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CHEMICAL MANUFACTURERS ASSOCIATION

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To: Chlorine Coordinating Council
Science and Health Work Group
CMA/CCC Matrix Team

From: Clyde Greenert Clyde Greenert

Subject: Cantox Study
"Plain Language Document" Draft

Attached is the August 13 draft of this summary of "The Interpretative Review of Potential Adverse Effects of Chlorinated Organics on Human Health and the Environment." Your review and comments would be appreciated.

Also, I'll buy lunch for the best alternate title suggested for this summary - "Plain Language Documents," does not do much for me!

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PLAIN LANGUAGE DOCUMENT

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CANTOX

INTRODUCTION

Since ancient times, humans have used chemicals as tools in the quest for improved quality of life. Originally, useful chemicals were obtained as natural extracts, but with the understanding of chemistry came the ability to synthesize specific chemicals for particular applications. Many of these specifically produced chemicals contain chlorine molecules as part of their chemical makeup. A chlorinated organic chemical is made up of atoms of carbon and hydrogen and chlorine. In addition to being synthesized for specific applications, chlorinated organic chemicals originate from natural sources and are also by-products or end-products resulting from various human activities including pulp and paper production, incineration, manufacture of numerous consumer products and disinfection of drinking water. Chlorine-containing chemicals are used in the production of numerous consumer goods including pharmaceuticals, food additives, crop protection agents, sunscreens, cosmetics, plastics, adhesives, paints, varnish, antifreeze, spandex and soft drink syrup, to name just a few. In addition, some alternative processes and chemicals may be less environmentally friendly, or the potential hazards have not been sufficiently well studied compared to those based on chlorine chemistry.

As the production of chemicals, including chlorinated organic chemicals, has increased to support the growing demands of society, so too have scientific knowledge and societal concern about the possible effects of chemicals released into the environment. Active field and laboratory research into the biological effects of specific chemicals has suggested an association between releases of large quantities of certain chemicals, resulting in increases in their concentrations in the environment, and adverse effects on wildlife. The chlorinated chemicals for which these associations have been observed represent a small subset of the entire universe of chlorinated chemicals. This small group of chlorinated chemicals has properties that result in their ability to accumulate in the tissues of organisms as they are passed from prey to predator up the food chain (a process known as bioaccumulation). The combination of their bioaccumulative properties and the quantities released into the environment results in great enough concentrations in animals at the top of food chains that adverse effects may occur. Numerous other chlorinated organic chemicals, that do not have these structurally and functionally bioaccumulative properties, do not result in such effects in the environment. These observations show that the mere presence of chlorine on a molecule does not cause it to have adverse effects in the environment. While there have been allegations that the bioaccumulative chlorinated chemicals can cause adverse effects at very small concentrations (parts per trillion and parts per billion in the environment), a detailed comprehensive review of the existing scientific evidence regarding the potential of these and other chlorinated chemicals to affect the environment or human health has not previously been undertaken. This study was conducted in order to produce an interpretive evaluation of the potential adverse effects of chlorinated chemicals on human health and the environment. This was achieved through the application of sound scientific principles to the assessment of the vast amount of data existing on these chemicals.

There are several thousand chlorinated organic chemicals, rendering it impossible to evaluate each one of them thoroughly, within the scope and time frame of this work. However, many have been studied in great detail through testing of animals in the laboratory, studying humans and wildlife exposed to chemicals in the environment, and measuring their concentrations in different media of the environment (*e.g.*, air, water, soil, sediments, animals). Since it was not practical nor feasible to assess the potential adverse effects of all chlorinated chemicals on human health and the environment, it was necessary to select a group of chemicals that could be studied. This selection process considered those chemicals which have been identified by different agencies as concerns due to potential adverse effects. In addition, consideration was given to the availability and completeness of information on which to base an assessment. Finally, consideration was given to usefulness of the chemical as a general example from which various scientific principles could be assessed for application in the development of new chemicals and products that would not be harmful to human health or the environment.

The chemicals were chosen to include representatives of the major classes of chlorinated organic chemicals that could serve as surrogates for those not studied in detail. In identifying the chemicals, the various types of product categories, in which chlorine is employed, were considered. The chemicals of greatest concern were selected from a list of 93 chlorinated chemicals identified by various agencies as potential concerns to the environment, including human health (Table 1). By considering total quantities of use and the potential for the chemical to produce harmful effects, 46 chlorinated chemicals were selected for detailed evaluation in the eight product categories (Table 2). The eight product categories cover a wide spectrum of chlorine chemistry used by society and are as follows:

i) molecular chlorine,
ii) polychlorinated biphenyls (PCBs),
iii) vinyl chloride/polyvinyl chloride (VCM/PVC),
iv) chlorine disinfection of drinking water and waste water,
v) incineration of chlorinated materials,
vi) wood pulp bleaching,
vii) chlorinated organic solvents and
viii) the use of chlorine in the development of pesticides.

For the first seven product categories, the possible harmful effects were evaluated, from past and present uses of the chlorinated chemicals included in each product category, and predictions of future safe use patterns were made. In the case of pesticides, the role of chlorine in pesticide activity was assessed, and the need to assess each chemical individually was discussed, based on its potential to cause hazardous effects relative to its potential benefits.

APPROACH TO THE SCIENTIFIC EVALUATION OF DATA

In order to evaluate the potential for a specific chemical to cause adverse effects on human health or the environment, the following questions must be addressed:

- is there opportunity for exposure of humans or the environment to the chemical?
- can the chemical interact with biological systems in a manner consistent with known biological principles?
- is there a scientific basis for concluding that specific adverse effects are associated with exposure to the chemical?
- is the degree of exposure sufficiently high to be likely to cause adverse effects?

If the available information is sufficient to answer these questions, then it is possible to evaluate the potential for adverse effects caused by environmental concentrations of specific chemicals.

In attempting to answer these questions for the representative chlorinated organic chemicals chosen for the current study, a rigorous scientific approach was taken to the interpretation of the published information. The amounts and types of information available varied among the different chlorinated chemicals, with most falling into the following categories:

- laboratory studies using individual cells, isolated cell components or specialized test organisms exposed to known concentrations of a single chemical;
- laboratory studies using animals exposed to known concentrations of a single chemical under controlled conditions for time periods ranging from days to their lifetime;
- field studies to assess possible adverse effects in animals by comparing populations with or without known exposures to mixtures of chemicals (known as eco-epidemiological studies);
- studies to assess possible adverse effects in humans by comparing populations with or without exposures to mixtures of chemicals (known as epidemiological studies);
- studies of concentrations of specific chemicals in air, water, soil, sediment and biological tissues.

In evaluating the available studies in these various categories, the scientific strengths and weaknesses of the supporting information were assessed, as it affected the validity of the conclusions. After reviewing numerous studies on each of the representative chlorinated organic chemicals, conclusions regarding the potential for each of them to cause adverse effects were made based on the overall weight-of-evidence. One of the most important outcomes of this type of weight-of-evidence analysis is the establishment of sound cause-effect relationships. The mere presence of a chemical in the environment in association with a particular adverse effect does not necessarily mean the observed effect was caused by that chemical. In assessing the plausibility of possible cause-effect relationships between chemicals and adverse health effects, the following considerations were made:

- does the adverse effect occur more frequently in populations of humans and/or animals known to be exposed to the chemical?
- is the adverse effect more severe in humans and/or animals exposed to higher concentrations?
- has the adverse effect been reported to be associated with exposure to the chemical by different investigators, in different places, at different times?
- does the adverse effect occur only after exposure to the chemical has begun?
- does the adverse effect disappear or become less severe when the chemical is removed or concentrations are lowered?
- is the chemical likely to be able to cause the observed effect according to known biological principles?
- have similar chemicals been associated with the adverse effect?

Once having established the plausibility of a cause-effect relationship, the relationship between the dose and the magnitude of the effect was examined. The purpose of this examination was to determine the highest dose of a chemical that could be tolerated by humans or wildlife without causing adverse effects. As the earliest toxicologists knew, it is the dose that makes the poison, with the most innocuous chemicals (such as water) capable of causing adverse effects when consumed in excessive quantities, and the most hazardous chemicals (such as cyanide) having no adverse effects when consumed in very small amounts. This determination of a no-effect or "safe" dose for each chemical is usually based on the results of controlled studies in laboratory animals, in which low, medium and high doses were given every day for life. This type of study, where the doses are known and only one chemical is given, provides a reliable means of determining the safe dose for an animal (usually rats or mice). The "safe" dose for humans was calculated either by the application of safety factors to the safe dose observed for animals in laboratory studies (*i.e.*, by dividing the safe dose for an animal by factors of 10, 100 or 1000, depending on the type of study, species tested, and severity and type of effect caused at higher doses in animals), or by the use of theoretical dose-response models.

