Evaluation of Community Exposure to Emissions from Madison Kipp Corporation.

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## Abstract

Over the past several years, an increasing proportion of the community surrounding Madison Kipp has expressed concern about the operation of this facility. Neighbors are concerned for several reasons that are identified in this report. This report evaluates the data available on Madison Kipp's emissions and identifies questions about exposures that are not answered by the available data.

Prior to this evaluation, WI Department of Natural Resources staff had determined that Madison Kipp is in compliance with ambient air quality standards. This evaluation finds that the available data does not identify an obvious human health threat to the community and does not support the performance of a health study based on environmental exposures. Clearly, the community is exposed to low levels of Madison Kipp's emissions. However, a study designed to measure health outcomes as they relate to these known exposures is unlikely to be conclusive because, generally, low-level exposure does not create enough variation in health outcomes to be detectable with epidemiological methods. While questions about Madison Kipp's environmental impact remain, these questions seem to be limited to specific details about the emissions that are not considered to have public health significance. As additional data becomes available, this exposure evaluation will be re-evaluated to determine if the potential for adverse human health effects has changed.

## Introduction

The purpose of this evaluation of exposure is to help guide the Madison Department of Public Health (MDPH) and the Health Study Workgroup in the process of designing and evaluating the efficacy of a health study in the community surrounding Madison Kipp Corp. A considerable number of Madison Kipp's neighbors are clearly concerned about this facility's emissions with respect to environmental and human health impacts. As a step in understanding, assessing, and addressing the health concerns of the community, MDPH determined the need to summarize the exposure and emissions data collected by Wisconsin Department of Natural Resources (WI DNR) and Madison Kipp Corporation staff in a formal exposure evaluation document.

This evaluation of exposure is the second half of the preliminary evaluation of the health concerns reported by the community surrounding Madison Kipp. A preliminary evaluation of reported health concerns is one of the first steps in the Guidelines for Investigating Clusters of Health Events developed by the US Centers for Disease Control and Prevention (CDC) (1). The first half of this preliminary evaluation was the assessment of health reports received by Madison Department of Public Health (2). An informal assessment of health reports received from January 1997 through December 1999 found a wide variety of relatively common

symptoms. No patterns in symptom groups were observed among those reporting illness. For these reasons, it was not possible to create a case definition that would describe illness reported in the community surrounding Madison Kipp. Without a strong case definition, epidemiological studies are likely to be inconclusive. However, continuing community concern about health impacts identified the need to evaluate potential exposures.

## Evaluation of emissions and exposures

Madison Kipp Corporation is an aluminum and zinc die casting facility located on the east side of Madison, WI. Processes performed at the Madison Kipp Corporation have the potential to emit various pollutants including chlorine ($Cl_2$), hydrogen chloride (HCl), nitrogen oxides ($NO_X$), sulfur dioxide ($SO_2$), carbon monoxide (CO), particulate matter and various volatile organic compounds (VOC) (3). In response to ongoing concerns of the neighborhood about exposure to these chemicals, the following report has been prepared to summarize the exposure data collected by WI DNR and others. This assessment will also attempt to identify exposure data gaps and the possibility, feasibility, and the usefulness of collecting this information.

### *Chlorine ($Cl_2$) and Hydrogen Chloride (HCl)*

Chlorine and HCl are released from Madison Kipp Corp due to the injection of $Cl_2$ into molten aluminum in order to remove magnesium from the aluminum. Depending on the concentration of magnesium, the temperature of the metal, and several other factors, $Cl_2$ may not completely react with the magnesium in the metal and can be released from the furnace to the stack. Hydrogen chloride will result when $Cl_2$ reacts with water vapor present in the furnace, stack, and ambient air. Both $Cl_2$ and HCl are released from the stack as a result of this process.

The potential for release of these chemicals is of concern to neighboring residents because they are potent irritants (4-5). Chlorine and HCl may cause adverse health effects resulting from irritation or tissue damage in the respiratory tract and mucous membranes depending on the level of exposure. They also have a low odor threshold, which allows detection of the chemicals even at levels that are unlikely to cause harm.

