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SUBJECT: CHLORINE GAS RULE MAKING PROPOSAL

Upon your request, we reviewed the 2012 Rulemaking Proposal to add chlorine gas to the list of California Restricted Materials (3CCR 6400). The rulemaking proposal makes reference to illnesses in California attributed to chlorine gas, alone or in combination with another pesticide, from 2000 to 2009. We reviewed the illness reports to verify that they indeed involved chlorine gas and that they fall under the use patterns specified in the rule making proposal. Below are our findings beginning with a discussion to distinguish between chlorine gas, chlorine dioxide, chlorine generators and other products that, when mixed with water (or other products), produce chlorine or hypochlorous acid which has an odor usually associated with chlorine.

Chlorine/Chlorine Gas

Chlorine, a naturally occurring element, is a highly reactive gas. Exposure to chlorine can occur in the workplace or in the environment following releases to air, water, or land. People who use laundry bleach and swimming pool chemicals containing chlorine products are usually not exposed to chlorine itself. Chlorine is generally found only in industrial settings (U.S. EPA OPPT 1994). Chlorine is formulated as a pressurized gas and distributed in large stationary containers such as tank cars or trucks and 150-pound to 1-ton cylinders.

Chlorine gas is used in water treatment to disinfect drinking water, swimming pools, ornamental ponds and aquaria, sewage and wastewater, and other types of water reservoirs. Chlorine gas is also used as a disinfectant, microbistat/microbicide and algicide in food processing systems, pulp and paper mill systems, and commercial and industrial water cooling systems. It is used in washing meat, fresh produce and seeds to control decay-causing microorganisms (U.S. EPA OPPT 1999, U.S. EPA 2010)

It is often impractical to store and use chlorine gas for water treatment, so alternative methods of adding chlorine are used. These include hypochlorite solutions, which gradually release chlorine into the water, and compounds like sodium dichloro-s-triazinetrione (dihydrate or anhydrous, aka "dichlor"), and trichloro-s-triazinetrione (aka "trichlor"). These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to poolwater or industrial water systems, the chlorine atoms hydrolyze from the rest of the molecule forming hypochlorous acid (HOCl), which acts as a general biocide (Wiberg *et al* 2001).

Chlorine in the form of hypochlorous acid is used to kill bacteria and other microbes in drinking water supplies and public swimming pools. In most private swimming pools, chlorine itself is not used, but rather sodium hypochlorite, formed from chlorine and sodium hydroxide, or solid tablets of chlorinated isocyanurates (Hammond 2000).

Chlorine Dioxide

Chlorine dioxide differs from chlorine in that it dissolves in water but does not react with water as chlorine does, so it is less affected by pH. Unlike chlorine, chlorine dioxide may be used in combination with acid. Chlorine dioxide does not form trihalomethanes or other chlorine-additive products. In addition, Chlorine dioxide does not form chloramines. Because Chlorine dioxide is not stable enough to be manufactured off-site and shipped, it must be created at the point of use and that requires a generator of some sort (Apel 1993). Chlorine dioxide is used primarily for bleaching of wood pulp, but is also used for the bleaching of flour and for the disinfection of municipal drinking water (U.S. EPA 1999). Chlorine dioxide is most commonly used in water treatment as a pre-oxidant prior to chlorination of drinking water to destroy natural water impurities that produce trihalomethanes on exposure to free chlorine (Sorlini and Collivignarelli 2005). Chlorine dioxide is also used in many industrial water treatment applications as a biocide including cooling towers, process water and food processing (Andrews e*t al* 2002). (Photo 1a, 1b and 2)

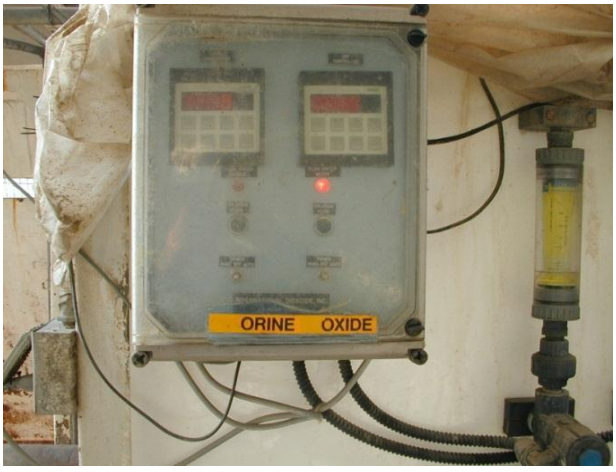

Photo 1.a) Chlorine dioxide generator at a food processing plant, b) Containers of reactants used to generate chlorine dioxide in the food processing plant. (Photos courtesy of Harvard Fong)

