. (1995) Time-Resolved Radio-Frequency Conductivity (TRRFC) Studies of Charge-Carrier Dynamics in Aqueous Semiconductor Suspensions. *Journal of Physical Chemistry* **99**, 16641-16645.

Hoffman A. J., Carraway E. R., and Hoffmann M. R. (1994) Photocatalytic Production of H<sub>2</sub>O<sub>2</sub> and Organic Peroxides on Quantum-Sized Semiconductor Colloids. *Environmental Science & Technology* **28**, 776-785.

Hoffman A. J., Mills G., Yee H., and Hoffmann M. R. (1992) Q-Sized CdS - Synthesis, Characterization, and Efficiency of Photoinitiation of Polymerization of Several Vinyllic Monomers. *Journal of Physical Chemistry* **96**, 5546-5552.

Hoffman A. J., Yee H., Mills G., and Hoffmann M. R. (1992) Photoinitiated Polymerization of Methyl Methacrylate Using Q- Sized ZnO Colloids. *Journal of Physical Chemistry* **96**, 5540-5546.

Hoffmann M. R., Martin S. T., Choi W. Y., and Bahnemann D. W. (1995) Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews* **95**, 69-96.

Hong A. P., Bahnemann D. W., and Hoffmann M. R. (1987) Cobalt(II) Tetrasulfophthalocyanine on Titanium-Dioxide - a New Efficient Electron Relay for the Photocatalytic Formation and Depletion of Hydrogen-Peroxide in Aqueous Suspensions. *Journal of Physical Chemistry* **91**, 2109-2117.

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Kesselman J. M., Lewis N. S., and Hoffmann M. R. (1997) Photoelectrochemical degradation of 4-chlorocatechol at TiO<sub>2</sub> electrodes: Comparison between sorption and photoreactivity. *Environmental Science & Technology* **31**, 2298-2302.

Kesselman J. M., Shreve G. A., Hoffmann M. R., and Lewis N. S. (1994) Flux-Matching Conditions at TiO<sub>2</sub> Photoelectrodes - Is Interfacial Electron-Transfer to O<sub>2</sub> Rate-Limiting in the TiO<sub>2</sub>-Catalyzed Photochemical Degradation of Organics. *Journal of Physical Chemistry* **98**, 13385-13395.

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Kormann C., Bahnemann D. W., and Hoffmann M. R. (1988) Photocatalytic Production of H<sub>2</sub>O<sub>2</sub> and Organic Peroxides in Aqueous Suspensions of TiO<sub>2</sub>, ZnO, and Desert Sand. *Environmental Science & Technology* **22**, 798-806.

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Martin S. T., Herrmann H., Choi W. Y., and Hoffmann M. R. (1994) Time-Resolved Microwave Conductivity .1. TiO<sub>2</sub> Photoreactivity And Size Quantization. *Journal of the Chemical Society-Faraday Transactions* **90**, 3315-3322.

Martin S. T., Herrmann H., and Hoffmann M. R. (1994) Time-Resolved Microwave Conductivity .2. Quantum-Sized TiO<sub>2</sub> and the Effect of Adsorbates and Light-Intensity on Charge-Carrier Dynamics. *Journal of the Chemical Society-Faraday Transactions* **90**, 3323-3330.

- Martin S. T., Kesselman J. M., Park D. S., Lewis N. S., and Hoffmann M. R. (1996) Surface structures of 4-chlorocatechol adsorbed on titanium dioxide. *Environmental Science & Technology* **30**, 2535-2542.
- Martin S. T., Lee A. T., and Hoffmann M. R. (1995) Chemical Mechanism of Inorganic Oxidants in the TiO<sub>2</sub>/Uv Process - Increased Rates of Degradation of Chlorinated Hydrocarbons. *Environmental Science & Technology* **29**, 2567-2573.
- Martin S. T., Morrison C. L., and Hoffmann M. R. (1994) Photochemical Mechanism of Size-Quantized Vanadium-Doped TiO<sub>2</sub> Particles. *Journal of Physical Chemistry* **98**, 13695-13704.
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- Peill N. J., Bourne L., and Hoffmann M. R. (1997) Iron(III)-doped Q-sized TiO<sub>2</sub> coatings in a fiber-optic cable photochemical reactor. *Journal of Photochemistry and Photobiology A-Chemistry* **108**, 221-228.
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Betterton E. A., Erel Y., and Hoffmann M. R. (1988) Aldehyde-Bisulfite Adducts - Prediction of Some of Their Thermodynamic and Kinetic-Properties. *Environmental Science & Technology* **22**, 92-99.