To evaluate the potential for adverse effects to occur from concentrations of chemicals in the environment, the exposures expected as a result of environmental concentrations are either estimated using exposure models or measured directly in tissues of exposed populations. If the estimated exposures (doses) are lower than the "safe" dose, then no adverse health effects might be expected. If the exposures exceeded the "safe" dose, there is the potential for adverse health effects. This type of assessment was conducted for all the representative chemicals in each product category, based on their rates of release and measured concentrations in the environment. In order to put the environmental concentrations of chlorinated organic chemicals associated with the product categories into perspective, the sources of such chemicals produced through natural processes, independent of human activities, also were evaluated.

To summarize, the following steps were taken in the assessment of the selected chemicals in each product category:

- Determination of sources and amounts of the selected chlorinated chemicals released to the environment from human activities and natural processes.
- Estimation of typical exposures to various organisms, including humans, using information on concentrations of the chemicals in air, water, soil and other environmental media.
- Assessment of the potential of the chemicals to cause harmful effects, and the use of this information to determine safe levels of exposure for each chemical.

- Assessment of the degree of concern or risk from the use of the chemical by comparing the exposures from environmental media against the upper exposure limit of the chemicals.

KEY FINDINGS FOR EACH PRODUCT CATEGORY

I CHLORINE

Sources of Chlorine

Sources of chlorine related to human activities include the following:

- the manufacture of plastics and adhesives;
- the manufacture of chlorinated organic chemicals;
- the manufacture of drugs;
- the manufacture of various household goods, including deodorants, cleaners and bleaches;
- use of chlorine for drinking and waste water disinfection.

The Environmental Protection Agency's Toxics Release Inventory estimated the total quantities of chlorine released into the environment by human activities in the United States to be between 35 and 36 million pounds per year over the period 1987-1990. This is approximately one tenth or less, of the annual production of chlorine from natural sources. Chlorine released into the environment rapidly reacts with water or water vapors to produce hydrochloric acid (HCl).

Natural sources of chlorine include:

- volcanic eruptions;
- the break-down of sea salt by ultra-violet light from the sun (known as photolysis).

Volcanic eruptions have been estimated to contribute from 0.4 to 11 million tons of chlorine/year (800 million to 22 billion pounds) on a global basis. The production of chlorine in the atmosphere by the photolysis of sea salt is believed, by Swedish scientists, to result in the deposit about 1 to 23 pounds of chlorine per hectare of land each year on a global basis.

Cause-Effect Relationship

The potential for harmful effects to the environment from chlorine is associated with the corrosivity of hydrochloric acid produced by the reaction of chlorine with water in the environment or in the respiratory tissues of air breathing organisms. Evidence from studies with laboratory animals and from accidental human exposures have shown that sufficiently high concentrations of chlorine gas or hydrochloric acid can cause irritation to tissues at the site of contact with effects becoming less severe at lower doses. At sufficiently low concentrations of hydrochloric acid no adverse effects occur.

Evaluation of the Potential for Adverse Effects from Chlorine

The conclusion of the interpretive review of the available information on chlorine is that, with the exception of spills related to transportation and use, and large accidental releases from point sources, the concentrations of chlorine in the environment over the past two decades have been below those expected to cause unwanted or harmful effects on human health or the environment.

Recommendations

Continued efforts are required to make sure that spills and accidents that release chlorine to the environment are minimized and those that occur are controlled as quickly as possible. The current trends in the adoption of best-available-technologies for systems that prevent the release of chlorine to the environment must continue, to ensure that potential harmful effects from the uses of chlorine are prevented in the future.

II POLYCHLORINATED BIPHENYLS (PCBs)

Sources of PCBs

Historically, the largest use of PCBs was in the electrical industry, because their superior heat absorbing capacity and electrical insulating properties provided greater safety (e.g., reduced fires and explosions) compared to alternative materials. PCBs are no longer manufactured, but are still in use in some closed systems. Until recently it was believed that there were no known natural sources of PCBs; however, PCBs, not related to any human activities, were identified in ash from the 1980 volcanic eruption of Mt. St. Helens in Washington state, indicating their formation from natural processes independent of human activities. The quantities of PCBs released to the environment from volcanic eruptions are unknown.

Physical and Chemical Properties of PCBs and Fate in the Environment

The term PCBs denotes a family of 209 chemicals with chlorine attached at various places on the molecule. Depending on the position and amount of chlorine, the different PCBs exhibit a wide range of physical and chemical properties. For example, the ability of the different PCBs to dissolve in water ranges over 5.5 million-fold and the potential for vapors to form in the air ranges 100,000-fold among the different PCBs. The ability of different PCBs to be stored in the body fat of animals ranges over 10,000-fold, and becomes greater with increasing amounts of chlorine on the molecule. Since the behavior of chemicals in the environment is determined by their physical and chemical properties, the differences in properties of the various PCBs are reflected in their distribution, disappearance and movements in the environment. Generally, as the amount of chlorine contained in PCBs increases, their disappearance or degradation in the environment becomes slower. Some forms of PCBs are stored in the fat of organisms following exposure. These PCBs are subsequently passed to predators and stored in the fat of the predator. Since elimination from biological tissues is very slow for some of these PCBs, their concentrations stored in fat gradually increase in organisms if their rate of exposure exceeds their rate of elimination. This leads to the potential for adverse effects especially in predators at the top of food chains, such as fish-eating birds and mammals.

The combination of unrestricted use and of physical properties, which favor long range atmospheric transport, bioaccumulation and slow breakdown of PCBs has resulted in their widespread distribution in the environment, including remote areas such as the Arctic and Antarctic. Due to their widespread occurrence, PCBs are found at low concentrations in tissues, (such as fat, liver, blood and breast milk) of people with no known occupational or unique environmental exposures. Concentrations of PCBs in various aquatic wildlife (*e.g.*, fish and fish-eating birds) are generally greater than those reported for humans, primarily because of the characteristics of aquatic food chains and the less varied diets of aquatic wildlife (*i.e.*, almost all fish) compared to humans.

The Cause-Effect Relationship

Laboratory studies on animals have indicated that PCBs have the potential to cause adverse effects on reproduction and that extreme doses of some PCBs can increase the incidence of liver cancer in rats. These effects have been shown to be dose-related (*i.e.*, they become less severe and less prevalent at lower exposures). There is good evidence indicating that sufficiently low exposures to PCBs do not cause adverse effects.

Certain adverse effects, such as eggshell thinning in some species of Great Lakes fish-eating birds and crossed bills in cormorants, increased in prevalence and severity as the concentrations of PCBs and several other chemicals in the environment increased, and have declined as concentrations have declined. This consequent decline in environmental concentrations of PCBs and the recovery of bird populations is consistent with a cause-effect relationship between PCBs and reproductive effects in fish-eating birds. It must be noted, however, that several other chlorinated and non-chlorinated chemicals were also present in these birds, and that controls over the release of these chemicals occurred during the same time period as the uses of PCBs were regulated. Therefore, it is not possible, based on the field data available, to separate the possible cause-effect relationships of such a mixture of chemicals. In addition, there is evidence suggesting that loss of habitat caused by increasing urbanization and faulty industrial practices occurring at the same time that concentrations of PCBs and other chemicals were increasing, also played a role in the population declines observed in certain wildlife species during this time water bodies, where they can be accumulated by various organisms. Therefore, future rates of decreases in concentrations of PCBs in the environment are expected to remain slow relative to those observed historically.

Based on current knowledge about dose-response relationships for the possible harmful effects of PCBs, mostly from laboratory studies, and from studies of human populations historically exposed to PCBs in the workplace, no harmful effects would occur from exposures of humans to current environmental concentrations of PCBs. However, there is a greater likelihood for harmful effects on certain wildlife than humans, due to dietary habits and position in the food chains. This greater possibility for harmful effects from PCBs is particularly pronounced in species that eat almost exclusively fish and other aquatic organisms. Concern about possible harmful effects in such species is understandably great in regions of the environment where the concentrations of PCBs, together with other chemicals, are markedly elevated (*e.g.*, various "hot spots"). With the exception of these localized "hot spots", caused by historical point-source releases of chemicals, any adverse effects on the environment expected from current environmental concentrations of PCBs should be minor. Although PCBs were once considered to be resistant to natural biological breakdown, there is now considerable laboratory and field evidence to the contrary, although their breakdown rate varies significantly depending on the numbers and positions of chlorine on the PCBs. As the environmental concentrations of PCBs and other bioaccumulative chemicals continue to decline, through restrictions on environmental release rates, through natural, physical and biological degradation processes, and through continued burial via sedimentation, the degree of harmful effects in localized "hot spots" will continue to decline.

Recommendations

Chemicals having physical and chemical properties similar to those of certain PCBs, which result in their accumulation in the environment, should not be used in ways that lead to their uncontrolled release into the environment. The knowledge that these types of chemicals can be widely distributed throughout the world and will degrade slowly, should govern the design and use of new chemicals so that the situation that occurred with PCBs and other bioaccumulative chemicals is not repeated.

III VINYL CHLORIDE AND POLYVINYL CHLORIDE

Sources of Vinyl Chloride and Polyvinyl Chloride

Vinyl chloride and polyvinyl chloride are products of the plastics industry. Vinyl chloride, as it is, is not used in commercial products, but is the starting product for the production of polyvinyl chloride (PVC). PVC (called polymers) is made by linking a large number of vinyl chloride units together to form a long chain of linked molecules. PVC is a solid material with great stability in the environment. Its most recognized use is in PVC pipe, used in many drainage and plumbing applications. Under good manufacturing procedures, the residual concentration of vinyl chloride in modern PVC products is below the lower limit of analytical detection limits.

