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Chlorine Gas Exposure & Trees

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Chlorine is both a useful element and a dangerous element. Chlorine is an essential element in trees. It is found in thousands of natural and manmade compounds and materials. Chlorine is essential for both human thought and activating pesticides. Living things use chlorine and generate thousands of different organic compounds. Animal immune systems incorporate chlorine into natural materials to fight infections. Chlorine-containing organic materials are released every day from decaying plant materials. Organo-chlorines are also generated when plant materials are burned. Earth's volcanoes emit chlorine materials. Some minerals contain chlorine. We are surrounded by a chlorine recycling geology and ecology which is essential to our lives.

Sometimes chlorine in the environment reaches a dosage or exposure level where it can impact trees and other landscape plants. This review examines chlorine gas (Cl_2) impacts on trees and their supporting landscapes. This is not a toxicology or environmental dosage review, but is designed to help tree health care professionals understand potential injuries sustained by trees and other landscape plants when exposed to chlorine gas.

History

The element chlorine is a constituent of the Earth's crust. In nature, chlorine is always combined with something else. Major minerals containing chlorine include: sodium chloride (table salt), carnallite (potassium magnesium chloride), and sylvite (potassium chloride). The element chlorine was discovered in 1774 and named in 1810. Because chlorine in a pure gas form (Cl_2) is greenish-yellow in color, its name was taken from the Greek "khloros" which means a greenish-yellow color (chlorophyll shares the same root word origin.) Chlorine was found to disrupt and destroy cell membranes and cell wall components, especially in bacteria and viruses. Human and animal health benefit uses of chlorine are numerous. Chlorine has been used as a disinfectant since 1846.

It's A Gas

Chlorine (Cl_2) is a yellow-green poisonous gas. Chlorine can exist in four isotopes, two stable, one long-lived (~300,000 years), and one short-lived. Chlorine gas is very reactive in pure form. Chlorine belongs to an element family (group) called the halogens which include fluorine, chlorine, bromine, and iodine. Halogens are almost always bound to another element which makes them easier to handle. Chlorine boils at -29^{o}F (-34^{o}C), and so, is a gas at room temperature. Chlorine gas is 2.3 times heavier than air, which means at room temperature it sinks and flows along the ground and into low places. Table 1. Humans make chlorine by taking salt water and running an electric current through it. The result is chlorine, sodium hydroxide (caustic soda), hydrogen, and oxygen.

Use & Value

Chlorine is used in medicines, disinfectants, plastics, pesticides, bleaches, polyesters, computer chips and paper making. Chlorine can be found in a mirror's reflectant surface, wood cabinet finishes, wall covering, carpet, deodorant, cosmetics, food packaging, and toothpaste. Our quality of life depends upon this almost universal manufacturing aid and ingredient – chlorine.

Chlorine & Trees

Chlorine is an essential element in trees. Chlorine is a common ion in many soils and can be a constituent in precipitation (i.e. both pollution and sea salt sources). Deficiency is rare, but toxicity is common. Chlorine is freely taken up by trees. Within a tree, chlorine can show the greatest variability of toxicity concentrations of any essential element, as much as 8,000 times. Many fertilizers use a chlorine containing salt to carry essential elements (i.e. KCl, $CaCl_2$, $MgCl_2$, and NH_4Cl). These salts can cause toxicity problems from root desiccation, as well as too high of chlorine concentration. Toxicity symptoms include shoot and root damage and death, and leaf marginal distortion, death, and premature abscission. Chlorine will readily leach from most soils.

Trees require small amounts of chlorine for a variety of uses. Chlorine is primarily associated with water control and photosynthesis. Chlorine is positioned to move water through tissues (i.e. an osmoticum). Chlorine and potassium (K) are used to open and close guard cells around stomates. Chlorine is part of the initial proton, electron, and oxygen generating step of photosynthesis (LHCII) along with manganese (Mn). Chlorine helps activate the proton gradient production rotor of ATP on cell membranes. It is found in many organic materials in trees. Chlorine also has limited disease resisting attributes.

Chlorine deficiency is rare in trees. Chlorine deficiency leads to tissue stunting. Tree leaves show marginal yellowing, wilting, distortion (curling / cupping) and death. Young tree shoots, roots, and leaves are especially vulnerable to damage. Roots will present with a stubby, thickened appearance. At the onset of chlorine deficiency, tree leaf tissue color will shift to more blue-green and then bronze.

Changing States

We are surrounded with chlorine compounds in our environment. Low temperature burning and smoldering fire conditions form (and reform) many compounds. Some compounds formed when organic materials and other chlorine containing materials are openly burned are dioxins, furans, particulate matter (which can carry materials like chlorine), and PAHs (polycyclic aromatic hydrocarbons). These are all air pollutants. The United States EPA estimates unregulated trash burning is a major source of dioxins in the environment.

Blowing In The Wind

When cool chlorine gas is released into the atmosphere it tends to stay close to the ground. Air temperature chlorine gas in a stable atmosphere will stay together and follow land contours, accumulating in low places and over the surface of lakes and streams. Any breeze or an unstable atmosphere tend to quickly dilute chlorine with surrounding air and dissipate it downwind. Any chlorine gas which is warm from a fire or from smokestacks will tend to rise into the atmosphere and eventually be mixed and diluted. A chlorine gas plume can be seen for many miles downwind.

Transformed

In a warm atmosphere, chlorine gas quickly begins a transformation into other products. The first atmospheric reaction is splitting chlorine gas into chlorine atoms: $Cl_2 + \text{sunlight} = Cl + Cl$. Bright sunlight is

symbol	gas	times heavier
Cl_2	chlorine	1.0X
CO_2	carbon dioxide	1.6X
O_2	oxygen	2.2X
N_2	nitrogen	2.5X
air	atmosphere	2.3X

X = number of times heavier chlorine gas (Cl_2) is compared to listed gas

Table 1: Relative weight of atmosphere and select gases compared with chlorine gas (Cl_2).

rich in wavelengths less than 475nm which have enough energy to separate the atoms in chlorine gas. Once chlorine atoms are separated, each atom usually reacts with one of three other materials. These three reactions are the dominant ways chlorine interacts with the atmosphere surrounding landscapes. Chlorine atoms can combine with hydrogen (H_2), methane (CH_4), or water (H_2O), with each forming hydrochloric acid (HCl) as one product. Figure 1. Chlorine gas in the atmosphere is quickly removed by its chemical transformations, especially under high humidity and sunlight.

Removed

Chlorine gas is also removed from the atmosphere by three other means: in rainfall; absorbed onto particulate matter surfaces; and, direct uptake at the soil surface. The soil surface, especially when moist, provides many reactions which destroy chlorine gas and generate chlorides. Chlorides can build up in soil but then can be rinsed away. The chemical reactions which produce chlorides, as well as any water used to rinse chlorides out of the soil, will initiate the loss of valuable tree-essential elements like calcium, magnesium, potassium, and nitrate-nitrogen from soil. Figure 2. All these reactions involving chlorine gas assures its removal from the landscape-atmosphere system in less than three weeks under the worst conditions. Under perfect weather conditions, chlorine gas can be removed from the landscape atmosphere in two days.

Whiff Of Death

Chlorine in the environment is quickly dissipated, chemically bound, and compartmentalized. Sunlight, organic matter in the soil, iron and manganese in soil, nitrogen fertilizers, good soil aeration, clay soils, and plenty of soil water help minimize impacts of chlorine. Figure 3. Living things like trees can be damaged by chlorine gas.

The circumstances surrounding exposure concentrations and duration of exposure (dosage) will determine the extent of damage to trees and landscapes. Table 2 provides a list of impact factors which influence chlorine gas exposure damage within a landscape. Note many different combinations of conditions can interact to minimize or maximize exposure and damage.

In addition to site conditions, some plant species tend to be more suseptable than other species to chlorine gas. Table 3 lists relative species tolerances to chlorine gas. Not all plants are damaged by chlorine gas to the same degree. Some plants develop fewer and less intense symptoms for the same level of exposure. The closer to the ground plant foliage grows, the more likely it is to be damaged. Note, because of dosage and circumstance differences, some plants are cited as both sensitive and tolerant.

Tree Reactions To Chlorine Gas Exposure

Tree reactions to chlorine gas, and associated injuries, are as varied as the circumstances and exposure. Generally in a tree, foliage has the most sensitive tissue with no inherent buffering or shielding, like soil-surrounded roots. The photosynthetic system in a tree leaf is most sensitive. The first few minutes of exposure causes enough damage to shut down the leaf. Foliage wilts upon exposure. It is important to not water during the gas exposure period as this will tend to keep stomates open and cause more damage. Spraying antitranspirants during the exposure period can reduce damage if the antitranspirant material is removed promptly after chlorine gas exposure. Antitranspirants will have the greatest positive impact on small, shaded trees.

in atmosphere

$$Cl_2 \text{ (in sunlight)} = Cl + Cl$$

$$Cl + H_2 = HCl + H$$

$$Cl + CH_4 = HCl + CH_3$$

$$Cl + H_2O = HCl + O_2$$

Figure 1: Chlorine gas interacts and is removed from the atmosphere in three primary processes. Chlorine atoms combine with hydrogen (H_2), methane (CH_4), or water (H_2O) with each forming hydrochloric acid (HCl) as one of the products.