Betterton E. A. and Hoffmann M. R. (1987) Kinetics, Mechanism, and Thermodynamics of the Reversible- Reaction of Methylglyoxal ( $\text{CH}_3\text{COCHO}$ ) with S(IV). *Journal of Physical Chemistry* **91**, 3011-3020.

Betterton E. A. and Hoffmann M. R. (1988) Henry Law Constants of Some Environmentally Important Aldehydes. *Environmental Science & Technology* **22**, 1415-1418.

Betterton E. A. and Hoffmann M. R. (1988) Oxidation of Aqueous  $\text{SO}_2$  by Peroxymonosulfate. *Journal of Physical Chemistry* **92**, 5962-5965.

Boyce S. D. and Hoffmann M. R. (1984) Kinetics and Mechanism of the Formation of Hydroxymethanesulfonic Acid at Low pH. *Journal of Physical Chemistry* **88**, 4740-4746.

Boyce S. D., Hoffmann M. R., Hong P. A., and Moberly L. M. (1983) Catalysis of the Autoxidation of Aqueous Sulfur-Dioxide by Homogeneous Metal Phthalocyanine Complexes. *Environmental Science & Technology* **17**, 602-611.

Collett J., Daube B., Munger J. W., and Hoffmann M. R. (1989) Cloudwater Chemistry in Sequoia National Park. *Atmospheric Environment* **23**, 999-1007.

Collett J. L., Daube B. C., Gunz D., and Hoffmann M. R. (1990) Intensive Studies of Sierra-Nevada Cloudwater Chemistry And Its Relationship to Precursor Aerosol and Gas Concentrations. *Atmospheric Environment Part a-General Topics* **24**, 1741-1757.

Collett J. L., Daube B. C., and Hoffmann M. R. (1990) The Chemical-Composition of Intercepted Cloudwater in the Sierra-Nevada. *Atmospheric Environment Part a-General Topics* **24**, 959-972.

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Colussi A. J. and Hoffmann M. R. (2003) In situ photolysis of deep ice core contaminants by Cerenkov radiation of cosmic origin. *Geophysical Research Letters* **30**, art. no.-1195.

Conklin M. H. and Hoffmann M. R. (1988) Metal-Ion Sulfur(IV) Chemistry .1. Structure and Thermodynamics of Transient Copper(II)-Sulfur(IV) Complexes. *Environmental Science & Technology* **22**, 883-891.

Conklin M. H. and Hoffmann M. R. (1988) Metal-Ion Sulfur(IV) Chemistry .2. Kinetic-Studies of the Redox Chemistry of Copper(II) Sulfur(IV) Complexes. *Environmental Science & Technology* **22**, 891-898.

Conklin M. H. and Hoffmann M. R. (1988) Metal-Ion Sulfur(IV) Chemistry .3. Thermodynamics and Kinetics of Transient Iron(III) Sulfur(IV) Complexes. *Environmental Science & Technology* **22**, 899-907.

Dubowski Y., Colussi A. J., Boxe C., and Hoffmann M. R. (2002) Monotonic increase of nitrite yields in the photolysis of nitrate in ice and water between 238 and 294 K. *Journal of Physical Chemistry A* **106**, 6967-6971.

Dubowski Y., Colussi A. J., and Hoffmann M. R. (2001) Nitrogen dioxide release in the 302 nm band photolysis of spray-frozen aqueous nitrate solutions. Atmospheric implications. *Journal of Physical Chemistry A* **105**, 4928-4932.

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Erel Y., Pehkonen S. O., and Hoffmann M. R. (1993) Redox Chemistry of Iron in Fog and Stratus Clouds. *Journal of Geophysical Research-Atmospheres* **98**, 18423-18434.