Vinyl chloride can be released to the atmosphere as a vapor, and it rapidly degrades by reactions with ultraviolet light. It does not accumulate through food chains and ultimately is completely broken down by biological systems. Vinyl chloride molecules are reactive and readily join together in the presence of oxygen, sunlight or heat to form stable PVC.

No information was available on the air concentrations of vinyl chloride at locations remote from production/manufacturing facilities. However, based on the concentrations reported near such facilities and the rapid rate at which it is destroyed in ambient air, the concentrations in air in remote locations would be expected to be very small, and not even measurable with current techniques.

The Cause-Effect Relationship

Laboratory studies using animals have demonstrated that high dose, long-term exposure to vinyl chloride can result in the development of liver cancer. In addition, exposures of humans to unacceptably high concentrations of vinyl chloride in some workplaces prior to the 1970s are believed to have resulted in increases in an unusual liver cancer (called angiosarcoma) in workers. Intermediate break-down products formed during the degradation of vinyl chloride are reactive and bind to genetic material (DNA) in cells. The reactions of these reactive intermediates with DNA are believed to be responsible for the cancer-producing activity of vinyl chloride.

Through changes in technology, the air concentrations of vinyl chloride in workplaces in the 1980s were reduced about 10,000- to 100,000-fold compared to the pre-1970 values. Lower concentrations in the workplace, combined with protective equipment used by workers, virtually eliminated risks of liver cancer from occupational exposures associated with the use of vinyl chloride.

Evaluation of the Potential for Adverse Effects from Vinyl Chloride and PVC

No harmful effects to human health or the general environment occur from PVC itself. The major concern regarding PVC is the possible exposure of workers to PVC dust arising from the use of PVC materials in manufacturing processes, and possible products (e.g., vinyl chloride monomer) arising during its production. Through modifications in the manufacturing processes, the concentrations in the workplace have been reduced to near analytical detection limits (about 5 parts per billion) and are not associated with adverse effects on humans or the environment.

Recommendations

The use of production and manufacturing technologies that eliminate releases of vinyl chloride to the environment should continue, thereby preventing air concentrations of vinyl chloride from exceeding current undetectable values and ensuring that no harmful effects on human health or the environment would occur. Continued care is required to ensure that spills and accidental releases of vinyl chloride are minimized, and if accidents occur, that the resulting releases are controlled to prevent harmful effects to human health or the environment.

IV CHLORINE DISINFECTION OF DRINKING WATER AND WASTE WATER

Production of Chlorinated Chemicals Through Disinfection with Chlorine

Chlorine is used in the disinfection of drinking and waste water in order to prevent the spread of waterborne diseases such as typhoid and cholera, diseases which used to claim the lives of millions of people in Western society prior to the development of water treatment techniques. Several chlorinated chemicals are produced as unwanted by-products of the chlorine disinfection process, and low concentrations of these remain in the finished water. Everyone consuming chlorine-disinfected tap water is exposed to low concentrations of these chemicals. These are not uniquely man-made chemicals. Most are also produced in significant amounts through natural processes, and exposure to humans and the environment would occur to some degree even if they were not found in treated drinking and waste water. In addition, improvements in the techniques of disinfection of drinking water with chlorine can substantially reduce the concentrations of these unwanted by-products in the finished water.

The Cause-Effect Relationship

The most significant chlorinated chemicals found in water disinfected with chlorine were evaluated in terms of their potential for causing adverse effects. For all these chemicals, substantial amounts of information were available allowing characterization of the types of effects they could cause and of the doses required to cause the effects. Doses were determined for each of the chemicals that would be expected to result in no occurrence of adverse effects on humans or the environment.

Evaluation of the Potential for Adverse Effects from Chlorinated Chemicals Produced During Disinfection with Chlorine

The majority of the chlorinated chemicals studied in drinking water are present in tap water at concentrations far less than the concentration at which adverse effects would be expected. Two types of chlorinated organic chemicals (chlorinated ketones and nitrogen compounds) could not be rigorously evaluated due to inadequacies in the toxicological data base; however, the very low concentrations (parts per billion) of these were considered not likely to be associated with adverse health effects. Two types of inorganic chemicals (chlorite and chlorate) have been detected in some drinking water samples at concentrations exceeding those recommended as allowable. This exceedance of the allowable concentration in some cases may not be significant in terms of potential adverse health effects, because of the highly conservative procedures followed in establishing the recommended maximum concentrations. Overall it can be concluded that disinfection of drinking water using chlorine results in the production of a safe water supply.

The concentrations of chlorinated organic chemicals in rivers, lakes or streams receiving waste water disinfected with chlorine were below those that would be associated with adverse health effects on aquatic organisms. In some cases the concentrations of one type of chemical (chlorinated phenols) exceeded surface water guidelines in the effluent, prior to entry into the receiving water. These occurrences were primarily historical and surface water quality guidelines were not exceeded once the effluent was diluted into the receiving water. Another group of chlorinated chemicals (chlorinated dioxins and furans) can occur at concentrations in waste waters (primarily from sewage treatment plants) that are high enough to warrant some concern. This concern stems from the potential for these compounds to bioaccumulate through the aquatic food chain. The chlorinated phenols and chlorinated dioxins and furans may have been present in the raw water prior to treatment and may not have been produced as a result of chlorination, and so no conclusion regarding the effect of chlorination on the potential for them to cause adverse effects can be made.

Overall the weight-of-evidence indicates that chlorine disinfection of drinking and waste water would not be associated with adverse effects on humans or the environment.

Evaluation of Alternative Methods of Water Disinfection

There are a number of other processes which can be used in the disinfection of drinking water and waste water, each of which was evaluated for suitability in terms of the following criteria:

- *production of chemicals at concentrations not associated* with adverse effects
- the availability of information on the types and quantities of various by-products from alternative water disinfection processes, and of information required to assess their potential harmful effects
- ability to effectively destroy bacteria, viruses and parasites in water
- retention of disinfection capability throughout the water distribution and storage system
- improve the taste, smell, clarity and color of the water after treatment

Disinfection using chlorine meets all these criteria, while the other methods of disinfection meet only some of them. In most cases, the available information required to assess alternative disinfection technologies is incomplete, particularly regarding the identification and quantification of by-products. A major deficiency in the use of ultraviolet light for water disinfection is the lack of residual disinfection capacity outside the water treatment plant.

The overall conclusion from the current assessment is that disinfection of drinking water and waste water by chlorination remains the method of choice.

Recommendations

- The scientific basis for the establishment of the maximum allowable concentration of chlorite and chlorate should be more rigorously defined.
- The maximum concentration of chlorate and chlorite in finished drinking water should be reduced, through adjustments and refinements of the disinfection process.
- Continued vigilance needs to be employed in the control of the waste water treatment process to ensure that the concentrations of chlorinated phenols do not exceed surface water guidelines.
- The source of chlorinated dioxins and furans in treated waste waters needs to be established, and a detailed risk assessment, incorporating analysis of the aquatic food chain, needs to be conducted to ensure that concentrations are below those that would cause environmental concerns.

V INCINERATION OF CHLORINATED MATERIALS

Production of Chlorinated Chemicals Through Incineration

Chlorinated chemicals can be emitted from incinerators as a result of incomplete burning of materials fed into the incinerator, or through chemical reactions occurring in the incinerator stack. Numerous chlorinated chemicals have been detected in emissions from incinerator stacks. Most of these are not uniquely man-made chemicals but are also produced in significant amounts through natural processes, particularly those involving high temperatures such as volcanic eruptions and forest fires. Human and environmental exposure to these chlorinated chemicals would occur even if incineration technologies were not used, and the available information demonstrates that insignificant additions of such chemicals arise from a properly operated, best-available-technology incinerator.

The Cause-Effect Relationship

The most significant chlorinated chemicals found in incinerator emissions were evaluated in terms of their potential for causing adverse effects. For most of these chemicals a substantial amount of information was available to allow characterization of the possible effects they may cause and the doses required to cause the effects. For each of the chemicals, upper dose limits were developed that would not be expected to result in the occurrence of adverse effects on humans or the environment.

Evaluation of the Potential for Adverse Effects from Chlorinated Chemicals Produced During Incineration

The potential for adverse effects from chlorinated chemicals produced through incineration was evaluated through the assessment of an actual facility employing the best available technology.

The steps taken in conducting this analysis included the following:

- prediction of concentrations of representative chemicals in air, water, soil and wildlife resulting from the incinerator emissions;
- prediction of exposure to humans and wildlife resulting from these environmental concentrations;
- comparison of expected exposure from the incinerator emissions with the maximum safe exposure limits for each chemical.