Tree Essential Elements Potentially Lost From Soil By Cl_2 / Chloride Rinsing	
nitrogen	(N)
potassium	(K)
calcium	(Ca)
magnesium	(Mg)
phosphorus	(P)
sulfur	(S)

Figure 2: Chloride formation in soil, and water used to rinse chlorides from soil, will cause the loss of many valuable tree-essential elements.

Lower Cl_2 Levels

1. **sunlight impact at soil surface.**
2. **iron & manganese oxidation.**
3. **binding onto organic materials.**
4. **binding into nitrogen containing compounds.**
5. **hydrochloric acid formation and nitrogen gas release**
6. **free chlorine remains available in soil water**

Higher Cl_2 Levels

Figure 3: Soil reactions which minimize free chlorine content in soil water as chlorine exposure increases.

impact factor	*comments on potential damage*
concentration in air	damage starting at 0.1 ppm & severe by 5.0 ppm
distance from source	closer to the source, the higher the concentration in air
duration of exposure	longer duration means more damage
meteorological conditions	warm, clear, bright, still, humid, high pressure, and inversions increase damage potential
topography	gas flows along ground settling into low areas
soil moisture	more soil moisture, more damage through open stomates
time of year	Spring during expansive growth is most potentially damaging season of exposure, followed by remainer of growing season
species	some species more sensitive
maturity of tissue	older, mature, & active tissues are prone to injury
health of tissue	other stresses prevent effective reactions to any new damage

Table 2: List of factors which influence chlorine gas exposure damage in a tree-filled landscape.

Common Names of Landscape & Garden Plants Cited As Tolerant:

arborvitae, autumn olive, azalea, beech, begonia, birch, boxelder, cactus, chrysanthemum, corn, cowpea, daylily, dogwood, eggplant, English ivy, fir, geranium, grass, hemlock, holly, iris, Japanese maple, red maple, English oak, red oak, oxalis, pear, pepper, pigweed, pine, Southern magnolia, spruce, soybean, tobacco, yew.

Common Names of Landscape & Garden Plants Cited As Sensitive:

alfalfa, amaranthus, apple, ash, aspen, azalea, barberry, bean, beech, birch, blackberry, black gum, boxelder, buckeye, catalpa, cherry, chickweed, coleus, corn, cosmos, crabapple, crapemyrtle, cucumber, dandelion, deodar cedar, dogwood, elder, elm, forsythia, grape, hibiscus, honeysuckle, hydrangea, juniper, larch, morning glory, mulberry, mustard, onion, peach, petunia, phlox, pin oak, jack pine, loblolly pine, shortleaf pine, slash pine, Virginia pine, white pine, poison ivy, pokeweed, poplar, primrose, privet, radish, redbud, rhododendron, rose, sassafras, serviceberry, silver maple, striped maple, sugar maple, spruce, sunflower, sweetgum, tobacco, tomato, tree-of-heaven, tulip, viburnum, violet, Virginia creeper, willow, witchhazel, yellow poplar, yellowwood, zinnia.

Table 3: List of relative species sensitivity to chlorine gas (Cl_2) cited in research literature by common name. Note, because of cited dosage and circumstance differences, some plants are listed as both sensitive and tolerant.

Developing Symptoms

After an exposure event, damage will be visible as many minute necrotic or discolored points across the leaf surface. This stippling or flecking can appear similar to mite or sucking insect damage. As damage accumulates and other organisms take advantage of injuries to enter leaves, damage will tend to be concentrated at leaf margins and between veins in mature and active leaf blades. Later onset symptoms include necrotic, bleached or brownish colored areas or spots. Leaf veins are the last to show damage. Scorching or bleaching will be concentrated initially at the tips and along the edges of leaves.

Older mature leaves will be more prone to damage than younger leaves. Young leaves not yet expanded and leaves enclosed within expanding buds usually show little damage from low exposure doses. Older leaf symptoms may include a spotty bleached appearance and sunken wet-looking spots. Needles can develop tip dieback. In pines, the newest active needles show significant damage while older needles show significant damage and drop-off. If damage is too great, leaves may senesce (systematic shut-down of living systems) and abscise (break-off and fall.)

Damage Forms

Tree reactions to chlorine gas can take many forms. Reactions can be summarized into four primary reactions:

1) a tree accidentally avoids chlorine gas by season of year, topographic position, crown height, etc.;
2) a tree tolerates chlorine gas by detoxifying, oxidizing, compartmentalizing, or incorporating (a stress);
3) a tree shows an temporary (elastic) strain by changing physiological functions;
4) a tree shows a permanent (plastic) strain from injury.

A Cute Leaf

Acute chlorine damage in trees is primarily confined to leaves, buds, and rarely tissues beneath lenticels on twigs. Chronic exposure leads to a buildup of various chlorides in tissues and on surfaces. Close to the chlorine gas source, or at high exposure dosages, leaves are killed, browned, and stay attached to the tree for some time. Figure 4. Leaf tissue at high exposure dosages can present bleaching within 24 hours and can be dead within 48 hours. Under high chlorine gas concentrations, buds are also killed and brown-out. Twig tissues are damaged at higher concentrations and exposure durations. As concentrations and durations of exposure build, whole trees can be killed. Figure 5.

Low to moderate acute exposures to chlorine gas initiate tree reactions at the site of contact on the tree, not systematically. As concentration of chlorine gas declines, and as distance from the source lengthens, most tree reactions to chlorine gas are exclusively concentrated in the leaves. Figure 6. Whether trees hold or lose their leaves, they are more prone to other pests and stresses after chlorine gas caused damage.

At low doses, no visible damage may occur, but over the next few months of the growing season leaf epinasty can occur. Epinasty is the twisting, cupping, or curling of developing leaf blades and petioles. Even though no visible injury was sustained, exposure has initiated growth disruption through auxin transport damage and generation of ethylene.

Seasons

Tree reactions to moderate and low exposure dosages of chlorine gas generate a series of symptoms which change over time and can progress from one set of reactions to the next. Tree reactions will also vary by

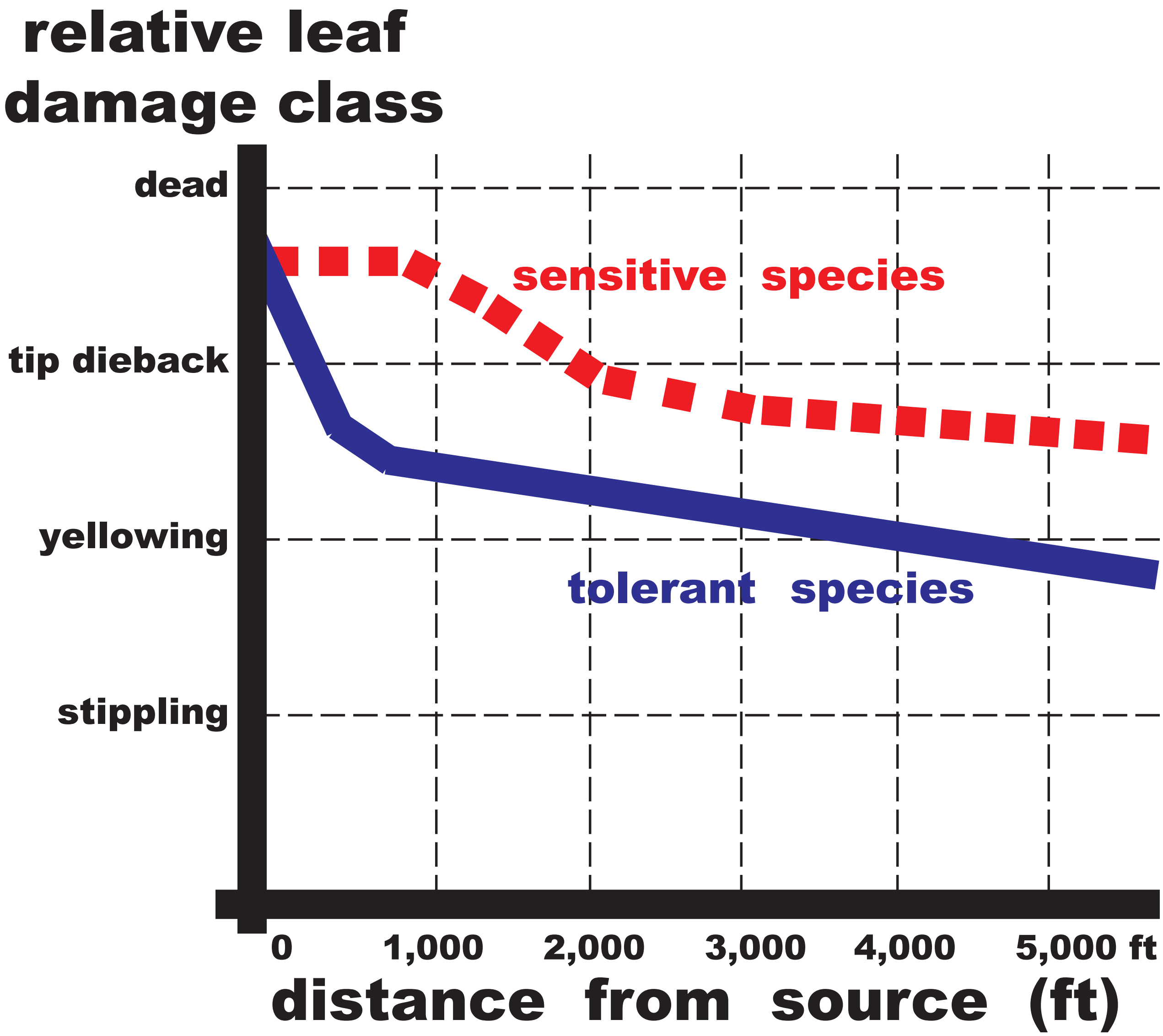

Figure 4: Historic leaf injury present for a sensitive and tolerant gymnosperm species downwind of a chlorine gas source two months after exposure.
(after Schreuder & Brewer, 2001)