Faust B. C. and Hoffmann M. R. (1986) Photoinduced Reductive Dissolution of Alpha-Fe<sub>2</sub>O<sub>3</sub> by Bisulfite. *Environmental Science & Technology* **20**, 943-948.

- Faust B. C., Hoffmann M. R., and Bahnemann D. W. (1989) Photocatalytic Oxidation of Sulfur-Dioxide in Aqueous Suspensions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. *Journal of Physical Chemistry* **93**, 6371-6381.
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- Gunz D. W. and Hoffmann M. R. (1990) Field Investigations on the Snow Chemistry in Central and Southern California .2. Carbonyls and Carboxylic-Acids. *Atmospheric Environment Part a-General Topics* **24**, 1673-1684.
- Hoffman A. J., Carraway E. R., and Hoffmann M. R. (1994) Photocatalytic Production of H<sub>2</sub>O<sub>2</sub> and Organic Peroxides on Quantum-Sized Semiconductor Colloids. *Environmental Science & Technology* **28**, 776-785.
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### **Overview of Past Research Accomplishments**

The past research accomplishments of Michael Hoffmann are in the topical areas of 1) heterogeneous atmospheric chemistry, and 2) pollution control chemistry and technology, and 3) environmental photochemistry. His research activities have involved both field and laboratory experimentation.

In the subject area of heterogeneous atmospheric chemistry (e.g., clouds, fogs, and haze aerosol), Hoffmann and his group made significant advances in the determination of the detailed kinetics and mechanisms of the reactions of dissolved sulfur dioxide with hydrogen peroxide, oxygen, and ozone, in advancement of our knowledge of the detailed thermodynamics, kinetics and mechanisms of the equilibrium formation of hydroxyalkylsulfonates from the reaction of dissolved sulfur dioxide with dissolved aldehydes (i.e., aldehyde-bisulfite complexes, in determination of the detailed chemistry of clouds and fogs in coastal and mountainous environments, in determination of the role of aqueous-phase photochemistry in relation to the *in situ* production of hydrogen peroxide, hydroperoxyl radical, and hydroxyl radical in illuminated clouds, and in the field-based determination of the redox states of dissolved metal ions (e.g., Fe(II) vs. Fe(III) and Cu(I) vs. Cu(II)) in clouds, fogs, and haze aerosol.

In the subject area of pollution control chemistry And technology, Hoffmann and his group made significant advances in our understanding of *a)* the basic chemistry And applications of homogeneous and heterogeneous catalysis involving metal-phthalocyanine complexes, *b)* in the chemistry And application of hydrogen peroxide for the oxidative elimination of hydrogen sulfide and other reduced sulfur compounds in water and wastewater, *c)* in the chemistry And application of quantum-sized semiconductor colloids for the oxidative and reductive elimination of chlorinated hydrocarbons and other contaminants from hazardous waste streams, *d)* in the examination of the underlying chemistry And physics of the application of ultrasonic irradiation in water for the destruction of chemical contaminants, *e)* for the development and advancement of the pulsed-power plasma process for the direct *in situ* destruction of hazardous wastes dissolved in water, *f)* for the development and advancement of metal-doped semiconductor electrodes for the electrochemical production of hydroxyl radical from water, *g)* for the development and characterization of semiconductor-coated fiber optic cable reactors for the heterogeneous photochemical destruction of chemical contaminants in water, and for *h)* the application of photochemically-activated periodate solutions for chemical compound oxidation.

In the subject area of environmental chemistry And photochemistry, Hoffmann and his research group focused their efforts on metal-ligand chemistry relevant to fresh waters, on the chemistry of aquatic humic substances and their interactions with first-

row transition metal ions, on the photochemistry of iron oxides and oxyhydroxides in the presence of naturally-occurring organic compounds, on the photochemistry of molecules trapped in ice and on snow, on the kinetics and mechanisms of redox reactions involving oxidants such as oxygen, hydrogen peroxide, peroxydisulfate, peroxydiphosphate, ozone, periodate, and hydroxyl radical, and on the kinetics and mechanisms of selected microbial processes involving the oxidation of reduced sulfur compounds, the oxidation of ferrous iron, and the reduction of ferric iron.