The predicted exposures of chlorinated organic chemicals from the case study incinerator were substantially lower than the maximum safe exposures, indicating that no adverse effects on human health or the environment would be expected. In addition, the predicted exposures to the chemicals were substantially (orders of magnitude) less than those associated with exposures from ambient background sources, independent of the incinerator. Although the amounts of chemicals emitted from an incinerator are dependent on a number of factors related to the design and operating conditions of the facility, the case study facility is considered representative of a modern day incinerator employing best available technology. Emission rates of chlorinated chemicals from any such facility would be very low and not associated with any adverse effects.

Recommendations

Outdated incinerator facilities should be upgraded or replaced to ensure that the best available technology is being employed. New facilities should be constructed using only the best available technology in order to ensure minimal concentrations of chemicals in emissions. Operating incinerators should be monitored to ensure they are operating properly.

VI WOOD PULP BLEACHING

Production of Chlorinated Chemicals Through Wood Pulp Bleaching

In order to manufacture high quality white paper, the wood pulp must be bleached. Historically, the only method of bleaching pulp was to use gaseous chlorine. This resulted in the formation of a number of chlorinated organic chemicals as the chlorine reacted with other chemicals used in the process and with chemicals from the wood itself. Most of these chemicals are not uniquely man-made chemicals, and many are produced in significant amounts through natural processes independent of wood pulp production. All the classes of chlorinated organic chemicals produced from pulp bleaching are represented by naturally occurring chemicals. Therefore, low concentrations of chemicals that are the same as or similar to those produced by pulp mills would be encountered by organisms in the environment, even if chlorine was not used in the pulping process.

Improvements in wood pulp bleaching technology and the development of new processes have led to the ability to whiten wood pulp using forms of chlorine other than gaseous chlorine. These modern processes result in the production of very low level chlorinated organic chemicals.

The Cause-Effect Relationship

Biological effects of pulp mill effluents can be evaluated in two ways:

- toxicity testing of effluent in the form that it is discharged from the mill;
- evaluation of toxicity of individual chemicals present in mill effluent.

Effluents from pulp mills using molecular chlorine are generally toxic to fish placed in tanks containing undiluted effluent. Since there are numerous chlorinated and non-chlorinated chemicals present in the effluent, it is not possible to determine from this type of study which particular chemical or mixture of chemicals is responsible for the toxicity of the effluent.

In field studies, adverse effects have been observed in fish downstream from some pulp mills. Recent studies have indicated that once the mills stop using chlorine in the bleaching process, some adverse effects on the fish continue to be observed. This suggests that non-chlorinated chemicals, and/or the disruption of habitat are at least partially responsible for the observed effects. Effluents from pulp mills using the best available technology are not lethal to fish, and in fact fish can survive without evidence of adverse effects when exposed for four days to undiluted effluents from such mills.

Individual chlorinated chemicals representative of the major classes of these chemicals were evaluated in order to determine whether any particular chemicals were present at high enough concentrations to cause adverse effects (*i.e.*, growth and reproduction effects) in fish downstream from pulp mills. Potential adverse effects on human health were evaluated on the basis of consumption of fish living downstream from pulp mills. This evaluation was based on mills using chlorine bleach or gaseous chlorine in the bleaching process, since very small amounts of chlorinated chemicals are produced by mills using modern methods.

For most of the representative chemicals, concentrations measured in rivers downstream of pulp mills are below those that could be associated with adverse effects. For two classes of chemicals insufficient data were available to allow a rigorous assessment to be conducted (chlorinated fatty and resin acids and chlorinated ketones).

There was only one group of chemicals for which concentrations in water gave cause for concern (chlorinated dioxins and furans). The concern regarding the chlorinated dioxins and furans stems from the facts that they can cause adverse effects on reproduction and that they bioaccumulate in the aquatic food chain. Since the potential effects of these chemicals are very site and mill specific, the assessment was based on a specific case study. Concentrations of chlorinated dioxins and furans in fish were measured downstream from a mill that used gaseous chlorine as the bleaching agent. This mill is remotely located, and fish living downstream are prevented from migrating by a dam on the river. These characteristics minimized the potential influences of factors unrelated to the pulp mill. The concentrations of chlorinated dioxins and furans in fish caught downstream were below those that would be associated with adverse effects in fish, although consumption of the fish by fish-eating mammals and birds such as otters and osprey could possibly result in accumulation in these species of enough chemical to adversely affect reproduction. Consumption of these fish by humans would not be expected to result in the accumulation of enough chemical to cause adverse effects.

In pulp mills not using gaseous chlorine for whitening pulp, chlorinated dioxins and furans cannot be detected in effluent. If it is assumed that concentrations of these chemical do exist at concentrations at the detection limit (10 parts per quadrillion), the resulting concentration in fish would not be expected to result in adverse effects in any species, including predators high on the food chain such as otters and osprey. Similarly, no adverse effects would be expected from the other chlorinated chemicals in the effluent from mills employing alternative methods for whitening pulp.

Recommendations

Pulp mills should use best available technology for producing and bleaching wood pulp so as to avoid the use of chlorine bleach or gaseous chlorine and thereby reduce or eliminate the discharge of chlorinated organic chemicals, particularly chlorinated dioxins and furans, to the aquatic environment. Research efforts should continue to focus on elucidating the factors or non-chlorinated chemical(s) responsible for the effects observed in fish populations near pulp mills.

VII CHLORINATED ORGANIC SOLVENTS

Sources of Chlorinated Organic Solvents

Chlorinated organic solvents are used in a wide range of production and manufacturing processes. Chlorinated organic solvents are generally small molecules that are derivatives of low molecular weight hydrocarbons. These chemicals include compounds such as chloroform, carbon tetrachloride, dichloromethane (methylene chloride), dichloroethane, and di-, tri-, and tetrachloroethylene. Chlorobenzenes are also widely used as solvents in the chemical industry.

During use, chlorinated solvents would be released into the workplace and the local environment surrounding production and manufacturing facilities. The implementation of more stringent effluent and emission criteria and improvements in operating technologies, based on a general improvement in the scientific understanding of the behavior and potential effects of chemicals on the environment, have resulted in decreased total quantities of chlorinated organic solvents released to the environment in the past decade. However, some environmental releases from these point sources still remain, even though they have become fewer with time and are within recommended limits. The chemicals from these point-source releases continue to disperse into the environment and contribute to the general ambient concentrations of these chemicals. Most of the chlorinated organic chemicals used as solvents are also released into the environment as by-products of a number of other human activities (*e.g.*, chlorine disinfection of drinking water, products of incomplete combustion (PICs), chlorine bleaching of paper pulp), and as products of a number of natural processes independent of human activities.

The Cause-Effect Relationship

The most significant chlorinated chemicals which are used as solvents, such as carbon tetrachloride, chloroform, the chloroethylenes and the chlorobenzenes, were evaluated with respect to their potential for causing adverse effects. For all these chemicals, substantial amounts of information were available. As a result, a detailed characterization of the types of effects caused and of the doses required to cause the effects was completed for each chemical. Doses were determined for each of the chemicals that would be expected to result in no occurrence of adverse effects on humans or the environment.

As a rule, the chlorinated solvents are of a relatively low order of toxicity, with the liver and kidney generally being the main organs affected in humans and/or animals receiving high doses. Some of the chlorinated organic chemicals have been reported to induce tumors in laboratory studies using animals, albeit through mechanisms which may be related to the extremity of the doses tested or to the specific physiology of the test animals. As a result, for some of the chlorinated organic solvents, the observation of tumors in certain animal studies is not likely to be relevant to degrees of exposure experienced by humans from the environment.

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Evaluation of the Potential for Adverse Effects from Chlorinated Organic Solvents

The evaluation of the potential adverse effects of chlorinated solvents on human health and the environment was based on exposures to ambient concentrations of the chemicals. It is not possible to conduct a general assessment of potential adverse effects that may be associated with point source releases because such assessments would be specific to the site, workers and processes involved.

With the exception of certain low molecular weight chlorinated chemicals such as chloroform and carbon tetrachloride, human and environmental exposures to chlorinated organic solvents from general ambient sources would be substantially below exposure limits considered to be protective of human health and the environment. In the case of chloroform and carbon tetrachloride, exposures to the average ambient environmental concentrations would be substantially below the exposure limits considered protective of human health and the environment. However, at the maximum ambient environmental concentrations reported historically at certain locations in specific urban centers, the recommended exposure limits would be exceeded by a small margin. This does not mean that adverse health effects would be associated with exposures to the maximum ambient environmental concentration since there are substantial margins of safety between the exposure limits and exposures that could produce observable adverse health effects.

The releases of solvents produced by human usage to the environment, particularly chloroform and carbon tetrachloride, have decreased over time, with increased usage in closed, non-emissive systems. In the case of chloroform, historical data on drinking water concentrations indicated that the procedures used for the disinfection of water supplies with chlorine were resulting in elevated levels of chloroform in the finished water; however data from systems using best-available-technologies for the disinfection of drinking water using chlorine demonstrate substantially lower concentrations of chloroform in the finished water (*e.g.*, approaching 10-fold lower concentrations). Therefore, the contributions of human activities to the concentrations of chlorinated organic solvents in the environment will continue to decline in the future with the increased use of improved technology. These declines would be coincident with decreasing human exposures and decreasing potential for the induction of adverse effects.