The amount of $Cl_2$ and HCl released during this process has been estimated by Madison Kipp and has been measured by WI DNR required stack testing. While operating the RCI furnace (chlorine-injection furnace) at full capacity, stack testing in 1995 showed that 1.02 pounds of $Cl_2$ and 3.97 pounds of HCl were released per hour from the stack (6). These values are slightly lower than the maximum theoretical emission rates reported in 1998 by Madison Kipp (1.28 lbs $Cl_2$/hr and 4.99 lbs HCl/hr) (7). The maximum theoretical emission rate is an estimate of the total amount of a chemical that may be released by a facility. These estimates are generally higher than the actual emissions released. Wisconsin DNR modeled the ambient air concentration of $Cl_2$ and HCl based on the 1998 estimated emissions.

**Table 1. Modeled Ambient Air Concentrations of Chlorine and Hydrogen Chloride**
(All Concentrations in μg/M³)

| | $Cl_2$ - 24 hr | HCl - 1 hr |
|---|---|---|
| Modeled[1] Ambient Air Concentration | 6.1 | 69 |
| Acceptable ambient concentration (AAC)[2] (current) | 72.0 | 700.0 |
| Percent of Current Standard[3] | 8.5% | 9.9% |
| Acceptable ambient concentration (AAC)[2] (proposed) | 34.8 | 746 |
| Percent of Proposed Standard[3] | 17.5% | 9.2% |

[1] As determined by DNR modeling of Madison Kipp's 1998 emissions inventory report (7).

[2] Acceptable ambient concentrations for toxic air pollutants are described in NR 445.

[3] The percent of the current/proposed AAC is calculated by dividing the modeled ambient air concentration by the AAC.

As shown in Table 1, these modeling results estimate that the amounts of $Cl_2$ released by this process are 12 times lower than the current acceptable ambient concentration (AAC) and 6 times lower than the proposed AAC. In the case of HCl, modeled ambient air concentrations were approximately 10 times lower than both current and proposed AAC. The acceptable ambient concentration (AAC) is a health-based standard that is set at a level where adverse human health effects are not expected to occur. The AAC are described in Chapter NR 445 of the WI DNR's regulatory code. Currently, the WI DNR is in the process of revising these regulations to be more reflective of the current scientific knowledge.

The WI DNR has also performed ambient air sampling to measure the level of $Cl_2$ and HCl in the neighborhood surrounding the Madison Kipp facility. In 1994 and 1995, there were several attempts to measure $Cl_2$ and HCl in ambient air. Table 2 describes the results of these tests (8,9). As a comparison, the lowest level of $Cl_2$ reported in the literature to result in an immediate or short-term response (tickling of the nose) is 40 to 157 μg/M³ (10). The lowest observable effect level for inhalation of HCl was not found in the literature reviewed. However, symptoms of throat irritation are seen at levels of 52,000 μg/M³ (5). Higher levels of exposure result in increasingly serious health effects. While the levels observed in ambient air are much lower than those reported to cause toxic effects, the ambient air testing data is fairly old. Due to changes at Madison Kipp in processes and production levels, it is reasonable to recommend that ambient air testing for these chemicals be repeated.

Both modeled and measured levels of $Cl_2$ and HCl give an indication of the potential for exposure. However, the actual exposure experienced by any one person will vary widely by location, time and activity of the person. The data presented here may not fully characterize the total amount of variation in ambient air levels of $Cl_2$ and HCl. The stack test cited above

was performed while the RCI furnace was operating at full capacity. This was done to generate the highest level of emission from the process. The modeling results reported in Table 1 also were based on maximum emission rates calculated from Madison Kipp's 1998 emission inventory report. Thus, it should be reasonable to expect that the modeled ambient air concentrations of $Cl_2$ and HCl represent maximum levels and that variation will result in levels

**Table 2. Measured Ambient Air Concentrations of Chlorine and Hydrogen Chloride**

| Date | Chemical | Concentration ($\mu g/M^3$) | Location of sampling | Duration of sample |
|---|---|---|---|---|
| 9/17/1994 | $Cl_2$ | * | S. Marquette St | |
| 9/17/1994 | HCl | * | S. Marquette St | |
| 9/30/1994 | $Cl_2$ | ND | S. Marquette St | 10.2 hrs |
| 9/30/1994 | HCl | ND | S. Marquette St | 10.2 hrs |
| 10/20/1994 | HCl | ND | S. Marquette St | 7.7 hrs |
| 11/30/1994 | HCl | 2.9 | S. Marquette St | 6.1 hrs |
| 12/1/1994 | HCl | 157.1 | Bike Path | 4.1 hrs |
| 12/1/1994 | HCl | ** | S. Marquette St | 4.1 hrs |
| 2/9/1995 | $Cl_2$ | 9 | Dixon St and Fairview St | 5.8 hrs |