### ***Specific Examples of Research Accomplishments and Advancements***

Some of the noteworthy creative advancements in environmental science and technology originating from the Hoffmann group will be highlighted in the several paragraphs emphasizing contributions in heterogeneous atmospheric chemistry, in pollution control chemistry and technology, and environmental photochemistry.

Hoffmann's detailed investigations of the kinetics and mechanism of the oxidation of dissolved sulfur dioxide in the form of bisulfite by hydrogen peroxide in acidic aqueous solution (Hoffmann and Edwards, 1975; mcardle and Hoffmann, 1983) established the state-of-the-art for our understanding of important pathways for the oxidation of sulfur dioxide to sulfuric acid in the atmosphere. This fundamental reaction is now recognized as the single most important pathway for the conversion of sulfur dioxide to sulfuric acid on a global basis. As much as 80% of the total sulfur dioxide on a global basis is oxidized via the cloud-processing pathway originally proposed by Hoffmann and Edwards (1975). The reaction mechanism involves the nucleophilic addition of hydrogen peroxide to the bisulfite ion to form a peroxymonosulfite intermediate, which, in turn, undergoes a proton-catalyzed rearrangement to give bisulfate as the final product. This mechanism has been formally named the "Hoffmann and Edwards' Mechanism." In a subsequent study, mcardle and Hoffmann (1983) extended the pH range of the initial study to very low pH values and confirmed an important prediction of the Hoffmann and Edwards' mechanism that the principal reactive species was bisulfite over the pH range of 0 to 8. Many other investigators over the next 10 years reexamined the kinetics of this reaction only to confirm the validity of the Hoffmann and Edwards' mechanism over a broad range of conditions relevant to atmospheric conditions.

The next major advancement by Hoffmann and his group involved a detailed field-oriented study of the chemistry of clouds and fogs. The primary focus of these studies was to obtain solid field-based observations of dynamic chemical changes within liquid water droplets and to very predictions of chemical kinetic models (e.g., Jacob and Hoffmann, 1983) for cloudwater acidification. In this regard, Hoffmann and co-workers developed several patented (US Patent Numbers 4,697,462 and 4,732,037) devices for the automatic time-series collection of cloud and fog water from ground-based sampling stations. In 1982, they published a seminal paper (Waldman et al., 1982) in *Science* entitled "The Chemical Composition of Acid Fogs," in which they determined the detailed chemical composition of hyperacidic clouds and fogs. Hoffmann and his

students measured pH values below 1.7 in coastal marine clouds and fogs. The occurrence of such highly Acidic clouds and fogs was not predicted. In later reports, Hoffmann and his group extended these early studies to a variety of different locations in California (Munger et al., 1983; Jacob et al., 1985; Jacob et al., 1986) and around the country.

During the course of their field studies, Hoffmann and his students discovered that many cloud systems in near urban environments were enriched in dissolved sulfur dioxide (i.e., S(IV)) and aldehydes such as formaldehyde, methyl glyoxal, glyoxal, and hydroxyacetaldehyde. Based on their initial observations they (Boyce and Hoffmann, 1984; Munger et al., 1984; Munger et al., 1986; Olson and Hoffmann, 1989) proposed that bisulfite and the aldehydes react in situ within cloud droplets via a classical reaction to form reversibly Aldehyde-bisulfite adducts or hydroxyalkylsulfonates as reservoir species for S(IV). A short time later, Hoffmann and his group a new analytical methods that allowed for the direct chromatographic determination of the hydroxyalkylsulfonates in ambient samples. They reported their discovery of the actual occurrence and quantification of these compounds in Science (Munger et al., 1986). In the laboratory, they studied the detailed thermodynamics (Betterton and Hoffmann, 1988), kinetics, and mechanisms of formation of a wide-range of hydroxyalkylsulfonates (e.g., Olson and Hoffmann, 1988ab; Olson et al., 1988).

Later work in the area of cloud and fog chemistry was focused on the detailed chemical speciation and photochemistry of iron-containing solids (e.g., Fe<sub>2</sub>O<sub>3</sub>, FeOOH, Fe(OH)<sub>3</sub>) present in aquated aerosol systems. Hoffmann and his co-workers were able to show that a substantial fraction of the total iron present in aerosols and clouds is found in the reduced ferrous state and that iron species mediate the in situ production of hydrogen peroxide and hydroxyl radical with the concomitant oxidation of organic compounds and sulfur dioxide (e.g., Faust et al., 1989; Erel et al., 1993; Pehkonen et al., 1993).