Recommendations

Efforts should continue to be directed toward reducing environmental releases of chlorinated organic solvents through the implementation of improved technologies (e.g., closed-systems, non-emissive procedures). Occupational exposures should continue to be monitored and best available technologies should be employed to continue to reduce human and environmental exposures to chlorinated organic solvents.

VIII THE USE OF CHLORINE IN THE DEVELOPMENT OF PESTICIDES

Many pesticides contain chlorine and many do not. The biological activity of pesticides does not correlate with the presence or absence of chlorine on the molecule. Non-chlorinated pesticides can be more toxic than chlorinated pesticides. Many pesticides are produced naturally by plants, and some of these contain chlorine, indicating that chlorinated pesticide were produced in nature before the advent of synthetic pesticides. Non-chlorinated pesticides produced by plants can induce at lower doses the same adverse effects than certain of the more publicized synthetic chlorinated organic pesticides.

While evaluating the potential for a pesticide to cause adverse effects on non-target organisms, the potential benefits associated with the use of the chemical must be considered. The chlorinated pesticide DDT provides a good example of a case in which the benefits have been ignored and the reasons for its widespread use forgotten in the wake of concern over potential adverse reproductive effects in birds. DDT is highly effective against disease-carrying insects, is significantly less likely to cause poisoning in humans or other mammals than alternative chemicals, and is cheap and easy to produce. At the time of its most widespread use, during the 1940s and 1950s, scientists, industry and end-users were unaware of its potential to bioaccumulate through the food chain. It is estimated that the death from malaria of over one billion humans and countless wild animals are prevented each year due to the World Health

Organization's mosquito control program using DDT, which still operates in many tropical countries. The use of DDT in Europe immediately after the second world war is believed to have prevented the deaths from disease of as many people as died from the war itself. It is easy to understand how DDT came into favor and widespread use, when the benefits were known and the potential for adverse effects on the environment was not clearly understood. Presently, DDT and other similar pesticides that bioaccumulate and have been associated with adverse effects on reproduction on fish eating birds, are banned from use in most countries, except in those threatened with malaria outbreaks.

The knowledge that certain structures of chemicals result in undesirable properties, such as toxicity to non-target organisms or bioaccumulation potential, has led to the ability to specifically design pesticides which do not have these faults. New pesticides are more specific in their action against pests and may be rapidly degraded in the environment. Some contain chlorine and some do not. Some are made using chlorine in the production process without containing chlorine in the final product. Because of their specificity and potency against target pests, the amounts used tend to be much smaller, thus reducing the already low risk of adverse environmental impacts.

Recommendations

The evaluation of the potential for pesticides to cause adverse effects should continue to incorporate an assessment of the potential benefits as well as the risks associated with their use, as is now the approach of regulatory agencies in most countries. The evaluation should be based on scientific data, not on whether or not a pesticide contains chlorine. The development of highly specific pesticides, that are rapidly broken down in the environment and need to be used only in small quantities should be encouraged.

CONCLUSIONS

Chlorinated chemicals are produced by natural processes and are ubiquitous in the environment. This provides evidence that organisms and ecosystems have evolved means of surviving in the presence of low concentrations of these types of chemicals. It is therefore expected that low concentrations of similar chemicals produced by human activities would not cause adverse effects. The results of the current study support this contention and indicate, with the exception of a few bioaccumulative chemicals present at excessive concentrations in localized areas, that chlorinated chemicals do not pose a threat to humans or the environment.

Those chlorinated chemicals that have been associated with adverse effects in the environment are all from one subset of the universe of chlorinated chemicals, those that have the ability to bioaccumulate through the food chains because of slow rate of excretion and breakdown in biological systems. These types of chemicals have been banned, or their use has been severely restricted, resulting in noticeable decreases in their concentrations in the environment over the years. The concentrations of these chemicals will continue to decline albeit slowly, and the recovery of affected species, already well underway, is expected to continue. Attention should also be directed toward the significance of habitat loss in the slow recovery of some species.

Known "hot-spots", where the concentrations of these chemicals are substantially elevated compared to the general environment, require continued attention to reduce release rates from point sources to the environment and to investigate possible remediation procedures if warranted. In addition, the knowledge gained on the properties and characteristics of chemicals that have been implicated in various environmental and human health problems must be used in the design and development of new products and processes to avoid a reoccurrence of such problems in the future.

Other chlorinated chemicals, which do not bioaccumulate through food chains and are readily degraded in the environment, have not been associated with adverse effects at concentrations at which they are found in the environment. Continued improvements in technologies (*e.g.*, the use of closed systems and non-emissive technologies) using and generating chlorinated chemicals, and increased vigilance in the prevention of spills and accidental releases of these chemicals will ensure further reductions in the future in the already low risks to humans and the environment from chlorinated organic chemicals.

Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
	Dibromochloropropane	●	●					
Chlorinated Alkanes (Continued)	1,2-Dichloropropane		●	●				
	1,2-Dibromo-3-chloro-propane			●				
Chlorinated Alkenes								
	Dichloroethylene		●					
	1,1-Dichloroethylene			●	●			
	1,2-Dichloroethylene (Cis)			●				
	1-2,Dichloroethylene (Trans)			●				
	Trichloroethylene		●	●	●			
	Tetrachloroethylene		●	●	●			
	1,3-Dichloropropene (Cis)			●				
	Pentachloropropene					●		
	Pentachlorobutadiene					●		
	Hexachlorobutadiene			●		●		
	Hexachlorocyclopentadiene			●				
	Hexachlorobutatriene					●		
	Vinyl Chloride			●	●		● (monomer)	
PVC								
	Polyvinyl Chloride						●	

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Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Inorganics								
	HCl				●		●	
	Chlorate	●						
	Chlorite	●						
Chlorinated Alkanes								
	Dichloromethane	●	●		●			
	Chloroform	●	●		●	●		
	Carbon Tetrachloride		●	●	●			
	Chloromethane			●	●			
	Bromodichloromethane	●	●	●				
	Chlorodibromomethane	●	●	●				
	Trichlorodihydroxyethane	●	●					
	Chloroethane	●	●	●				
	Dichloroethane	●	●					
	1,1-Dichloroethane			●	●			
	1,2-Dichloroethane			●	●			
	Trichloroethane		●					
	1,1,1-Trichloroethane			●				
	1,1,2-Trichloroethane			●	●			
	1,1,2,2-Tetrachloroethane			●	●			
	Bromodichloroethane			●				
	Hexachloroethane			●				
	Pentachloroethane			●				

Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Acids								
	Monochloroacetic Acid	●	●					
	Trichloroacetic Acid	●	●					
Chlorinated Ketones								
	Trichloroacetone					●		
	Tetrachloroacetone					●		
	1,1-Dichloropropanone	●	●					
	1,1,1-Trichloropropanone	●	●					
	Dichlorocyclopentene-1,2-dione (various isomers)					●		
	3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	●	●			●		
Chlorinated Benzenes								
	Chlorobenzene		●	●				
	Dichlorobenzene		●					
	1,2-Dichlorobenzene			●	●			
	1,3-Dichlorobenzene			●				
	1,4-Dichlorobenzene			●	●			
	Trichlorobenzene		●					
	1,2,4-Trichlorobenzene			●	●			
	Pentachlorobenzene			●				
	Hexachlorobenzene			●	●			
	Dichlorotoluene		●					
	2-Chloroethylbenzene		●					

Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Phenols, Catechols, Guaiacols								
	2-Chlorophenol	●	●	●				
	2,4-Dichlorophenol	●	●	●	●	●		
	2,6-Dichlorophenol					●		
	2,4,5-Trichlorophenol			●	●			
	2,4,6-Trichlorophenol	●	●	●		●		
	2,3,4,5-Tetrachlorophenol					●		
	2,3,4,6-Tetrachlorophenol		●	●		●		
	Pentachlorophenol			●	●	●		
	Tetrachlorophenol					●		
	Dichlorocatechol					●		
	Tetrachlorocatechol					●		
	Trichlorocatechol					●		
	3,4,5-Trichlorocatechol					●		
	4,5-Dichloroguaiacol					●		
	Dichloroguaiacol (other isomers)					●		
	Tetrachloroguaiacol					●		
	Trichloroguaiacols					●		
	Trichlorodihydroconiferyl Alcohol					●		
	Chlorovanillin					●		
	Trichlorovanillylalcohol					●		
	Trichloroacetosyringone					●		