* = sample was not valid
ND = non-detectable
** = amount of HCl in the sample was less than or equal to the blank

lower than those reported in Table 1. However, an ambient air sample collected by WI DNR (Table 2) identified a concentration of $Cl_2$ that exceeded the modeled concentration reported in Table 1 but was still lower than the current and proposed AAC. To better understand the actual variation in $Cl_2$ and HCl, it may be possible to calculate daily $Cl_2$ emission rates from $Cl_2$ use data if appropriate emission factors are available. Madison Kipp records the amount of $Cl_2$ injected with computerized data recorders. Variation could also be determined through ambient air monitoring. However, monitoring for $Cl_2$ and HCl is limited because methods for continuous monitoring do not exist for the levels of these chemicals present in ambient air. Also, it may not be feasible to site a sufficient number of monitors in the area to account for changes in wind and weather conditions.

To this point, $Cl_2$ and HCl levels have been evaluated based on relatively short-term exposure periods of 24 hours and 1 hour, respectively. However, there is considerable concern among the neighbors that low-level exposure to $Cl_2$ and HCl over long periods of time may also affect human health. At this time, the data on $Cl_2$ and HCl in air are not capable of answering this question. With appropriate data, it may be possible to determine if long-term levels of these chemicals pose a long-term health risk. One method for answering this question is to compare ambient air concentrations with the US Environmental Protection Agency (EPA)

reference concentrations (RfC) for these chemicals. Reference concentrations are based on scientific research of the chemical and developed to protect sensitive populations from any adverse health effect over a lifetime of exposure. At this point, the US EPA has not finished development of the RfC for inhalation of $Cl_2$ (11). The RfC for HCl inhalation is 20 $\mu g/M^3$ (12). Comparison of this RfC with the HCl test results above is not appropriate because the modeled and measured concentrations given above do not account for the same amount of time as the RfC. The modeled ambient air concentration for HCl in Table 1 represents a maximum level of exposure over one hour. It is reasonable to expect that average daily and yearly concentrations of HCl in ambient air are lower than the HCl value reported in Table 1. The ambient air sampling data is also not comparable to the RfC because they are averages over several hours and were collected during a time when $Cl_2$ use was high. Clearly, $Cl_2$ and HCl levels are expected to vary over time. In order to compare test results with the RfC, it is necessary to know the average 24-hour HCl concentration in ambient air.

*Areas lacking data, Chlorine and Hydrogen Chloride*

1) Testing results for $Cl_2$ and HCl are relatively old and levels of these chemicals in ambient air may have changed over this period of time.
    a) Additional ambient air testing should be considered to ensure that ambient air concentrations of these chemicals have not changed.
2) Variation in $Cl_2$ and HCl levels in ambient air may not be fully characterized.
    a) Modeling of daily $Cl_2$ and HCl levels from $Cl_2$ use data and emission factors may be the most feasible method of obtaining this information.
3) Long-term (daily and yearly) ambient air concentrations for $Cl_2$ and HCl have not been determined.
    a) Modeling daily $Cl_2$ and HCl levels from the $Cl_2$ use logs may also give useful information for comparison with published RfC values and comparison with other respiratory irritants.

*Oxides of Nitrogen ($NO_X$), Sulfur Dioxide ($SO_2$) and Carbon Monoxide (CO)*

Oxides of nitrogen, sulfur dioxide and carbon monoxide are generated as a result of the combustion of natural gas, propane, and diesel in the furnaces and emergency power generators (3). Given sufficient exposure, these chemicals may result in toxic health effects. However, based on stack testing and WI DNR modeling analysis, these compounds are not expected to achieve ambient air levels that may result in adverse health effects (Table 3) (13). These modeling results are based on established emission factors for the combustion of natural gas, propane, and diesel.

As shown in Table 3, Madison Kipp's modeled ambient air concentrations and the total ambient air concentrations (the sum of Madison Kipp's modeled emissions and the current background concentrations) of CO, $NO_X$, and $SO_2$ are less than the National Ambient Air Quality Standard (NAAQS) set to protect human health and the environment. The total ambient air

concentration gives the reader an ability to compare the maximum potential impact of Madison Kipp emissions on ambient air quality in the neighborhood.