Photo2. Chlorine dioxide generator used to fumigate a hospital in Oxnard (Ventura County) in 2007. (Photo courtesy of Harvard Fong)

Chlorine Generators in residential pools

A chlorine generator's main function is to produce chlorine. This eliminates the need to buy, store or handle pool chlorine products. Chlorine generators, when functioning correctly, produce chlorine constantly (when the pump is running) with most units. This keeps a residual of chlorine in the pool that prevents algae from growing. Through the process of electrolysis, water passing over the chlorine generator cell produces chlorine that is instantaneously transformed into Hypochlorous acid. Its effectiveness is dependent on balanced water conditions and, more importantly, proper pH (Woodhurst 2012).

Illnesses Due to Chlorine

From 2000 to 2009, there were approximately 73 case reports in which health effects were evaluated as definitely, probably or possibly related to "chlorine." Pesticide Illness Surveillance Program (PISP) staff conducted an in depth review of each case to confirm the formulation of the products involved. After we reviewed all 73 cases, we found that not all were due to chlorine gas, but also to chlorine yielding products, such as chlorinating tablets, chlorine generators, and chlorine dioxide.

Exposure to pressurized chlorine gas was confirmed in 58 of the 73 cases (79%).

Table 1. Individual Illnesses and Number of Episodes Associated with Exposure to Pressurized Chlorine Gas from 2000-2009 [1]

Pesticide	Total Episodes[2]	Total Cases[3]
Pressurized Chlorine Gas	36	58
Chlorine Dioxide*	7	10
Chlorine (from tablets)	2	2
Chlorine (generated on site)	2	2
Unidentified Chlorine Product	1	1
TOTAL	**48**	**73**

[1] Data for the years 2000-2009 generated May 7, 2012 by Nino Yanga, Worker Health and Safety Branch, Pesticide Illness Surveillance Program, Department of Pesticide Regulation. Data includes the use of a chlorine type product in combination with other pesticides.

[2] An episode refers to any single pesticide-related event (application, accidental spill, mix/load) that resulted in 1 or more illnesses.

[3] A case refers to a single person reporting symptoms.

* Priority Episode 56-SBT-09 crosses years (2009 & 2010). This episode affected 18 total workers; four cases were assigned in 2009 and 14 in 2010.

Ten of the 73 cases (14%) were due to chlorine dioxide while the remaining five cases (7 %) involved the use of chlorine yielding products (Table 1), including one unidentified chlorine product. Four of the 10 (40 %) cases involving chlorine dioxide occurred at crop/livestock processing facilities where it was used to clean equipment or control microbes in flume water. Three cases (30 %) occurred at water treatment plants. Two non-occupational cases (20 %) that were part of the same episode occurred at a single family home. While helping out in their daughter's barn, the mother found a half filled bottle in the refrigerator. She thought that the bottle was half-filled with water so she filled up the bottle with water and both she and her husband drank from it. They developed symptoms of coughing, headache and vomiting. The chlorine dioxide solution in the bottle was intended to treat fungus on horse hooves. The other case (10 %) occurred at an office where a mailroom clerk developed symptoms after a technician sprayed chlorine dioxide solution to a ventilation system to disinfect it.

Of the five cases that involved chlorine yielding products, two resulted from the use of chlorine tablets. In one case, a six year-old boy ran to a shed when he heard his father say the pool chlorine level was low. He tried to get chlorine tablets from the bucket, was overcome by vapors and started coughing. He was taken for care. In the second incident, a homeowner developed symptoms after inhaling vapors from a chlorinator. He was installing a new swimming pool device when he opened the lid of a chlorinator and the enclosed pressure released the vapor. He went to the hospital 12 hours later. There were two incidents involving chlorine generated on

site. One incident involved a water treatment operator conducting a routine check of metering gages on a prototype machine that mixed chemicals to generate chlorine gas. The chlorine gas was used to treat the city's water. Because he had smelled a slight odor, he approached the new chlorine generator, unaware that the machine had a leak. He developed irritant symptoms immediately and went for care the next day. In the second incident a municipal water system worker inhaled chlorine gas when the sodium chloride salt he added to the hopper displaced the chlorine gas. He suffered respiratory problems and sought medical attention. Since that incident, the employer has required the use of a respirator for that task. There was only one case in which the formulation of the chlorine could not be determined. A driver was reportedly mixing chlorine with water when the solution splashed into his left eye. He rinsed his eyes thoroughly and sought care. The formulation of the chlorine product could not be verified since the driver was uncooperative and did not want to provide the investigator further information.