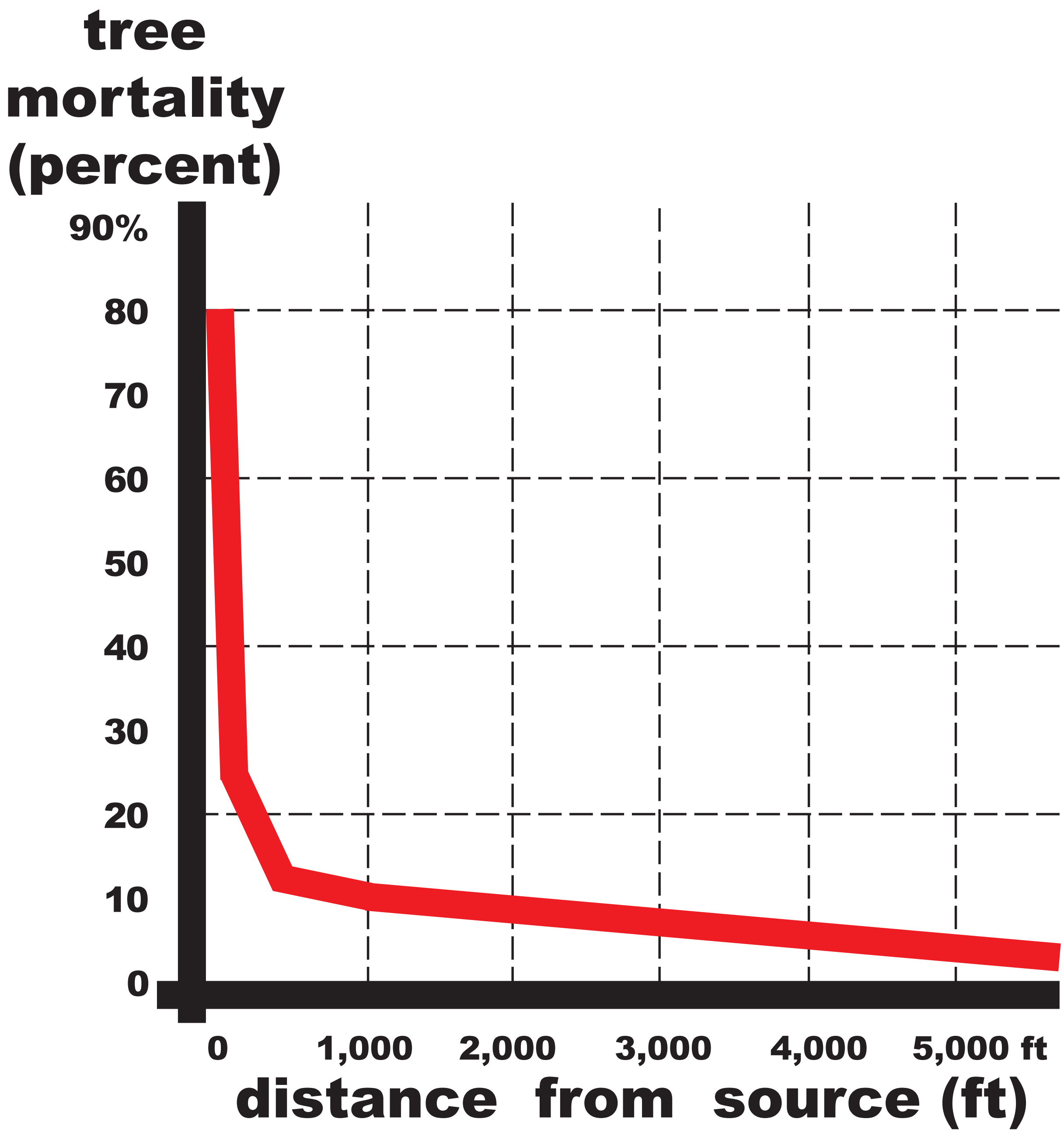

Figure 5: Historic mortality curve for a sensitive gymnosperm species downwind of chlorine gas source three years after exposure.

(after Schreuder & Brewer, 2001)

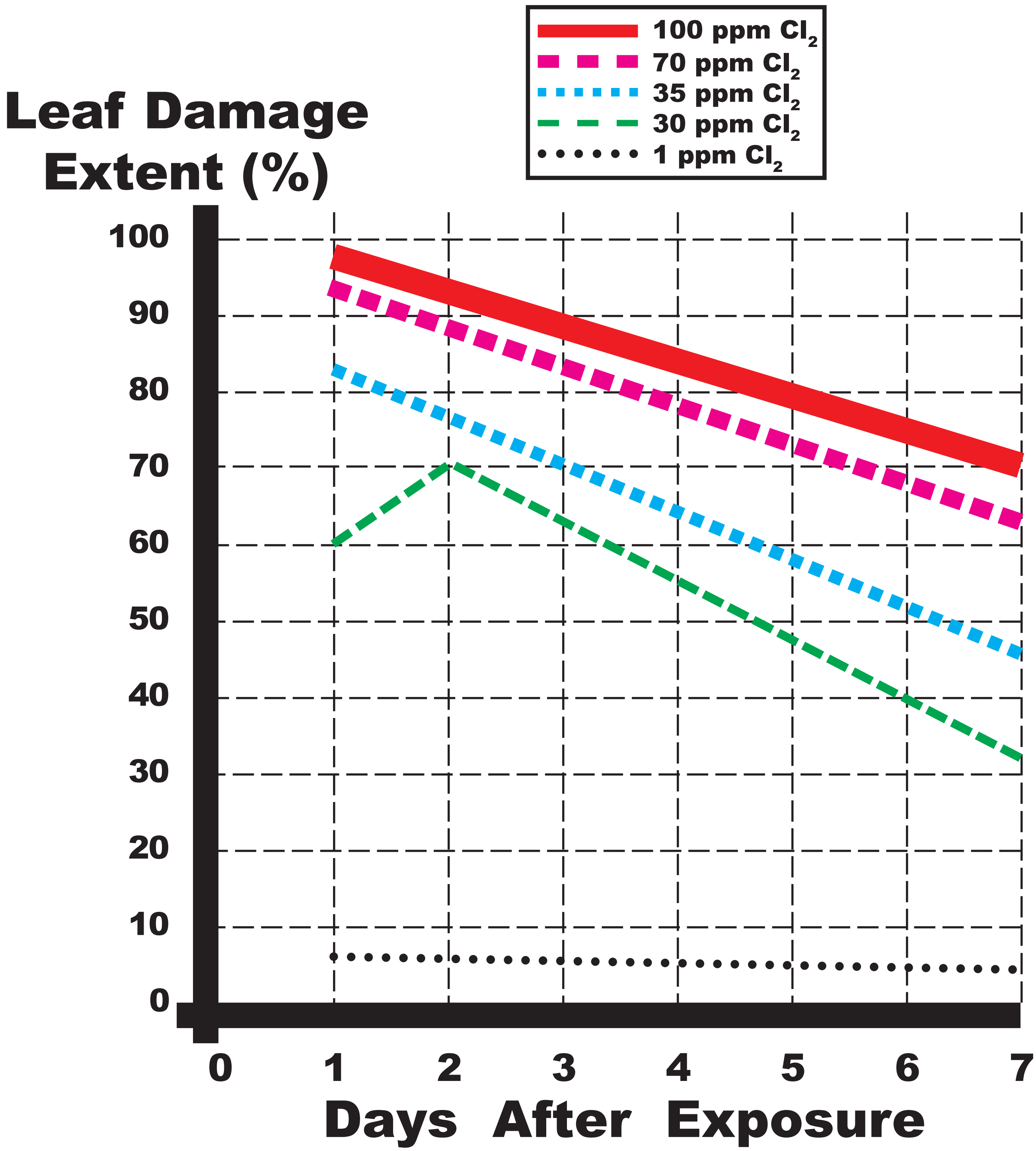

Figure 6: Laboratory chlorine exposure experiment examining plant leaf damage (100% is complete leaf damage and 0% is no leaf damage) over a one week period at five initial chlorine gas concentrations. Total chlorine gas exposure duration was 10 minutes. (after Griffiths & Smith, 1990).

tree life-stage and season. If leaves are not present, less visible reactions occur and less injury can result. The Spring time period when leaves are expanding is the worse time of year for exposure. The next most critical time for exposure is any time in the rest of the growing season after full leaf expansion.

Foliage damage in late Summer and Fall may have relatively less impact because exposure accelerates normal senescence and abscission processes. The Winter dormancy period, with accompanying lower temperatures, no deciduous foliage, and trees in a resting phase provides the least potential injury. Evergreen trees under warm day and night temperatures can be severely damaged even in Winter. Older-aged needles are lost first. Figure 7.

Damage Trail

Chlorine gas exposure can be seen to follow a distinct and rapid damage pathway in tree leaves. The first damage is on the underside of leaves in cells surrounding stomates. Damage is next apparent in leaf mesophyll (photosynthetically active) cells adjacent to air spaces just inside stomates. Cellular damage will continue to expand through more and more mesophyll cells. The next impacts can be seen in the more densely packed leaf palisade cells in contact with injured mesophyll cells.