**Table 3. Modeling of Carbon Monoxide, Sulfur Dioxide and Nitrogen Oxides**
(All Concentrations in μg/M³)

| Pollutant (Averaging time) | CO 1 hr | CO 8 hr | $SO_2$ 3 hr | $SO_2$ 24 hr | $SO_2$ Annual | $NO_X$ Annual |
|---|---|---|---|---|---|---|
| Ambient Air Concentration[1] (MKC) | 550.9 | 272.0 | 529.5 | 222.2 | 15.0 | 69.5 |
| Ambient Air Concentration (Background) | 3,475.2 | 2,527.4 | 137.5 | 40.8 | 8.5 | 17.9 |
| Total Ambient Air Concentration | 4,026.1 | 2,799.4 | 667.0 | 263.0 | 23.5 | 87.4 |
| NAAQS Standard for Ambient Air | 40,000 | 10,000 | 1,300.0 | 365.0 | 80.0 | 100.0 |
| Proportion of Standard (MKC emissions) | 1.4% | 2.7% | 40.7% | 60.9% | 18.8% | 69.5% |

[1]The ambient air concentration attributed to Madison Kipp is considered to be the potential to emit if the facility is operating at maximum capacity.

Carbon monoxide levels in ambient air resulting from Madison Kipp are a small percentage of the background levels of this chemical and the NAAQS standard. Acute toxic effects of CO exposure are documented to occur at exposures greater than or equal to 80,000 μg/M³ (14). Chronic effects may occur at levels exceeding 28,000 μg/M³, especially in persons suffering from heart disease. Given this information, CO emissions from Madison Kipp do not represent a human health threat.

Modeling of Madison Kipp's $SO_2$ and $NO_X$ emissions at full operating capacity has determined that ambient air concentrations of these chemicals are less than the NAAQS standards. At high levels, sulfur dioxide ($SO_2$) and oxides of nitrogen ($NO_X$) may cause respiratory irritation and tissue damage (15,16). Oxides of nitrogen include several different nitrogen compounds. One of the most important oxides in this group is nitrogen dioxide ($NO_2$). Both $SO_2$ and $NO_2$ can affect the respiratory system directly and decrease a person's natural ability to respond to respiratory diseases (15, 16). A long-term exposure study in British steel workers found no long-term health effects resulting from exposure to $SO_2$ at 900 μg/M³ (15). A study comparing healthy non-smokers to persons with mild asthma found that short-term exposure to 1,300 μg/M³ of $SO_2$ caused a slight impairment in respiratory function in the asthmatics but had no effect in those without asthma. After exposure to about 500 μg/M³ of $NO_2$, persons with mild asthma experienced slight changes in bronchial responsiveness (16). Exposure to $NO_2$ levels of 3,800 to 9,400 μg/M³ in indoor air has been

shown to have some effect on the immune system. The current annual ambient air standards of 80 μg $SO_2/M^3$ and 100 μg $NO_X/M^3$ appear to be protective of human health.

*Particulate Matter*

Madison Kipp generates particulate matter during the combustion of natural gas or propane in the furnaces and diesel fuel in emergency generators (3). Particulate matter may also result during the aluminum melting and cleaning process and during die-casting of aluminum and zinc. Table 4 provides the WI DNR modeling results for particulate emissions from Madison Kipp (13). The emission rates used in this modeling were the maximum potential emissions from all processes generating particulate matter.

**Table 4. Particulate Matter, NAAQS Analysis Results**

(All Concentrations in $\mu g/M^3$)

| | $PM_{10}$ - 24 hr | $PM_{10}$ - Annual | TSP - 24 hr |
|---|---|---|---|
| Ambient Air Concentration (from MKC) | 73.5 | 13.6 | 73.5 |
| Ambient Air Concentration (Background) | 48.4 | 22.6 | 72.7 |
| Total Ambient Air Concentration | 121.9 | 36.2 | 146.2 |
| NAAQS Standard for Ambient Air | 150.0 | 50.0 | 150.0 |
| Proportion of Standard (MKC emissions) | 49% | 27.2% | 49% |

WI DNR modeling shows that MKC's contribution to the regional ambient air concentrations varies depending on the time frame of measurement. The maximum 24-hour ambient air concentration of particulate matter 10 microns or smaller ($PM_{10}$) and total suspended particulate (TSP) resulting from Madison Kipp processes exceeds the highest 24-hour ambient air background concentration. However, the sum of Madison Kipp emissions and background concentrations does not exceed the NAAQS standard for either of these measurements. The "Total Ambient Air Concentration" provided in Table 4 for $PM_{10}$ - 24 hr and TSP - 24 hr estimates the maximum level of particulate matter in the area from all sources. When averaged over one year, Madison Kipp's contribution of $PM_{10}$ is less than the regional background levels of $PM_{10}$ and is 27.2% of the ambient air concentration standard.