Fifty five of the 58 cases (95%) associated with pressurized chlorine gas were occupational. Of the three non-occupational cases (5%), the first two involved 7-year old girls taking swimming lessons at a public pool. They developed respiratory symptoms when they inhaled chlorine vapors suspected to have come from an air pocket created by the chemical feed lines. The third non-occupational case involved a resident who was exposed to chlorine when he was getting his pool serviced.

The rulemaking proposal specified use patterns that would require that chlorine gas be categorized as a restricted use pesticide. These use patterns include food processing, public/commercial pools, commercial and industrial water treatment systems and for use to control biofilm/algae in agricultural irrigation. Residential pool treatment and municipal water and sewer treatment uses were excluded from the proposal.

Over the ten year period reviewed, only 22 (38 %) of the 58 chlorine gas related cases fell under the specified use patterns (Table 2).

Table 2. Cases Involving Chlorine Gas and Equipment Malfunction, 2000-2009.

Incident Setting[1] (site)	**No. of Cases**	**No. of cases with Equipment Malfunction**
Specified Use Patterns		
Crop/Livestock Processing Facility	14	12
Park (Public Swimming Pools)	3	2
Service Establishment (Private Pool)	3	3
Office/Business (Private Pool)	1	0
Farm	1	1
Total	**22**	**18**
Excluded Use Patterns		

Other (Telephone Poles, Fences, etc.)	27	14
Industrial or Other Manufacturing Facilities	6	0
Single Family Home	1	0
Landscape, Other	1	0
Unknown	1	0
Total	**36**	**14**

[1] **Incident Setting:** Location where the incident occurred. The location may not coincide with the application site. Identified incident settings include:

Crop/Livestock Processing Facility: Facilities involved in packing, manufacturing or processing foods or beverages for human consumption and feed products for animals and fowl. This includes facilities that sort, grade and pack fresh fruits and vegetables.

Farm: Areas where agricultural crops are grown. This excludes the following: 1) nurseries and greenhouses which are classified under "Nursery"; 2) livestock and poultry farms; and 3) forestry operations.

Industrial or Other Manufacturing Facility: Facilities involved in the mechanical or chemical transformations of materials or substances into new products. This excludes: 1) facilities engaged in manufacture or formulation of pesticides which are classified under PESTICIDE MANUFACTURING FACILITY (Code 30); and 2) facilities engaged in treatment of wood to protect against pest damage which are classified under WOOD TREATMENT.

Landscape, Other: Landscaped ornamental shrub and tree areas. This excludes ornamental shrub and tree areas in the following locations: 1) road/rail or utility right-of-ways; 2) parks; and 3) golf courses.

Office/Business: Commercial establishments including public and private business offices. This excludes "Retail establishments" and "Service establishments".

Other: Location of exposure occurred at a site not adequately described in any other incident setting category. This includes water supply systems and waste water treatment plants.

Park: An area of public land set aside for recreation. This includes public swimming pool facilities**.** This excludes private recreational facilities such as amusement parks, physical fitness facilities, etc. which are classified under "Service establishments".

Service Establishment: Establishments engaged in providing services to individuals, businesses and government. This includes restaurants, laundries, etc. This excludes medical service establishments.

Single Family Home: The house and other structures on property intended for use by a single family. This includes swimming pools, but excludes landscaped areas on the property which are classified under either LANDSCAPE, LAWN or LANDSCAPE, OTHER .

Unknown: The location of the incident is unknown.

Of the 22 cases falling under the specified use patterns, 14 (64 %) occurred at crop/livestock processing facilities. Twelve of these 14 cases were associated with a single priority episode investigation (16-KER-07) that occurred at a carrot processing facility. Although air monitoring

equipment detected no chlorine in the air, employees reported problems during an 11-day period. The employees reported symptoms of headache, eye and respiratory irritation. When maintenance personnel could not determine the source of the problem, the company brought in their engineering department. They determined that a malfunction of the damper sensors in the chlorinator caused chlorine to build up and be released into the plant. The engineering department made some changes and since then, no additional complaints have been received.

The remaining two cases that occurred at a crop/livestock processing facility stemmed from two separate incidents. In both instances, chlorine gas was used to treat water. In the first incident, a mechanic developed eye irritation when he cleaned weeds from a potato washing tank and a few drops of chlorinated water splashed into his left eye. The second incident involved a potato sorter, who developed symptoms after three weeks of work. She developed eye redness and irritation that she attributed to working near a chlorine bath about 75-feet away. She claimed the amount of chlorine used had increased, but the company denied it and said the chlorine was only used to bleach the potatoes. No violations were noted.