Damage next appears on both upper and lower leaf surfaces. All thin-walled cells of the leaf begin to crumple and collapse, forming more air spaces just below the tough epidermis (surface) cell layer. Water begins to accumulate in open spaces and appear to saturate leaf tissues. Finally, epidermal cells start to pull apart from each other. As the damage progresses through a leaf, veins are the last affected.

Acid & Bleach

Chlorine gas is absorbed into the water layer covering mesophyll cell walls inside leaves. As chlorine gas is dissolved in this water, hydrochloric acid (a strong acid (HCl)) and hypochlorous acid (a bleaching agent (HOCl)) are formed. Cell wall areas enclosing living tissues become highly acidic. The pH of this water has been measured as low as a pH of 1.8 after chlorine gas exposure, which is similar to battery acid. Water on the exterior surfaces of a leaf do not have a significant impact on leaf damage. Figure 8. As the leaf initially sustains damage, stomates are closed and wilting occurs -- which tends to reduce further leaf damage.

Death By Chlorides

Living cells in leaves attempt to oxidize chlorine into chlorides as long as food supplies are available and membrane permeability remains stable. Any chlorides produced are pushed out of the cells and passively transported to evaporating surfaces such as leaf tips, edges and stomates. These chlorides can build-up, representing high salt loads on leaf surfaces. Chlorides pull water out of living cells causing severe desiccation and more physical distortion of cells. Chloride accumulations in soil are particularly damaging to tree roots and disrupts water uptake. Ephemeral absorbing roots are damaged by acids and chlorides.

Dying Cells

Internal damage accelerates with increasing exposure, involving more biological and structural systems within a leaf. Generally, damage from chlorine gas starts with a reduction in photosynthesis and an accumulation of acidity, bleaching and oxidized products in a leaf. The drier a leaf is internally when exposed, the less damage it sustains because its stomates are more likely to be closed. Drought conditions leading into and during exposures reduce potential damage from chlorine gas entrance into a leaf. Once chlorine gas does enter a leaf, less internal water can lead to higher concentrations and less dilution of damaging agents which, in turn, leads to increased damage.

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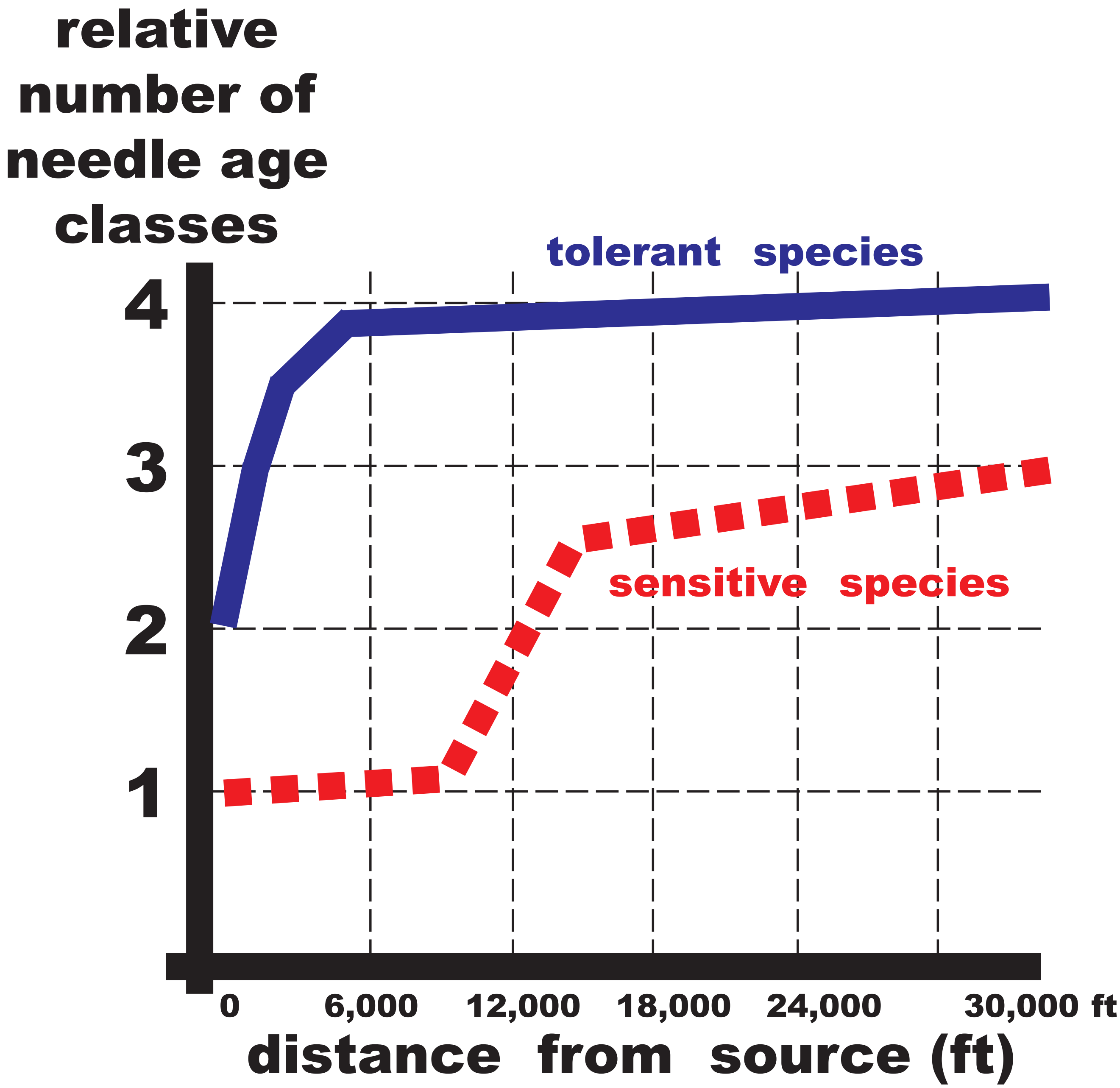


Figure 7: Historic needle age classes present for a sensitive and tolerant gymnosperm species downwind of chlorine gas source after two years from exposure. The fewer age classes, the more damage from exposure.
(after Schreuder & Brewer, 2001)

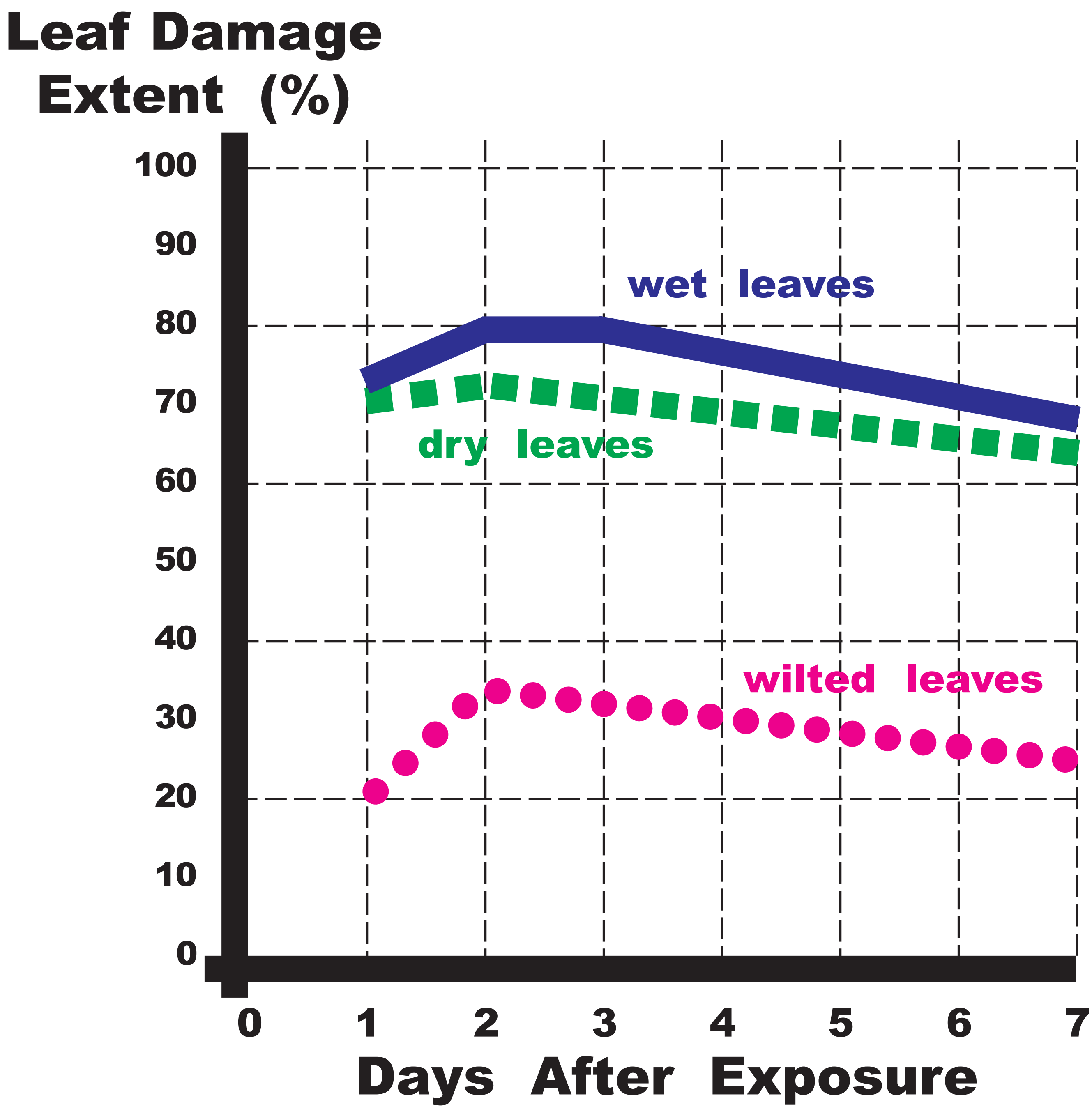


Figure 8: Laboratory chlorine exposure experiment examining plant leaf damage (100% is complete leaf damage and 0% is no leaf damage) over a one week period for three leaf conditions at exposure: wet, dry, and wilted. Chlorine gas exposure was 20 ppm for 10 minutes. (after Griffiths & Smith, 1990)

An additional interaction for leaf damage and chlorine gas is the light environment during and immediately after exposure. Darkness during and after exposure to chlorine gas reduces damage compared with full sunlight conditions. Even cloudy conditions significantly reduce damage compared with full sunlight. Figure 9. All chlorine damaging circumstances conspire to make a leaf progressively less resistant to more chlorine exposure.