From March 1998 through December 2000, 95% of measured total suspended particulate levels for the area have been less than the level predicted by WI DNR modeling for Madison Kipp. Monitoring for total suspended particulate is performed by a monitor that was placed near the bike path and Madison Kipp in March 1998. This monitor collects a 24-hour sample of air every six days and records the concentration of particulates. In this time period, one measurement in April 2000 measured TSP at a level of 180 $\mu g/M^3$ (17). Review of wind

data and analysis of the particulates collected suggest that the source of the particulates collected on this day was another local business located northwest of the air monitor. Microscopic analysis of the particulates collected determined that the majority of the particulates (54%) were calcium carbonate rocks and minerals in the 110-micron size range. Another 19% of the sample collected was quartz and feldspar mineral fragments in the 120-micron size range. In addition to other local businesses, other potential sources of particulate in this area are, most notably, the local vehicle traffic and the combustion of natural gas and other fuels in neighboring homes.

While ambient air monitoring has found that the majority of TSP samples in the area are fairly low, this is an incomplete answer to the question of particulate exposures. Research has shown that particulate matter ≤2.5 microns ($PM_{2.5}$) and 2.5 to 10 microns ($PM_{10}$) have a greater effect on health than the larger particulates (18). Although infrequent, air monitoring has shown the potential for high particulate levels to exist in the community. For this reason, there is a need to determine the amounts of $PM_{2.5}$ and $PM_{10}$ that are present in the total particulate load in the community. This would help ensure that particulate levels in the neighborhood are in agreement with air quality standards.

*Areas lacking data, Particulate Matter*

1) The amount of $PM_{2.5}$ and $PM_{10}$ particulate matter in the neighborhood is unknown.
    a) Due to the potential for high TSP in the area, measurement of the smaller size fractions of particulate matter may be necessary to ensure compliance with air quality standards.

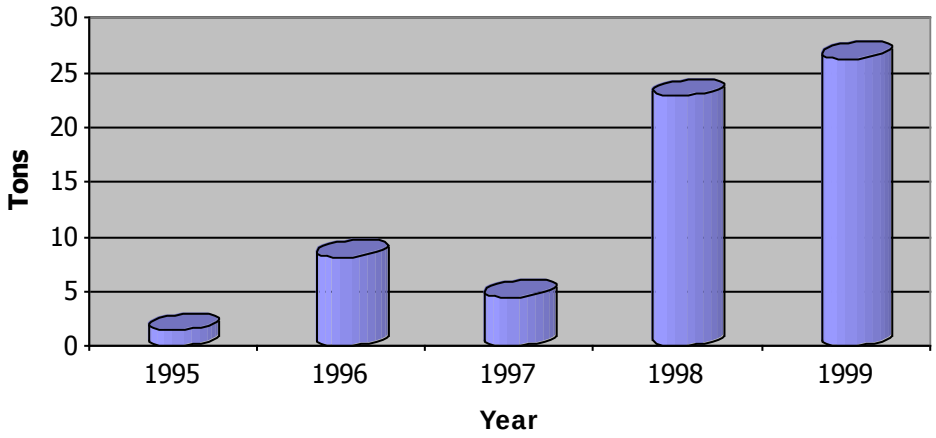
*Organic Chemical Emissions*

Organic chemicals emitted by Madison Kipp result from the combustion of natural gas and propane, the vaporization of die lube and shot beads during the die casting of aluminum and zinc, and from the remelt of aluminum and zinc die cast scrap (3). Many of the organic chemicals released by these processes are considered to be volatile organic compounds (VOC). As a group, VOCs are regulated to control the generation of ozone. Organic chemicals, including those that are VOCs, are also regulated individually based on their toxic properties.