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Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
	Dichloro-3,4-dihydroxy-propiophenone					●		
Chlorinated Nitrogenous Compounds								
	Dichloroacetonitrile	●	●					
	Nitrochloroform	●	●					
Chlorinated Aldehydes								
	Trichloroethanal	●	●					
	Chloropropenal					●		
	Chloromethoxydibenzaldehyde					●		
	Chloralhydrate	●						
Chlorinated PCDDs, PCDFs								
	2,3,7,8-T_4CDD		●		●	●	●	●
	1,2,3,7,8-P_5CDD		●		●	●	●	●
	1,2,3,4,7,8-H_6CDD		●		●	●	●	●
	1,2,3,4,8,9-H_6CDD		●		●	●	●	●
	1,2,3,6,7,8-H_6CDD		●		●	●	●	●
	1,2,3,4,6,7,8-H_7CDD		●		●	●	●	●
	O_8CDD		●		●	●	●	●
	2,3,7,8-T_4CDF		●		●	●	●	●
	2,3,4,7,8-P_5CDF		●		●	●	●	●
	1,2,3,7,8-P_5CDF		●		●	●	●	●
	1,2,3,4,7,8-H_6CDF		●		●	●	●	●
	1,2,3,7,8,9-H_6CDF		●		●	●	●	●

Table 1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
	1,2,3,6,7,8-H_7CDF		●		●	●	●	●
	2,3,4,6,7,8-H_7CDF		●		●	●	●	●
Chlorinated PCDDs, PCDFs (Continued)	1,2,3,4,6,7,8-H_7CDF		●		●	●	●	●
	1,2,3,4,7,8,9-H_7CDF		●		●	●	●	●
	O_8CDF		●		●	●	●	●
PCBs								
	PCBs							●
Chlorinated Fatty Acids	Dichlorostearic Acid					●		
Chlorinated Resin Acids	Chlorodehydroabietic acid					●		
	Dichlorodehydroabietic acid					●		
Chlorinated Amines	3,3'-Dichlorobenzidine			●				
	4,4'-methylene-bis-(2-chloroaniline)			●				
Chlorinated Ethers	Bis(2-chloroethyl)ether			●				
Chlorinated Sulfones and Thiophenes								
	Chloro-2-[illegible] Acid					●		
	Chlorothiophenedicarboxylic Acid					●		
	1,1-Dichlorodimethylsulfone					●		
TOTAL NO. CHEMICALS	93	22	49	44	37	54	20	18

Table 2 Representative Priority Chemicals Assessed in Stand-Alone Documents

CHEMICAL GROUP	PRODUCT CATEGORY								
	Chemical	Chlorine	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Inorganics									
	Cl_2	■							
	ClO_2		■						
	HCl							■	
	Chlorate		■						
	Chlorite		■						
Chlorinated Alkanes[a]									
	Chloroform		■	■		■	■		
	Carbon Tetrachloride			■	■	■			
	Dichloromethane								
	1,1-Dichloroethane		■	■	■	■			
	1,2-Dichloroethane		■	■	■	■			
	Dichloromethane	■	■	■	■				
	1,1,1-Trichloroethane				■				
Chlorinated Alkenes[a]									
	Trichloroethylene			■	■	■			
	1,1-Dichloroethylene				■	■			
	Tetrachloroethylene				■				
	Vinyl Chloride [illegible]					■		■	
	Hexachlorobutadiene						■		
Chlorinated Acids[a]									
	Trichloroacetic acid		■	■					

Table 2 Representative Priority Chemicals Assessed in Stand-Alone Documents

CHEMICAL GROUP	PRODUCT CATEGORY								
	Chemical	Chlorine	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Ketones[a]									
	Trichloroacetone						■		
	Tetrachloroacetone						■		
	1,1-Dichloropropanone		■	■					
	1,1,1-Trichloropropanone		■	■					
	Dichlorocyclopentane-1,2-dione						■		
	3-Chloro-4-[dichloromethyl]-5-hydroxy-2(5H)-furanone		■	■			■		
Chlorinated Benzenes[a]									
	Hexachlorobenzene				■	■			
	Dichlorobenzene			■	■	■			
	1,4-Dichlorobenzene								
	1,4-dichlorobenzene			■	■				
	1,2,4-Trichlorobenzene			■	■	■			
Chlorinated Phenols, Catechols, Guaiacols[a]									
	Pentachlorophenol			■	■	■	■		
	2,4,6-Trichlorophenol		■	■	■		■		
	2,4-Dichlorophenol		■	■	■	■	■		
	Chlorocatechols[a]						■		
	Chloroguaiacols[a]						■		
Chlorinated Nitrogenous Compounds[a]									
	Dichloroacetonitrile		■	■					
	Nitrochloroform		■	■					

Table 2 Representative Priority Chemicals Assessed in Stand-Alone Documents

CHEMICAL GROUP[b]	PRODUCT CATEGORY								
	Chemical	Chlorine	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Aldehydes[a]									
	Trichloroethanol		■	■					
	Chloralhydrate		■	■					
PCDDs/PCDFs[c]				■			■	■	
PCBs[a]									■
Chlorinated Fatty Acids[a]									
	Dichlorostearic acid						■		
Chlorinated Resin Acids[a]									
	Chlorodehydroabietic acid						■		
	Dichlorodehydroabietic acid						■		
Chlorinated Sulfones and Thiophenes									
	1,1-Dichlorodimethylsulfone						■		

[a] Environmental effects to be discussed for the group of chlorinated chemicals in the preliminary list (see Table 1-1).
[b] Human and mammalian toxicity data to be discussed for the chemical group.
[c] 2,3,7,8- substituted dioxin and furan isomers.

Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment

- Vinyl Chloride (VCM) and Polyvinyl Chloride (PVC) -

Report of an Expert Panel

May 26, 1993

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Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment

- Vinyl Chloride (VCM) and Polyvinyl Chloride (PVC) -

Report of an Expert Panel[1]

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[1] This report was prepared, under the direction of the Expert Panel, by CanTox Inc. with supervision by Robert F. Willes, Ph.D. The Expert Panel provided direction in the preparation of the documents and critical scientific interpretation of the issues addressed in each product category document. The documents provide an interpretive review of the significance of observed past, present, and predicted future environmental concentrations of chlorinated organic chemicals to human health and the environment.

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Members of the Expert Panel and Area of Their Expertise

Dr. Elizabeth Delzell, Ph.D., is Professor of Epidemiology, School of Public Health, University of Alabama, Birmingham. Dr. Delzell is an expert in the field of epidemiology and has provided critical review and analysis of the interpretation of the epidemiological and case studies of the chemicals included in the product category documents.

Dr. John Doull, Ph.D., M.D., is Professor of Pharmacology and Toxicology, and Director, Center for Environmental and Occupational Health, University of Kansas Medical Center. Dr. Doull is an expert in human toxicology, and provided critical review and analysis in the areas of mammalian toxicology, metabolism and carcinogenicity of the chemicals included in the product category documents.

Dr. John Giesy, Ph.D., is Distinguished Professor of Fisheries and Wildlife, Michigan State University in East Lansing. Dr. Giesy is an expert in aquatic toxicology, and provided critical review and analysis in the areas of aquatic and wildlife toxicology and the interpretation of natural and anthropogenic sources, environmental concentrations and environmental fate of the chemicals included in the product category documents.

Dr. Donald Mackay, Ph.D., is Professor, Department of Chemical Engineering and Applied Chemistry, and Chairman, Environmental Engineering Program, University of Toronto. Dr. Mackay is an expert in the environmental fate of organic chemicals, and provided critical review and analysis in the area of environmental chemistry and fate, and sources and environmental concentrations of the chemicals included in the product category documents.

Dr. Ian Munro, Ph.D., is President, CanTox Inc. and an expert on toxicology and health safety and highly experienced in dealing with complex regulatory issues related to product safety. Dr. Munro provided critical review and analysis of the major components considered in the safety assessment of the chlorinated chemicals and in the area of regulatory toxicology.

Dr. Gary Williams, M.D., is Director of the American Health Foundation, Valhalla, NY, and a Research Professor, Department of Pathology, New York Medical College, Valhalla, NY. Dr. Williams is an expert on chemical carcinogenicity/mutagenicity, and provided input into the critical area of biochemical aspects of toxicity and carcinogenicity of the chemicals included in the product category documents.

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Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment

- Vinyl Chloride (VCM) and Polyvinyl Chloride (PVC) -

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VRD 0002048887

PREFACE

Over the past two to three decades, concerns about chlorinated chemicals have increased and there are divergent opinions regarding how society should react to the use of these chemicals. Sound scientific information has historically been the driving force behind the identification of concerns regarding the adverse effects of chemicals in the workplace and environment. Similarly, future actions governing the production and use of chemicals by society should also be based on the best possible scientific evaluation of the consequences of their uses with respect to maintaining a viable balance between environmental quality and providing clear benefits to society. Such scientific evaluation requires an understanding of i) the potential for chlorinated organic chemicals to produce adverse effects on the ecosystem, including humans, ii) the contributions of both anthropogenic (*i.e.*, related to human activities) and natural (independent of human activities) sources of chlorinated chemicals to total concentrations versus the environment, iii) the environmental fate of the chemicals that determine the distribution and losses from the environment, and iv) the determination of the degree of anthropogenic activities that could be sustained without exceeding the assimilative capacities of the environment and the occurrence of adverse effects.