Final Failing

As more leaf cells die, larger damaged areas are formed between veins. All living cells surrounding damaged areas progressively fail in attempting to compartmentalize damaging materials and damaged cells. This disruption and dysfunction within a leaf generates a reduction in the amount and quality of tree food produced and transported, as well as disrupting growth regulator production and transport. Susceptibility to pests and injury increase as defensive capabilities decline and structural units are compromised.

Internal & External Tree Reactions To Chlorine Gas

Primary tree reactions to chlorine gas, both internally and externally, are reviewed below. This subject matter treatment is not a toxicology or environmental dosage review, but is designed to help tree health care professionals understand potential injuries sustained by trees and other landscape plants when exposed to chlorine gas.

Tree leaf reactions classes to chlorine gas exposures include: chlorosis, flecking, glazing and wet spots, and scorching.

Chlorosis: Chlorosis is a yellowing caused by many things which slow or damage the photosynthesis process or production of chlorophyll. Photosynthesis is extremely sensitive to gas exchange, intercellular acidity and cell water contents. The green pigments of photosynthesis are concentrated in bundles called chloroplasts within leaf cells and are the first to show change. The first ephemeral leaf color change is a gray-green color which most people do not notice due to its quick passage into chlorosis.

The chlorotic leaf color change is caused by a decrease in chlorophyll content which exposes some of the auxiliary pigments, many of which are yellowish in color. The combination of lightening green leaf color and exposure of yellows are what is termed chlorosis. General chlorosis can be leaf-wide with some areas between veins showing more intense chlorosis. With time, chlorosis symptoms can lead to a bleaching (whitening) of tissue as pigments are destroyed.

The final damage in tissue which was originally chlorotic is necrosis (death), which shows colors ranging from tan to reddish to brown to black, depending upon what materials are present in living cells when injured and how quickly cell death occurred.

Flecking / Stippling: Flecking, stippling and mottling are words describing the appearance of minute and larger spots on leaf surfaces. A number of air pollutants and pests can cause flecking. Flecking has three phases on tree leaves. First is the appearance on the underside of leaves around stomates. As damage progresses to more cells, both lower and upper side of leaves show flecking.

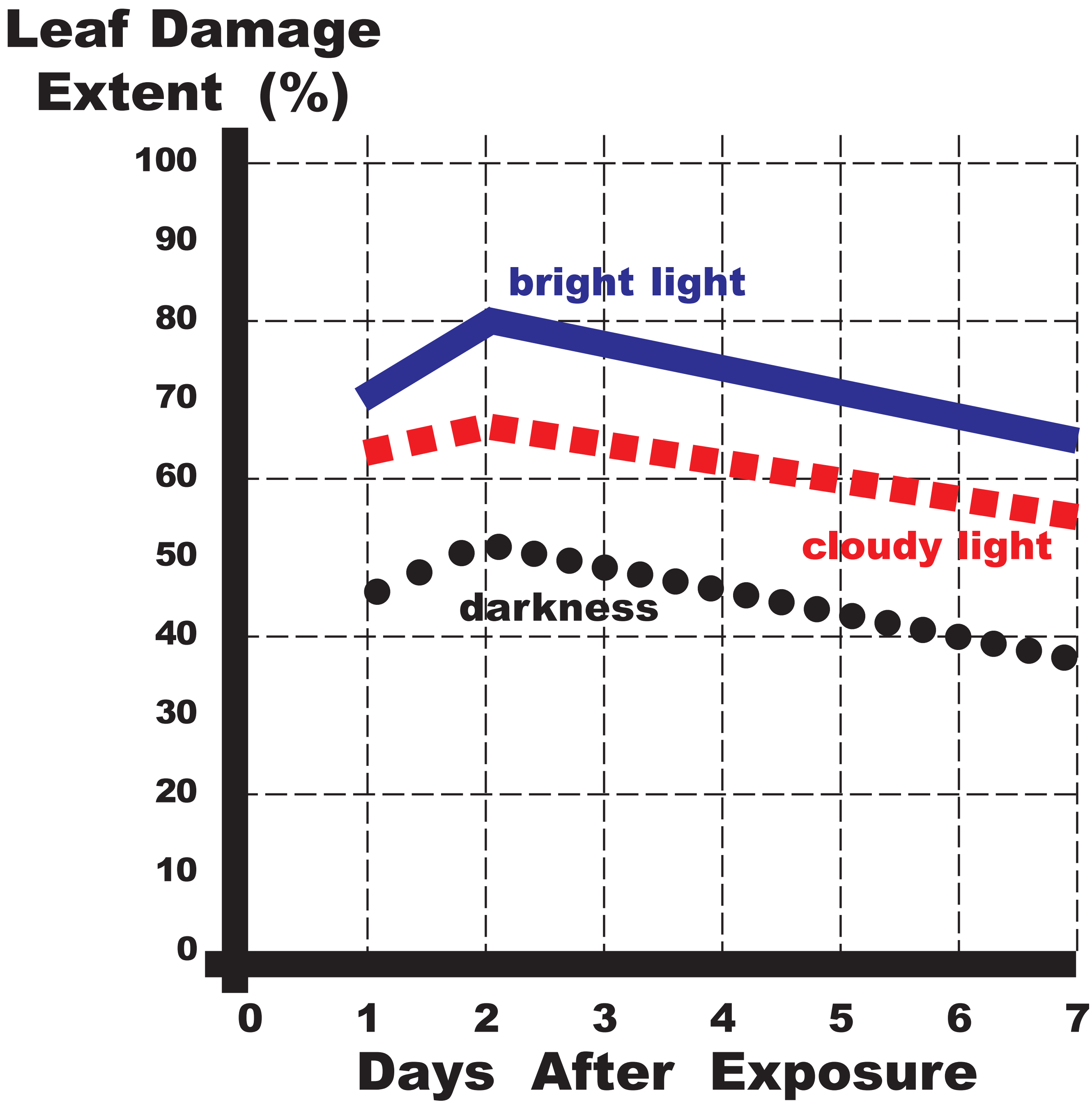


Figure 9: Laboratory chlorine exposure experiment examining plant leaf damage (100% is complete leaf damage and 0% is no leaf damage) over a one week period. Chlorine gas exposure was 20 ppm for 10 minutes under three light levels. (after Griffiths & Smith, 1990).

The second phase of flecking is spots beginning as chlorotic flecks usually progressing to dead spots which are brown or black in color. Bronzing is flecking across a wide area or in larger spots where tissue color in spots is light tan to brown, sometimes with faint tinges of red or orange.

The final phase of flecking is tissue death in spots of different sizes which can be either brown in color or in higher chlorine exposures can be orange-brown in color.

Glazing / Wet Spots: One symptom visible after a period of time in leaves is a "silver" or "glazed" appearance. This symptom is a result of increasing air spaces just below the leaf epidermis (surface layer). Light reflectance off a leaf is changed by air spaces leading to a glazed appearance. These air spaces can become saturated with water generating a symptom known as wet spot or water logging. As tissue is damaged and water is pulled from cells, cell wall areas and intercellular air spaces become saturated with an acidic and high salt content solution. These spots can continue to develop into reddish-brown to black dead spots.

Scorching: Scorching is death of large areas of leaf tissues, usually initially concentrated at leaf margins and tips. The more exposure to chlorine, the greater leaf volume damaged and the more scorching. Large areas of necrotic tissue (dead areas) may appear to have developed from many flecks and dead spots coalescing into large dead spots, or from massive dead spots developing spontaneously.

Scorching can appear quickly and progress until almost the entire leaf is brown. Whole leaf browning and death can lead to leaves staying on a tree if the injury was fast, or can lead to a fast senescence and abscission process if the leaf tissue and twig had a longer time to react. Either result is a loss of leaf area to make food for a tree. Partial scorching can lead to leaf cupping and distortion.

Let's Compare

Chlorine gas is not a rare air pollutant, but is not considered common. As such, many diagnostic guides choose to compare chlorine gas symptoms with other air pollutants. Because trees only have a few reactions to a host of damaging agents, and because the massive number of tree-damaging agents impact the most sensitive and visible portions of tree biology, chlorine gas exposure can be said to mimic other types of pollution.