Seven cases occurred at public or private club swimming pools. One case involved a swimming pool supervisor who developed an itchy rash. Chlorine levels were determined to have been in range. The employee's mother mentioned that her son had similar problems in the past, which made her doubt the chlorine involvement. Another incident took place at a private pool club and affected three landscape workers. These workers attempted to assist the pool maintenance man when a leak from a chlorine gas cylinder occurred. They experienced respiratory symptoms and sought care. In another incident, two 7-year old girls developed symptoms of difficulty breathing and coughing when they were overcome by chlorine vapors while taking swim lessons at a public pool. It was suspected that the chlorine vapors came from an air pocket made by the chemical feed lines. Both girls were taken for care. One girl was kept in the emergency room for 4 hours, but both were released the same day. The last case involved a pool service technician who developed symptoms while servicing a pool at an office/business. He hurriedly filled a chlorine cylinder and turned the valves in the wrong sequence, causing the tank to release chlorine gas into his eyes.

There was only one agricultural case involving chlorine gas that occurred on a farm. A trained irrigator drove by a chlorination system and detected a strong chlorine odor being emitted. Without hesitation, he attempted to shut down a malfunctioning chlorine injection system without using respiratory protection and inhaled the vapors. He immediately became lightheaded and dizzy and was taken for care. The chlorine was used to control algae in the drip irrigation system. Investigation of the incident revealed that the company used a product that was not registered in California for agricultural use in irrigation systems

We noted equipment malfunctions associated with the chlorination system or chlorine gas cylinder apparatus in 18 (82%) of the 22 cases (Table 2). One could ask whether these exposure situations could have been avoided had a routine maintenance schedule been in place. 40 CFR §

170.234 (b) (Subpart C – Standard for Pesticide Handlers, Safe Operation of Equipment) states that "The handler employer shall assure that , before each day of use, equipment used for mixing, loading, transferring, or applying pesticides is inspected for leaks, clogging, and worn or damaged parts, and any damaged equipment is repaired or is replaced." Title 3 of the California Code of Regulations (3 CCR) Section 6744 (Equipment Maintenance) states that "Persons who own or operate pesticide mixing, loading, or application equipment shall inform each employee under their control who may be involved in the cleaning, servicing or repair of that equipment of the hazards of the pesticides that a person may encounter, and the methods of protecting against personal injury. If such cleaning, servicing or repairing is to be performed by persons not under the control of the owner or operator of the equipment, he/she shall so notify the person in charge of performing these services. Employees who clean, service, or repair mixing and application equipment shall be provided with any necessary protective equipment or clothing by their employer, and shall be instructed and supervised in the maintenance operation in a manner that will reduce work hazards." We are uncertain as to whether existing regulations require a routine maintenance program for the gas cylinders and chlorination systems in facilities using chlorine gas.

Of the excluded cases, 26 of the 27 cases that were classified under the Incident Setting "Other (Telephone Poles, Fences, etc.)" occurred at municipal water and sewer treatment facilities. The remaining case under this incident setting involved one of two utility workers who noticed a chlorine gas cloud while they were installing a fiber optic inter duct to a telephone pole. As they lowered their aerial bucket, they passed through the chlorine gas and one of the workers experienced breathing difficulty and vomited. The gas cloud came from a new chlorine line being tested nearby. Over half of the cases occurring in the Incident Setting "Other (Telephone Poles, Fences, Etc)" (n=14) involved some sort of equipment failure such as tank leaks and chlorinator malfunctions.

All six of excluded cases in the incident setting "Industrial or Other Manufacturing Facilities" occurred at a roof manufacturing plant. Chlorine odors drifted over from a neighboring pool chemical plant and caused these six workers to experience symptoms of shortness of breath, nausea and dizziness. Approximately 60 workers were evacuated. The pool chemical manager caused the leak by failing to shut off the valve after filling a small container with liquefied chlorine gas. The one incident that occurred at a "Single Family Home" involved a homeowner who was getting his pool serviced. As he stood near the pool maintenance worker who was changing the valve on a chlorine gas cylinder, some trapped gas escaped. The homeowner inhaled the vapors, developed breathing difficulties and sought care.

Under the incident setting "Landscape/Other", a lake and pond service technician developed symptoms when he added chlorine to a water feature. Some of the chemical splashed onto his pants, irritating his right thigh. He sought care four days later. A violation was noted since he did not wear his hip waders.