In an effort to assist continued progress in the application of sound scientific principles to the assessment of the potential adverse effects of chlorinated chemicals, a series of documents have been prepared, under the direction of an expert panel, that provide a detailed review and interpretive evaluation of the scientific information available on the historical, current and future status of chlorinated chemicals in the environment. The objective of this interpretive review was to provide an overview perspective on the potential adverse effects on the environment of chlorine and chlorinated organic chemicals for eight categories of products that involve specific chlorinated organic chemicals. The product categories identified included: chlorine, polychlorinated biphenyls, vinyl chloride/polyvinyl chloride, chlorinated organic solvents, chlorine disinfection of drinking water/waste water, incineration of chlorinated materials, bleaching wood pulp for production of paper, and the use of chlorine in the development of pesticides. For each of the first seven product categories, an interpretive review of the potential effects on human health and the environment of representative chlorinated chemicals of potential concern has been prepared. For the eighth product category, pesticides, a slightly different approach was adopted which addressed the issue of risk/benefit analysis as applied to the use of chlorine in the development of pesticides. Copies of all documents are available from the Chlorine Institute

The protocol followed in preparation of the seven product category documents has been outlined below.

- A preliminary list of chlorinated chemicals of the greatest concern and of the most relevance to each of the product categories was developed based on published quantitative analytical and hazard data. A total of 93 chlorinated chemicals were identified and were grouped by chemical class (*i.e.*, chlorinated inorganics, chlorinated alkanes, chlorinated alkenes) (see Table 1-1).

- It was beyond the scope and intention of the interpretive review to conduct a detailed assessment of the environmental and health effects of all 93 chlorinated chemicals. The use (*i.e.*, chlorine disinfection) as well as alternatives were examined and considered in the final conclusions regarding the human health and environmental effect of each product category, where information on alternatives were available.

Table 1-1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Alkanes (Continued)	1,2-Dichloropropane		●	●				
	1,2-Dibromo-3-chloro-propane			●				
Chlorinated Alkenes								
	Dichloroethylene		●					
	1,1-Dichloroethylene			●	●			
	1,2-Dichloroethylene (Cis)			●				
	1-2,Dichloroethylene (Trans)			●				
	Trichloroethylene		●	●	●			
	Tetrachloroethylene		●	●	●			
	1,3-Dichloropropene (Cis)			●				
	Pentachloropropene					●		
	Pentachlorobutadiene					●		
	Hexachlorobutadiene			●		●		
	Hexachlorocyclopentadiene			●				
	Hexachlorohexatriene					●		
	Vinyl Chloride			●	●		● (monomer)	
PVC								
	Polyvinyl Chloride						●	
Chlorinated Acids								
	Monochloroacetic Acid	●	●					
	Trichloroacetic Acid	●	●					

Table 1-1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Phenols, Catechols, Guaiacols								
	2-Chlorophenol	●	●	●				
	2,4-Dichlorophenol	●	●	●	●	●		
	2,6-Dichlorophenol					●		
	2,4,5-Trichlorophenol			●	●			
	2,4,6-Trichlorophenol	●	●	●		●		
	2,3,4,5-Tetrachlorophenol			●		●		
	2,3,4,6-Tetrachlorophenol		●	●		●		
	Pentachlorophenol		●	●	●	●		
	Tetrachlorophenol					●		
	Dichlorocatechol					●		
	Tetrachlorocatechol					●		
	Trichlorocatechol					●		
	3,4,5-Trichlorocatechol					●		
	4,5-Dichloroguaiacol					●		
	Dichloroguaiacol (other isomers)					●		
	Tetrachloroguaiacol					●		
	Trichloroguaiacols					●		
	Trichlorodihydroconiferyl Alcohol					●		
	Chlorovanillin					●		
	Trichlorovanillylalcohol					●		
	Trichloroacetosyringone					●		
	Dichloro-3,4-dihydroxy-proplophenone					●		

Table 1-1 Preliminary List of Chemicals of Concern Per Product Category

CHEMICAL GROUP	PRODUCT CATEGORY							
	Chemical	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated PCDDs, PCDFs (Continued)	1,2,3,4,6,7,8-H_7CDF		●		●	●	●	●
	1,2,3,4,7,8,9-H_7CDF		●		●	●	●	●
	O_8CDF		●		●	●	●	●
PCBs								
	PCBs							●
Chlorinated Fatty Acids	Dichlorostearic Acid					●		
Chlorinated Resin Acids	Chlorodehydroabietic acid					●		
	Dichlorodehydroabietic acid					●		
Chlorinated Amines	3,3'-Dichlorobenzidine			●				
	4,4'-methylene-bis-(2-chloroaniline)			●				
Chlorinated Ethers	Bis(2-chloroethyl)ether			●				
Chlorinated Sulfones and Thiophenes								
	Chloro-2-thiophenic Acid					●		
	Chlorothiophenedicarboxylic Acid					●		
	1,1-Dichlorodimethylsulfone					●		
TOTAL NO. CHEMICALS	93	22	49	44	37	54	20	18

Table 1-2 Representative Priority Chemicals Assessed in Stand-Alone Documents

CHEMICAL GROUP	PRODUCT CATEGORY								
	Chemical	Chlorine	Drinking Water	Waste Water	Solvents	Incineration	Pulp & Paper	PVC/VCM	PCBs
Chlorinated Ketones[a]									
	Trichloroacetone						■		
	Tetrachloroacetone						■		
	1,1-Dichloropropanone		■	■					
	1,1,1-Trichloropropanone		■	■					
	Dichlorocyclopentene-1,2-dione						■		
	3-Chloro-4-[dichloromethyl]-5-hydroxy-2(5H)-furanone		■	■			■		
Chlorinated Benzenes[a]									
	Hexachlorobenzene				■	■			
	Dichlorobenzene			■	■	■			
	1,4-Dichlorobenzene								
	1,4-dichlorobenzene			■	■				
	1,2,4-Trichlorobenzene			■	■	■			
Chlorinated Phenols, Catechols, Guaiacols[a]									
	Pentachlorophenol			■	■	■	■		
	2,4,6-Trichlorophenol		■	■	■		■		
	2,4-Dichlorophenol		■	■	■	■	■		
	Chlorocatechols[b]						■		
	Chloroguaiacols[b]						■		
Chlorinated Nitrogenous Compounds[a]									
	Dichloroacetonitrile		■	■					
	Nitrochloroform		■	■					

VINYL CHLORIDE MONOMER (VCM) AND POLYVINYL CHLORIDE (PCV)

EXECUTIVE SUMMARY

This document focuses on the interpretation of the potential adverse effects of vinyl chloride monomer (VCM) and polyvinyl chloride (PVC) on human health and the environment. Potential secondary effects related to pyrolysis products from VCM and PVC are addressed in the Product Category document entitled "Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment - Incineration of Chlorinated Chemicals -". The assessment of the potential adverse effects of VCM and PVC has been based on the application of the dose-response principles that govern the actions of chemicals on biological systems as outlined in a document entitled "Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment - Introduction and Methods -".

The overall conclusions of the interpretive review of the available information on VCM and PVC are:

i) No potential adverse effects to public health or the general environment would occur from PVC. The primary concern regarding PVC relates to occupational exposures to PVC dusts arising from the use of PVC materials in manufacturing processes.

ii) Historical (pre-1970s) concentrations of VCM in work environments of production/manufacturing facilities were excessive (in the range of 100 to 1000 ppm), and resulted in increased risks of liver angiosarcoma in workers.

iii) Although no data were identified on the concentrations of VCM in air at locations remote from production/manufacturing facilities, based on the concentrations reported near such facilities and the rapid rate of disappearance half-life of VCM in ambient air, the concentrations of VCM in air in remote locations would be expected to be infinitesimal.

iv) Following an in-depth, detailed review of the available epidemiological information on VCM, Sir Richard Doll (1988) concluded that "according to any reasonable criterion, the hazard to the general public (if there is any at all) must be negligible" from VCM exposures at locations remote from VCM production/manufacturing facilities. This conclusion is in agreement with the prediction that the concentrations of VCM in air in remote locations would be infinitesimal, and substantially less than current analytical detection limits (< 5 ppb).

v) With the exception of spills related to transportation and use, and accidental releases from point sources, the predicted risks to populations assumed to be constantly exposed to the detection limit for concentrations of VCM in air (< 5 ppb as reported in the mid-1980s within a few hundred meters of production/manufacturing facilities), would be in the range of one per million to one per 10 million.

vi) The implementation of non-emissive technologies would be expected to diminish the already undetectable concentrations of VCM in air near production/manufacturing facilities, and thereby further diminish the already infinitesimal, and unmeasurable potential risk to human health and the general environment. However, continued product stewardship is required to ensure spills and accidental releases are controlled to prevent the future occurrence of adverse effects to human health or the environment.

The supporting evidence for this conclusion is based on an assessment of sources, environmental fate, hazard potential and environmental concentrations of PVC and VCM.

Physical/Chemical Properties and Environmental Fate

PVC is a polymer of VCM, and is a very stable, solid material that is relatively inert chemically, environmentally and biologically. PVC does not depolymerize or degrade under natural environmental conditions. One of the historical concerns of the presence of non-polymerized VCM in PVC products has been largely addressed by modified manufacturing and production techniques. Under good manufacturing procedures, the residual concentration of VCM in modern PVC products is below analytical detection limits.