For example: rapid interveinal leaf chlorosis and death is like sulphur dioxide; marginal and leaf tip dieback (scorching) is like hydrogen fluoride; leaf tissue bleaching is like ozone; and, the overall leaf damage is like acid rain. If good symptomology is developed for these other pollutants, then comparison of damage might be initially helpful in diagnosing chlorine gas damage to tree leaves.

Internally Yours

Internally, chlorine gas initiates a variety of changes within tree leaves. These internal changes are concentrated around photosynthesis and physical changes to leaf surfaces which impact water content. Short term changes in leaves arise from lowering of pH as cell spaces become more acidic. Long term leaf changes arise from the transformation and accumulation of chlorides. Note that chloride concentrations alone in tissues are NOT a proxy to determine damage extent or exposure concentrations.

Internal impacts of chlorine gas on tree tissues are concentrated around the photosynthetic systems and tissue water control. The primary impact of chlorine gas is the entrance into the stomate and its dissolving in the cell wall water, allowing chlorine (in several damaging forms) to reach living cell membranes. Membrane permeability is altered and osmotic changes occur disrupting both chloroplasts and mitochondria. Cell regulatory links become severed and fail leading to cell death.

Photosynthesis: Photosynthesis is the first process to be impacted with exposure to chlorine gas. Photosynthesis is extremely sensitive to even minor water content changes, and the water content changes from chlorine damage can be massive. The efficiency of the entire process falls rapidly as compounding damage accumulates. As water contents change, stomate control is lost and acidification of cell wall water disrupts carbon-dioxide uptake and cell wall permeability in both directions (out and in of the cell). The photosynthesis processes are reduced by loss of materials leaking out of cells, lack of chloroplasts generating a gradient of protons, and disruption of chlorophyll maintenance and production sequences.

Magnesium atoms, used as the centerpiece of working chlorophyll molecules are replaced (bumped out) by hydrogen atoms in the acidic environment, rendering chlorophyll inoperative. The repair enzymes which would normally correct structural problems in chlorophyll are also shut-down. The primary full sunlight chlorophyll molecule (chlorophyll a) breaks down four times more quickly in acidic conditions than the shade dominant chlorophyll (chlorophyll b). Other pigments which protect chlorophyll from sunlight or chemical damage are themselves destroyed.

The amount of light during and immediately after exposure modifies damage levels seen in leaves. Bright light tends to allow more leaf damage to be visible, while a dark period reduces damage potential. Most light effects are due to stomatal opening and closing which affects internal leaf exposure to chlorine gas.

Leaf Surfaces & Water Content: As acidity increases in the leaf (pH falls), living cell membranes are damaged. Surface structures on membranes are disengaged or destroyed. As membranes become more disabled, more materials hoarded for essential processes leak from cells. As more materials build-up outside cells, more water flows out of cells and builds-up in intercellular spaces. Without positive water pressure (turgor), cells begin to pull away from cell walls and collapse. Water loss from cells, and from leaves in general, cause stomates to close.

Turgor loss causes wilting, collapse, cupping and shrinking of leaves. Water loss from leaves generates a severe drought-like desiccation. The epidermis cells separate and lose continuity with each other from both internal and external acidification. Desiccation from damaged leaf surfaces (epidermis, trichomes, and cuticle) can influence growth for more than a year after chlorine gas exposure. A final interaction occurs as water loss accelerates from leaf surface damage -- leaf surface wettability increases which allows for longer moisture residence times on a leaf increasing leakage of materials and potential for successful pest entrance.

Whole Tree Growth

On a whole tree basis, the precipitous drop in photosynthesis and continued desiccation leads to food allocation problems and measurable growth changes lasting as much as five years. The most noticeable impact with trees not killed outright, is an early on-set of senescence in the year of exposure. A shortened growing season leads to less food produced and stored, as well as modified defensive processes during a longer warm period without active crown productivity. On both evergreen and deciduous trees, leaf longevity is compromised and decreased. On otherwise stressed trees with evergreen leaves, loss of additional perennial leaves is a tremendous resource loss.

Stem growth is greatly reduced from chlorine gas exposure. In one study, tree crowns initially reacting with mostly chlorotic symptoms had 25% less stem growth after three years, while trees initially reacting with mostly necrotic crowns had 55% less stem growth after three years. In trees with greater than 85% initial defoliation, death was the usual result. Reproductive tissues are also severely damaged by chlorine gas exposure. In pines, female cone production has been cited as greatly reduced (60% less) following chlorine gas exposure. Tree fruiting may be impacted through premature fruit abortion upon exposure.

Chlorine Gas Dosage, Damage & Treatments

The damage extent in trees from chlorine gas and associated water solution products depends upon exposure dose. Exposure dose depends upon:

-- how much damaging agent is present (concentration);
-- how long of time tree is exposed (duration);
-- how accessible are living cells of tree (entrance); and,
-- the time of year exposed (season).

The greater the concentration, duration, entrance avenues, and exposure in the early part of a growing season, the greater damage potential to trees because the exposure dose is increased.

Poison Dose

Across many species and different climatic and topographic circumstances, concentrations and duration values can be roughly defined which initiate damage in trees. Concentrations of 0.5 to 5.0 ppm initiated chlorosis and tissue death in tree leaves. Figure 10. A standard dose appears to be 3 hours at 1 ppm to initiate tree damage, but dosage could vary from 0.5 ppm for 8 hours to 5.0 ppm for 10 minutes. The amount of leaf tissue damage quickly builds with small increases in exposure concentrations. Visual symptoms rapidly increase between 1-30 ppm. Figure 11.

Assessing Potential Damage

One standard formula for estimating changes in leaf damage is:

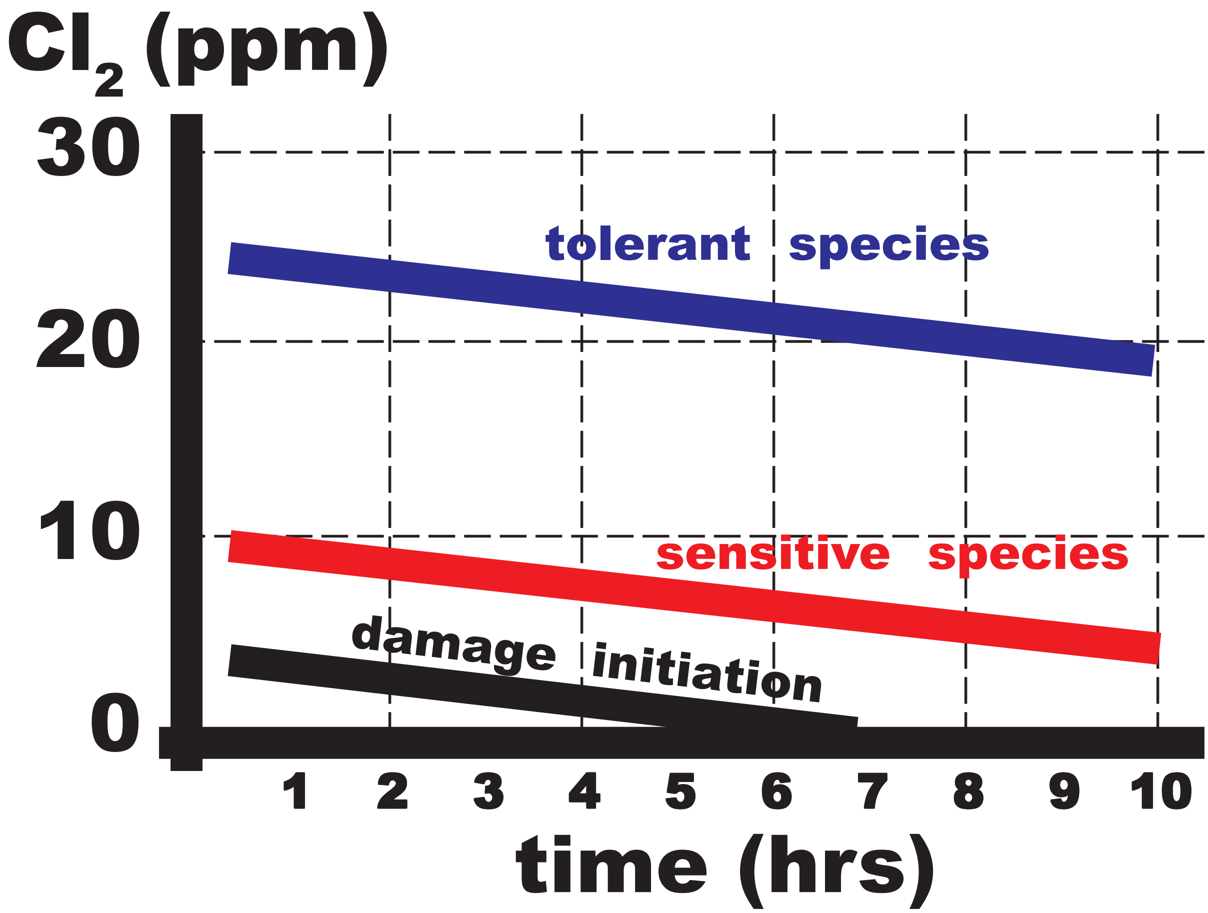
$$\textbf{potential leaf damage level} = (\textbf{ chlorine gas concentration })^2 \times \textbf{ time}$$

This formula demonstrates chlorine gas concentration increases greatly outpace duration effects in impacting leaf damage.