In the field of pollution control chemistry, Hoffmann (1977) investigated the detailed kinetics and mechanism of the oxidation of hydrogen sulfide by hydrogen peroxide over a broad pH range and proposed that this reaction could be used to conveniently control H<sub>2</sub>S in water and wastewater systems. Today this simple chemical system is widely used to control the odor, corrosion, and toxicity problems posed by H<sub>2</sub>S in engineered systems. In the next major advance, Hoffmann and his students (Hoffmann and Lim, 1979; Boyce et al., 1983; Hong and Hoffmann, 1987ab, Leung and Hoffmann, 1989ab) synthesized a series of metal phthalocyanine complexes that were highly effective homogeneous catalysts of the oxidation of hydrogen sulfide in water by molecular oxygen, which is a slow reaction in the absence of any catalytic influences. These catalytic systems were then extended to active (Hong et al., 1987ab) and passive (Hong et al., 1989) porous support systems that could be used in industrial-scale catalytic reactors.

Over the same period of time, Hoffmann and his students (Kormann et al., 1988; Bahnemann, et al., 1987; Hong et al., 1987ab; Choi et al., 1994; Martin et al., 1994abc)

carried out a detailed series of investigations in the photochemistry And photophysics of colloidal metal oxide semiconductor systems that could be used for the effective elimination of chemical contaminants from water or for the *in situ* production of hydrogen peroxide. For example, Hoffmann and colleagues were the first to synthesize nano-sized colloidal zno in the quantum-size domain (i.e., the photochemical characteristic such as the band-gap energy increase with decreasing particle size) and show that as the particle sizes decrease toward 2 nm in diameter the quantum yield for the photoreduction of dioxygen to form hydrogen peroxide approaches unity (Hoffman et al., 1994). This research also led to the development of hybrid photocatalytic systems involving the chemical coupling of Co(II)tetrakisulfophthalocyanine catalysts to the surface of TiO2 to produce an unusually high reactivity photocatalyst (Hong et al., 1987ab). In the case of the photooxidation of SO2 by oxygen, the measured quantum yield in the presence of the hybrid photocatalyst was greater than 1000, which indicated that the reaction proceeded via the photolytic induction of a free-radical chain reaction on the surface of the functionalized titanium dioxide (Hong et al., 1987b).

Research in the area of metal-doping of the quantum-size semiconductor photocatalysts led directly to the successful development of niobium (V)-doped TiO2-coated titanium anodes for the direct electrochemical production of hydroxyl radical from the oxidation of hydroxide ion and water with current efficiencies approaching 98%. This novel electrochemical system (Kesselman et al., 1997) led to the granting of 3 patents (Weres and Hoffmann, U.S. Patents 5,364,508, 5,419,824; and 5,439,577) and to direct commercialization of the electrochemical reactor system for water and wastewater treatment applications. Several Fortune 500 companies such as the Eaton Corporation are using these commercially-available treatment systems in large-scale applications.

Further advances in the application of semiconductor photocatalysis by the Hoffmann group; include the development of TiO2-coated fiber optic cable reactors for heterogeneous photocatalysis (Peill and Hoffmann, 1995; 1996; 1997; 1998). These novel photoreactors employ quartz fiber-optic cables to deliver focused UV or solar irradiation over long-distances to an active reaction zone in which the polymeric coating of the fiber optic cables has been replaced by TiO2 or metal-doped TiO2 coating. Once the propagated light reaches the semiconductor coating the UV light is refracted out of the fiber and into the TiO2 coating, which then leads directly to photoactivation of the catalyst. This invention has also led to the formal approval of another US Patent (Serial Number 08/654,093)). These reactors can be used, for example, for the *in situ* photocatalytic treatment of contaminated groundwater or for the photocatalytic treatment of contaminated air streams from industrial sites. At present, this technology is being explored by the Northrop-Grumman Corporation for chemical and biowarfare agent control.