The last excluded case involved a pool maintenance worker exposed to chlorine while servicing a client's pool at an undetermined location. As he uncoupled a hose after treating the pool, he apparently turned the valve the wrong direction, causing chlorine gas to shoot onto his face when he disconnected the hose. He experienced symptoms of shortness of breath.

A**gricultural use of chlorine gas**

A possible reason for writing the proposal was to address worker safety concerns related to how chlorine gas tanks - used to treat irrigation drip lines - are transported and/or left in agricultural fields. Some growers have been observed using tool carriers to transport these chlorine gas tanks or "pigs" to the field (Figure 3a). The hazard from this practice stems from the possibility that these tanks could move around during transport, collide with each other and possibly release chlorine gas. Another hazard associated with chlorine gas used in agricultural fields is that tanks may be left unattended in the fields (Figure 3b). These tanks are exposed to the elements which may cause faulty tank valves that may result in accidental and/or uncontrolled release of the chlorine gas. These tanks are also subject to acts of vandalism that may result in the unintentional release of the gas in the environment. Of the 73 pesticide illness reports we received from 2000 to 2009 in which health effects were evaluated as definitely, probably or possibly related to "chlorine", only one involved chlorine gas in an agricultural field setting. In this particular incident, a trained irrigator checked a drip system and noticed a strong chlorine odor. He shut off the chlorinator without using respiratory protection, inhaled some gas, and became ill. The chlorination product involved was not registered at that time.

Photo 3.a) Tool carriers used to transport chlorine tanks ("pigs"), b) Unattended chlorine tank in a field. (Photos courtesy of Harvard Fong)

The Department of Pesticide Regulation does not regulate the transport of chlorine. Instead, this activity falls under the federal Department of Transportation. Regulations pertaining to the

transport of chlorine are found in Title 49 Code of Federal Regulations (CFR) with the two main sections being the Hazardous Material regulations and the Motor Carrier Safety regulations (The Chlorine Institute 2007).

The Hazardous Materials regulations are found in Title 49 Code of Federal Regulations (CFR) Parts 171 to 180. These parts cover the classification of the material, the qualifications for containers, and includes labeling, placarding, marking, training, loading and unloading. The transportation of hazardous waste is also included in these regulations (The Chlorine Institute 2007).

The Motor Carrier Safety regulations are found in 49 CFR parts 40, 380, 382, 383, 387, 390, 391-397, 399 and Appendix G – Minimum Periodic Inspection Standards. These regulations cover topics from the action of the drivers to maintenance of the vehicles.

More recent episodes of concern (2010 – 2011)

Since 2010, there has been only one large episode involving chlorine gas (11-RIV-10). A crane sorting scrap metal at a metal recycling yard punctured a four-inch hole in an eight foot long, one-ton metal pressurized cylinder, releasing a chlorine gas cloud to nearby-businesses. Seventeen persons were exposed and developed symptoms but only two were taken to a local hospital. The investigation revealed that the chlorine tank had been taken to the recycling center in Indio after it had been found abandoned in the desert. Ownership of the tank could not be determined, so any enforcement action was not possible.

At the time the rule making proposal was written, two episodes originally thought to have involved chlorine gas, turned out to involve other chlorine yielding products instead. In Sacramento County (49-SAC-11), more than 20 persons in a water park were exposed to chlorine when a chlorine injection device malfunctioned. The chemical monitoring system was not working as intended and the chlorine and acid chemical pumps continued to pump chlorine and muriatic acid into the return line of the filter system where there was no water flow. The introduction of chlorine and acid into the return line from the filter system that had no flow allowed the two substances to mix in sufficient levels to create chlorine “gas”.

Another incident in 2011 occurred in Yolo County (51-YOL-11). The episode involved chlorine dioxide. Workers at a tomato cannery were exposed when a gas cloud of chlorine dioxide formed over a water tank feeding the flume system that conveyed tomatoes.

Summary

After a more thorough review of the 58 illness investigations associated with chlorine gas from 2000 - 2009, we found that only 22 cases fall under the use patterns specified in the rule making proposal. Eighteen of these 22 cases involved equipment failure. Only one of these 22 cases

occurred in a farm. This case did not involve an illness or injury related to how the chlorine tanks are improperly transported or stored, an issue that the rule making proposal may have intended to address. We also determined that the two large multi-person priority episodes that occurred in 2011, and mentioned in the rule making proposal, did not involve chlorine gas.

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