Another formula used for unconstrained outdoor exposures is:

$$\textbf{potential leaf damage level} = \textbf{chlorine gas concentration} \;/\; \textbf{wind velocity}$$

This formula demonstrates how more wind means less residence time for chlorine gas around the tree.



LINE EQUATIONS FOR GRAPH ABOVE (use time in minutes):

initiation of leaf damage --	Cl_2 ppm = -0.01 * (time) + 4. Time = (ppm - 4) / -0.01.
damage to sensitive tree foliage --	Cl_2 ppm = -0.01 * (time) + 10. Time = (ppm - 10) / -0.01.
damage to tolerant tree foliage --	Cl_2 ppm = -0.01 * (time) + 25. Time = (ppm - 25) / -0.01.

Figure 10: Composite dosage and damage potential for chlorine gas on leaves of chlorine-sensitive and chlorine-tolerant trees. Graph developed from summarizing diverse laboratory and field information without regard to humidity and precipitation.

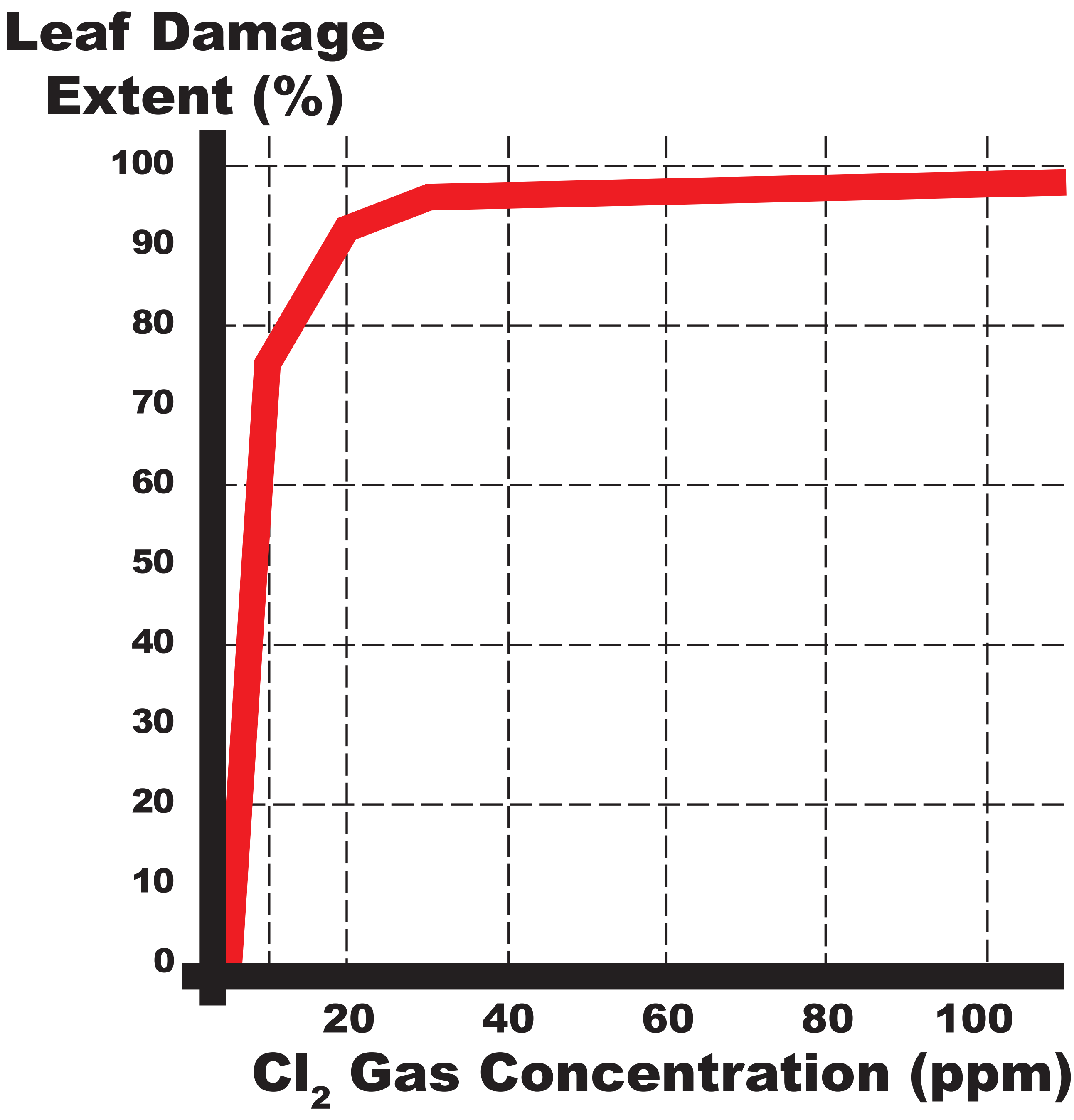


Figure 11: Laboratory chlorine exposure experiment examining plant leaf damage (100% is complete leaf damage and 0% is no leaf damage) across chlorine gas concentrations. Chlorine gas exposure duration was 10 minutes. (after Griffiths & Smith, 1990).

The Coder formula, which can be used in the field as a rule of thumb for potential leaf damage assessment, is a modification of the proceeding two formula:

potential leaf damage level =
((chlorine gas concentration)^3 X (time)^2) /
((distance from source)^2 X wind velocity)

Any time dose components increase, or wind velocity and distance from source decrease, relative leaf damage will increase.

Human PPMs

Humans start to smell chlorine in the air at approximately 1 ppm, with a strong odor sensed around 3 ppm. Chlorine gas coloration in the air can be seen at about 2 ppm. For humans, 50% mortality averages are reached at dosages of 150 ppm for 1.7 hours, 350 ppm for 10 minutes, 800 ppm for 1 minute, or 1-2 breaths at 1,000 ppm.

A Good Mixer

As chlorine is released into the atmosphere, the more unstable the atmosphere and the more wind present, the more dilution and mixing. A stable atmosphere (inverted) and no wind, allows for extended exposures to chlorine gas to locally exist. Figure 12 gives a chlorine gas concentration level over distance downwind and downslope from a cool source where chlorine gas was channelled and concentrated by topography.

In general, foliage damage classes can be defined by the distance from a cool exposure source. A simple distance based system is:

1 mile from exposure source -- all trees can be severely injured;
2 miles from exposure source -- chlorine-tolerant trees show little damage;
6 miles from exposure source -- sensitive trees show little damage; and,
11 miles from exposure source -- visible foliage damage can still occur but with little long term impact

All of these classes assume the chlorine gas stays close to the ground and is not quickly diluted or rapidly blown away.

Water Treats

Tree treatments for chlorine gas exposure revolve around preventing increased dosing and dissipating damaging agents. During exposure, irrigation, watering, or foliage spraying should not occur. Watering trees during exposure will cause a greater access to living cells for chlorine gas and associated damaging materials. Wetland trees can be especially hard-hit by being low in the landscape topographically, with open stomates for a relatively longer duration per exposure.

After the source has stopped emitting chlorine gas and the gas dissipated, watering, sprinkling and irrigation of soil should commence. Use plenty of water to both dilute and rinse away chlorine products. A little water may actually be more detrimental than none at all. Use water to rinse plant surfaces and soil. Water will help dilute acid and help to more quickly transform and transport damaging materials. The additional benefit of