Hoffmann and his group explored the application of several forms of electrohydraulic cavitation for the elimination of hazardous chemical compounds from water. They Advanced the general understanding of the chemistry And physics of ultrasonic irradiation in water and advocated its application of the destructive elimination of

chemical contaminants such as carbon tetrachloride, pentachlorophenol, TNT, parathion, triethanolamine, and methyl tertiary-butyl ether from groundwater. Hoffmann and his students demonstrated that electrohydraulic cavitation induced by ultrasonic irradiation over the frequency range of 16 to 1,100 kHz results in the complete oxidative and pyrolytic degradation of a wide range of organic and inorganic compounds in water (Kotronarou et al., 1991; Kotronarou and Hoffmann, 1992; Hua and Hoffmann, 1996; Hua and Hoffmann, 1997; Kang and Hoffmann, 1998). They have shown that the chemical pathways resulting from the violent collapse of cavitation bubbles include direct pyrolytic decomposition within the vapor-phase of the collapsing bubbles, oxidation by hydroxyl radical produced from the pyrolytic decomposition of water, and by transient supercritical water reactions resulting from the extremely high temperatures and pressures generated within a bubble during sonolytic cavitation. This technology also has many commercial applications.

In a related application of electrohydraulic phenomena, Hoffmann and his group (Wilberg et al., 1996; Lang et al., 1998) have developed a reactor system known as the pulsed-power plasma discharge reactor. In this unique reactor system, a large capacitor bank is charged up to a level of several thousand volts (i.e., 10,000 volts) and then over a period of nanoseconds this stored energy (up to 10 kJ) is discharged across two tantalum electrodes with the resulting conversion of water directly into a 50,000 K plasma state. The  $H_2O^+$  and electron plasma produces a blackbody emission centered at about 100 nm. At these wavelengths, water is photodecomposed to produce hydroxyl radical and hydrogen atom. Within the plasma volume (4 ml), all chemical compounds are instantly degraded during the net lifetime of the plasma (e.g., 40  $\mu$ s). At the plasma water interface, the  $H_2O^+$  ions from the gas-phase react with water to produce hydroxyl radical, which in turn is used to oxidize organic compounds and their degradation intermediates. Recent work (Lang et al., 1998) has shown that 200  $\mu$ M TNT can be totally eliminated from 4 liters of water within a power utilization time of only 0.2 ms. This technology is also being developed for commercial applications by several small technology companies.

Recent research has been focused on photochemical transformations in ice and snow. Ice core contaminants are thought to provide permanent paleoclimatic records if, as it is generally assumed, they remained frozen in place and isolated from sunlight by the reflectivity of overlying snow layers. However, recent observations of CO and CO<sub>2</sub> excesses from Greenland air bubbles in ice relative to Antarctic records prior to ca. 1500 AD suggests *in situ* production of CO<sub>2</sub> in ice cores. In the past, the possibility of photochemistry in deep ice has been generally dismissed, due to the high reflectivity of the snow cover to the ultraviolet sunlight and the lack of a conceivable radiation source *in situ*. However, ultraviolet radiation of cosmic origin has been detected at large depths, in connection with the search for intergalactic neutrinos. The density of the photon flux field has been recently quantified, showing that photochemistry can be driven by the Čerenkov radiation continuously emitted within deep ice cores by relativistic muons of cosmic origin is a "reasonable mechanism" for the photogeneration of CO *in situ* as shown recently by Colussi and Hoffmann (2003).

Hoffmann and his group have shown that environmentally important organic compounds can undergo photochemical transformations in ice. They have investigated the photochemistry of pyruvic acid, which is found in polar ice cores, in frozen aqueous solutions. They found the ice phase photolysis products were found to be 2-hydroxy-3-butanone and CO<sub>2</sub>. They Also used solid state MAS <sup>1</sup>H-NMR to determine that pyruvic acid reversibly reacts with free molecular water to form a gem-diol in the ice phase. These results show that pyruvic acid embedded with water ice releases CO<sub>2</sub> when exposed to actinic UV radiation. Therefore, they concluded that this process is quite likely to occur in polar ice at all depths as driven by the photon field generated *in situ* by penetrating muons of cosmic origin.