VCM (also referred to as chloroethene, chloroethylene or monochloroéthylene) is a molecule of two carbon atoms joined by an unsaturated bond and containing three hydrogen atoms and one chlorine atom. VCM has a high vapor pressure and is slightly soluble in water, consequently volatilization into the atmosphere is the major transport process in the environment. VCM is reactive, and readily polymerizes in the presence of oxygen, sunlight or heat to form PVC. VCM rapidly degrades in the troposphere *via* photochemical oxidation. As indicated by the low log K_{ow} of 1.38, VCM does not adsorb to organic carbon of soils/sediments or accumulate in biological tissues. Certain strains of microorganisms (*e.g.*, *Mycobacterium*) can use VCM as a carbon and energy source under aerobic conditions. Biological degradation of VCM to CO_2 can occur under both aerobic and anaerobic conditions.

Hazard Potential of VCM

As with other chemicals, the potential for adverse effects of VCM depends on the concentrations that occur in target tissues within the body where adverse effects develop. These tissue concentrations depend on the bioavailability of the chemical from various environmental media through different routes of exposure.

At room temperature, VCM is a gas. As such, inhalation is the most significant route of exposure in the environment and in occupational settings. VCM is readily and rapidly absorbed by the lung and readily metabolized to the reactive epoxide intermediate, chloroethylene oxide, which can rearrange spontaneously to chloroacetaldehyde, then undergo further metabolism. VCM does not accumulate in tissues.

VCM is not a potent acute toxic agent, and acute lethality is not observed until air concentrations reach 113,000 to 230,000 ppm (294 to 595 g/m^3). At these high exposures VCM acts as a narcotic or anaesthetic agent. In addition, at acutely toxic doses, tissue damage to lung, liver and kidneys has been observed. Following repeated, non-lethal exposures, the principal target organ for VCM is the liver. VCM was not found to be teratogenic in a number of laboratory studies on mammals.

VRD 0002048894

Evidence for the carcinogenicity of VCM in animals is conclusive based on positive data from numerous laboratory studies on animals. Both IARC and the U.S. EPA have concluded that there is sufficient evidence for VCM carcinogenicity in humans based upon the epidemiological data on workers exposed to high concentrations between the 1940s and late 1960s. VCM exposure has been associated with the development of a specific cancer (angiosarcoma) of the liver. There is disagreement in the reported literature regarding the potential for VCM to produce other types of cancer; however, there of some evidence for such concerns among persons with extreme exposures such as those that occurred historically in occupational settings.

The results of *in vitro* mutagenicity studies and observations of chromosomal aberrations in peripheral blood lymphocytes in workers indicate a DNA-reactive mechanism for the mutagenicity/carcinogenicity of VCM. VCM has also been shown to be activated, via P450 enzyme systems, to a reactive epoxide intermediate that is believed to result in alkylation of DNA.

Sources and Environmental Concentrations

The majority of VCM is produced for use in the production of vinyl chloride homopolymer and copolymer resins. VCM is also used to a lesser extent as a component in the synthesis of methyl chloroform and as a co-monomer with vinylidene chloride to produce resins. A former use of VCM was as a propellant in aerosol cans and as a refrigerant. PVC resins manufactured from VCM are used in the manufacture of a variety of industrial and commercial products ranging from building materials to household and medical items.

Undefined quantities of VCM can be produced from biotic and abiotic transformation of chlorinated solvents such as 1,1,1-trichloroethane and 1,1-dichloroethane. 1,1,1-Trichloroethane and 1,1-dichloroethane both have a number of anthropogenic and natural sources. The natural sources of these VCM precursors suggest that there may be sources of VCM produced by natural processes independent of human activities, although such sources have not been unequivocally identified to date.

The primary source of VCM in the environment is from emissions and effluents from VCM and PVC production and manufacturing facilities. Such releases rapidly volatilize into the atmosphere. Since 1979, VCM emissions from production facilities have been regulated in both Canada and the United States. Prior to 1975, it was estimated that PVC plants released 22.7 million kg of PVC and 110 million kg/year of VCM into the environment in the United States. Implementation of regulatory standards have substantially reduced total environmental releases of VCM and PVC, and currently the major sources are from accidental releases and spills.

The concentrations of VCM in air are greatest near industrial facilities involved in its production and use in various manufacturing processes. Average concentrations of VCM in air in the late-1970s were 44 $\mu g/m^3$ near production facilities for Houston, Texas, and 10 to 40 $\mu g/m^3$ near facilities in England. Air concentrations near production facilities were generally below analytical detection limits (< 13 $\mu g/m^3$ or 5 ppb) by the mid-1980s. In the work environment, air concentrations of VCM have decreased over the years with the reduction of emissions through improved operating technologies. Workplace concentrations in the Netherlands decreased from approximately 1000 ppm in 1945-1955 to 5 ppm after 1975 (Barnes, 1980), and data from the late 1980s to the present indicate workplace air concentrations generally <0.1

ppm with occasional values near 1 ppm in specific production/handling areas. Since production and manufacturing facilities are major sources of VCM, decreases in workplace concentrations would be expected to coincide with decreases in environmental releases. This relationship is supported by the declining environmental concentrations of VCM reported near production and manufacturing facilities observed between the 1970s and early 1980s.

Potential Significance of Environmental Concentrations of VCM

The available information on the physical/chemical properties, environmental fate characteristics and sources of VCM indicate that the major environmental concerns for VCM come from exposures of production and manufacturing workers and possibly populations living near such facilities. There would be little opportunity for exposures, and therefore risks of adverse effects, to the general public, or aquatic and terrestrial wildlife from VCM at locations distant from production and manufacturing facilities. As outlined above, the air concentrations near such facilities (within a few hundred meters) were historically in the range of 10 - 40 ppb in the mid-1970s, and had decreased to values below detection limits ($< 13\ \mu g/m^3$ or 5 ppb) by the mid-1980s. Based on current concentrations of VCM in air in the work environment (generally in the range of 0.1 to 0.2 ppm), the concentrations near facilities would be expected to be substantially less than analytical detection limits at the present time, and in the future.

The characterization of the potential health risks that could result from exposures to such concentrations of VCM in air requires the comparison of resulting levels of exposure against a cancer potency estimate. The U.S. EPA has, over the years, proposed cancer potency slope values for VCM of 0.0174, 0.0295 and 2.3 (mg/kg body weight per day)$^{-1}$, based on lung and liver tumors, respectively, following inhalation exposure to up to 30,000 ppm VCM and oral exposure to 0-17 mg/kg body weight/day (5 days/week) in laboratory rats. These cancer potency slopes translate into RsD (Risk Specific Dose) values of 0.575, 0.339 and 0.00435 μg/kg body weight/day at a lifetime risk of one per 100,000, a range of 132-fold, based on available laboratory information and the EPA risk assessment approach.

Cancer potency factors estimated from epidemiological studies of workers exposed to VCM in the 1940s, 1950s and 1960s, range from 0.00024 to 0.000024 (mg/kg body weight/day)$^{-1}$. These estimates assume exposures to 100 to 1000 ppm VCM resulted in a mortality incidence due to liver cancer of 2 per 100. The cancer potency estimates derived from the epidemiological data would translate into RsD values of approximately 42 to 420 μg/kg body weight/day at a lifetime risk of one per 100,000. These exposure limits are starkly different from the greatest potency value proposed by EPA, and indicate that VCM is less potent by some 9500- to 95000-fold. Such large differences in estimates of cancer potency, using different data and approaches, result in equivalent differences in the risk estimates, and therefore, in the interpretation of the potential significance of the environmental concentrations of VCM near production/manufacturing facilities.

Risk estimates based on the EPA values range from approximately 15 to 7700 per 100,000 for the air concentrations of VCM near production facilities in the mid-1970s, and from 7.4 to 980 per 100,000 for the mid-1980s air concentrations of VCM near production facilities. Risk estimates based on the epidemiological data range from 0.08 to 0.2 per 100,000 for the mid-1970s air concentrations, and from 0.01 to 0.1 for the mid-1980s air concentrations.

Based on a critical evaluation of the available epidemiological evidence available from workers exposed to VCM between the early 1940s and the 1960s, Doll (1988) concluded that potential risks from VCM to the "general public (if there is any at all) must be negligible". This conclusion is in agreement with the risk assessment summarized above using cancer potency estimates based on epidemiological data. Based on the environmental fate of VCM, the potential health risks to the general public in regions remote from VCM production and manufacturing facilities would be even more negligible, and certainly unmeasurable using conventional epidemiological study approaches. The maintenance of procedures for non-emissive uses of VCM and strict attention to operations to avoid accidental releases are needed to ensure that the current status of no adverse effects on human health and the environment is maintained. In the future, improved production and manufacturing control technologies and attention to accident prevention, in keeping with policies of progressive product stewardship, will continue to reduce emissions of VCM from production and manufacturing facilities, thereby further reducing the already negligible and unmeasurable risks predicted from current environmental concentrations of VCM near production and manufacturing facilities.