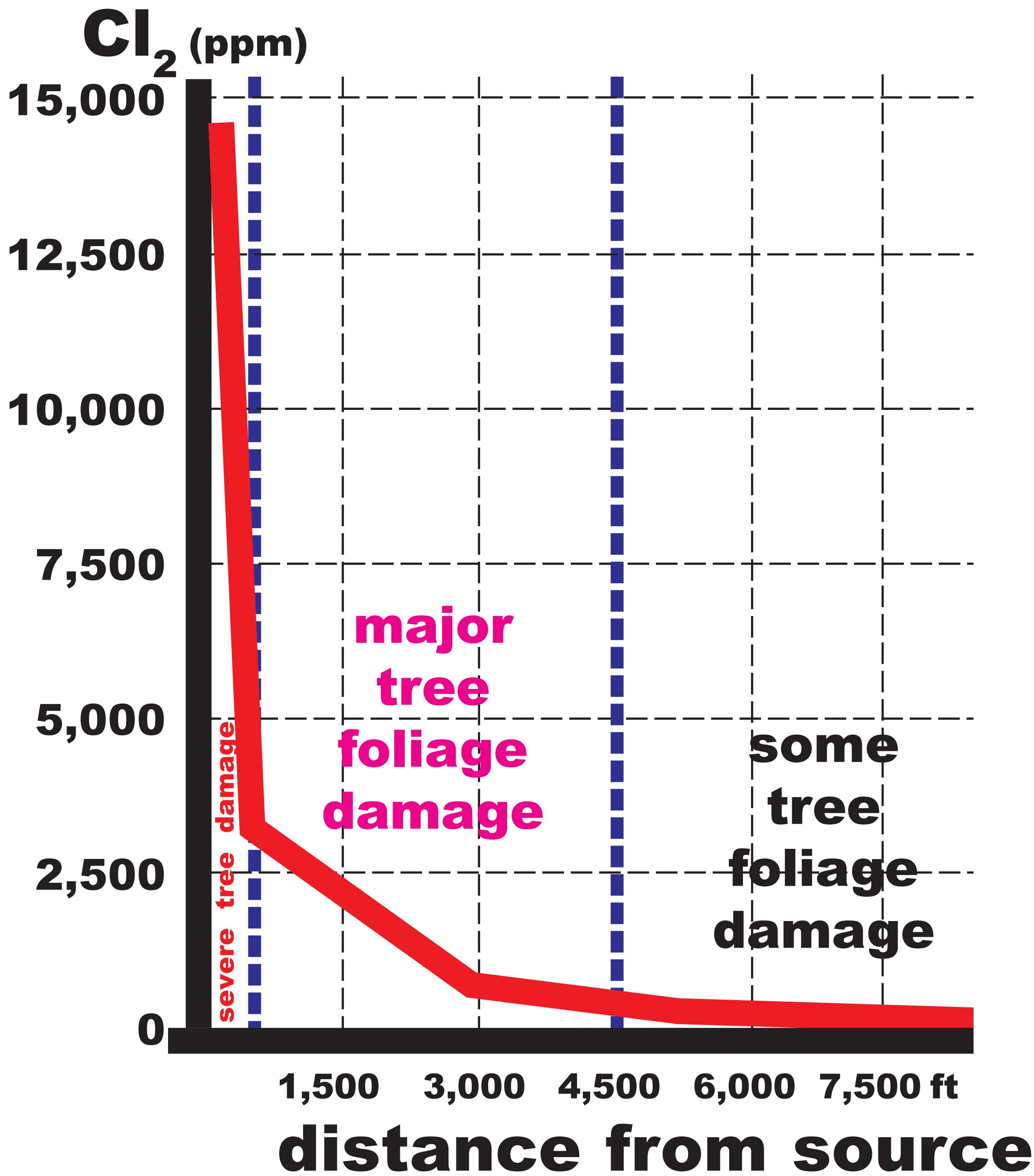


Figure 12: Historic dilution curve of the highest chlorine gas concentrations measured in ppm over distances down-wind from a source in a location with constraining topography.

Dotted lines separate severe, major, and generalized damage zones.
(5 ppm reached at 30,000ft downwind)

water is to keep tree systems functioning biologically in order to effectively deal with damaging materials and repair internal damage quickly, especially essential processes like photosynthesis.

Site Treatments

Treatments in areas where landscapes have been exposed to chlorine gas could include: irrigate soil and wash plant surfaces to remove acidic materials, particulate matter, and accumulated chlorides; light fertilization with a slow release nitrogen to increase the ecological vitality of the site; application of a dolomitic limestone amendment to replenish base elements; and, assure adequate drainage of soil water – do not allow water accumulation. Plentiful rainfall can help rinse plant surfaces and soils.

Remember, chlorides are rinsed away by water but they take important essential elements with them. These elements need to be replenished through careful fertilization and liming of soil. Dolomitic limestone should be added back to soil because calcium and magnesium will be essential for tree recovery. A light fertilization with slow release nitrogen and plenty of potassium and phosphorus can help in the recovery process. Do not over-fertilize.

Future Expectations

Ecological and growth changes caused by chlorine gas exposure can last beyond 5 years close to the source. The farther away from the source, the less residual damage should be experienced in landscapes. The primary residual effect is a disruption and slowing of growth which accentuates other stresses. Long term damage is usually most noticeable on young, small, and short trees. Generally, drought tolerant species and trees with strong water use efficiencies (WUE) are less prone to long term damage, while bottomland trees and wetland species are more prone to long term damage.

An accelerated tree health care program should be put in place for at least three full growing seasons because of the threat of pests. Extreme vigilance must be shown to valuable trees which have been damaged because of potential bark beetle and ambrosia beetle attacks. Drought stress and heat stress syndrome will be much more damaging in chlorine gas damaged trees. Less food production by a tree will lead to less growth and potentially poorer reactions in defense, reproduction, and resource gathering and control.

Special Problem: Landscapes, Humans, & Calcium Hypochlorite

Calcium hypochlorite ($CaCl_2O_2$) is a chemical compound which is quite common in our lives. It is a defender of our health and used for a variety of different uses. Sometimes this common chlorine containing chemical escapes from normal use and becomes potentially damaging in the environment and within landscapes. A closer look at this chemical agent is needed because of it yeild of chlorine gas. Seek immediate medical assistance if exposed, and review all regulatory and safety data sheets for this compound before use and for storage.

Judging Character

Calcium hypochlorite is a common, manufactured, chlorine-containing product used for disinfection of water, such as for swimming pool sanitation. Calcium hypochlorite is a white solid at room temperature.

Calcium hypochlorite is heavier than water and quite soluble. It decomposes in water, or when heated past 210°F (99°C), and forms oxygen and chlorine. It has a chlorine odor.

Calcium hypochlorite is an artificial compound, not occurring in nature. Accidents and improper use of calcium hypochlorite can cause short-term, high concentration exposures of chlorine gas within a landscape. Leaks around water treatment plants and swimming pools are extremely rare but have occurred.

Intense Reactions

Calcium hypochlorite is an oxidizing chemical, allowing combustible materials to burn well. It is not flammable itself, but can react explosively with ammonia, amines, carbon-tetrachloride, charcoal, oils, organic sulfides, sulfur, and thiols. Metal oxides help catalyze the chemical decomposition of calcium hypochlorite. Contact with alcohols, glycols, glycerols, and phenols can result in ignition. Calcium hypochlorite should be stored in a dry, ventilated area below 120°F (49°C). Acids, ammonia, amines, other chlorinating agents, and other types of oxidizing compounds should be removed from the area.

Water Water Everywhere

Calcium hypochlorite ($CaCl_2O_2$) added to water generates a calcium ion (Ca^{++}) and two hypochlorite ions (OCl^-). The hypochlorite ions are in a pH dependent equilibrium with hypochlorous acid (HOCl) in water. This water solution is found in household bleach. Most drinking water systems use a hypochlorous acid concentration of around 0.6ppm for disinfection. Other names used for calcium hypochlorite include hypochlorous acid, calcium chlorohydrochlorite, calcium salt, chlorinated lime, lime chloride, calcium oxychloride, and perchloron.

Great Escape

When exposed in the environment, calcium hypochlorite breaks apart due to interactions with sunlight and atmosphere. In soil, calcium hypochlorite breaks apart into calcium ions and hypochlorite ions. These ions can interact with many different soil and water constituents. Iron, manganese and nitrites can be oxidized by chlorine. The chlorine combines with organic materials in soil water including nitrogen containing materials. With increasing concentrations of chlorine, the chlorine containing nitrogen compounds are broken down into hydrochloric acid and nitrogen gas. Calcium hypochlorite or chlorine does not accumulate ecologically in food webs.

Humans!

People are exposed to calcium hypochlorite and associated materials in everyday products like household bleach, in the water of many swimming pools, and in municipal drinking water. Bleaching of textile and paper are other places where people can be exposed to calcium hypochlorite and its ions in solutions.

Humans are impacted by small amounts of calcium hypochlorite and associated materials, presenting symptoms of irritated skin and mucus membranes. Eyes and open skin can be irritated at low doses, and inflamed and blistered with more exposure. This material is corrosive to living surfaces. The chlorine gas generated as calcium hypochlorite decomposes can irritate nasal passages and cause sore throats and coughing with small exposures, and serious breathing constrictions with greater exposures. Children tend to be more vulnerable to the corrosive nature of this chemical.

Gassed

Children are especially at risk from chlorine gas injury. Chlorine gas released from calcium hypochlorite causes eye and nasal irritation, sore throat, and coughing at low concentration exposures. Inhalation of greater amounts of chlorine gas leads to respiratory distress through airway constriction and accumulation of liquid in lungs. Exposure can lead to rapid breathing and wheezing. Breathing reactions usually occur 5 minutes to 15 hours after exposure.

There is no specific antidote for calcium hypochlorite exposures other than removal from the exposure area, and water rinsing and cleansing of body and clothes. Flush hair and skin with large amounts of warm water. Irrigate eyes with saline or other appropriate material for an extended time. Seek immediate medical assistance. Chlorine exposure can lead to "reactive airway dysfunction syndrome" (RADS), a chemical irritant type of asthma.

Because chlorine, oxygen and calcium are essential elements for living things, general medical tests of blood and urine for these materials are not useful. Tests can be used to show extent of damage. People exposed to large concentrations of calcium hypochlorite dust can be corrosive to other people and can release chlorine gas impacting anyone rendering aid. People exposed to only the chlorine gas released from calcium hypochlorite pose little risk to aid providers.

Conclusions

Trees and chlorine gas do not mix!

Tree reactions, both internally and externally, generate growth and health problems when exposed to chlorine gas.

Short-term and long-term tree problems occur.

Usually the dosage of any exposure determines damage. In trees, other environmental stresses, both before and after exposure, can further compound problems.

Understanding tree reactions and recognizing symptoms are key to formulating tree health care prescriptions.

A good tree health care program, including monitoring for secondary problems while reducing other stressors, will be critical for trees exposed to chlorine gas.

Tree health care professionals can conserve trees by preventing any more damage, removing damaging materials on plant surfaces and in soil, and by enriching soil with essential resources.

Citation:

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The literature on chlorine gas damage to trees is based either upon laboratory exposures of trees (usually small and juvenile trees) to chlorine gas and hydrochloric acid, or upon accidental releases of chlorine gas into the environment. Accidental releases are valuable for assessing damage but it should be remembered: data control is poor; observations of damage is assumed to be directly related to accidental exposure without proof of exposure; and, information about climatic factors at the time of exposure may be limited. Trees exposed to chlorine gas vary in their reaction ranges from no visible symptoms to death.

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