Volatile organic compounds are reported in Madison Kipp's emission inventory report each year (19). In this report, VOC emissions are calculated based on VOC emission factors for each of Madison Kipp's VOC emitting processes. The emission of VOC from the combustion of natural gas and propane are calculated by multiplying the quantity of natural gas or propane consumed over one year by emission factors established by the US EPA. Because VOC emission factors are not established for die casting processes, WI DNR required Madison Kipp to analyze the VOC emissions from the die casting process. This testing resulted in quantifying the total amount of VOC emitted from the die casting process and the development of total VOC emission factors for die-casting. From these test results, WI DNR determined that Madison Kipp would not be in violation of the VOC emission rules. Volatile organic compound emission data reported to the WI DNR over the last 5 years is given in Figure 1. The values in Figure 1

are reported in tons of VOC emitted per year because ambient air concentrations for VOCs have not been modeled. Wisconsin DNR has not pursued modeling of VOC as a group because there is currently no acceptable model for estimating the ozone generation potential from VOC emissions. The dramatic increase in VOC levels between 1997 and 1998 is likely to be the result of changes in Madison Kipp's reporting procedures. Levels of VOC emissions for 1995 through 1997 are expected to be similar to those reported in 1998 and 1999.

**Figure 1. Total VOC Emissions (both Waubesa and Fair Oaks facilities)**




While the total amount of VOC emitted has been estimated, the chemical composition of organic chemicals emitted by Madison Kipp may not be complete. The specific organic chemicals emitted from the combustion of fossil fuels at the facility can likely be estimated using US EPA's established emission factors. As mentioned above, no such emission factors exist for the die-casting or furnace processes. An environmental consultant for Madison Kipp gathered the only data available on the organic chemicals generated by the die-casting process in February 1998 (20). This analysis involved collecting die-casting process emissions in a 6-liter summa canister and analyzing them by GC-MS. The organic chemicals generated by the vaporization of the die lube and shot beads (plunge lube) are provided in Table 5. The GC-MS scan (EPA Method TO-14) attempted to identify 61 individual organic chemicals. Only those with detectable concentrations are reported in Table 5. Also reported in Table 5 are acceptable ambient concentrations (AAC) for each of the chemicals. Except for benzene and 1,3-butadiene, the levels of these chemicals are much smaller than the AAC. Even though levels of benzene and 1,3-butadiene were closer to the AAC, the fact that the sample was taken directly above the die-casting machine must be considered before determining potential exposure to residents in the surrounding community. Neither the manufacturer of the die-lube nor technical specialists with North American Die Casting Association were able to provide additional data on the organic chemical emissions from the die casting process.

Organic chemicals may also be emitted from the aluminum melt furnace when metal with lubricant residue is charged to the furnace. The identity and quantity of organic chemicals

**Table 5. VOCs emitted from the aluminum die casting process**

| Product (Chemical Composition) | VOC identified | Concentration (ppb) | Acceptable Ambient Concentration (ppb) |
|---|---|---|---|
| Die Lube (15-25% proprietary lubricant blend, 1-3% alkanolamine, remainder water) | Ethanol | 3,500 | 24,000* |
| | Unknown alkane 1 | 63 | NA |
| | Unknown alkane 2 | 78 | NA |
| Shot beads (100% polyethylene) | Ethanol | 950 | 24,000* |
| | 1,1,1-Trichloroethane | 4.4 | 8,400* |
| | Benzene | 6.5 | 12** |
| | Toluene | 6.2 | 1,200 |
| | 1,3-Butadiene | 16 | 48 |
| | Acetone | 23 | 12,000* |
| | Unknown hydrocarbon | 90 | NA |
| | 1-Hexene | 20 | 720 |
| | Unknown alkane 3 | 29 | NA |
| | Unknown alkane 4 | 40 | NA |
| | Unknown alkene | 25 | NA |

NA = not applicable. Acceptable ambient concentration (AAC) can only be determined for specific chemicals.

* This AAC was calculated by dividing the current TLV by 0.024 because this chemical is not listed in NR 445 as a hazardous air pollutant.

** This AAC was calculated by dividing the current TLV by 0.024 because benzene is not regulated according to the AAC.

generated by this process are unknown. However, several members of the community are concerned that dioxin is a potential emission from this process. Madison Kipp disagrees with this conclusion. In 2000, the City of Madison collected soil samples from the neighborhood and several locations around the City for dioxin analysis. Low levels of dioxin were identified in each of the samples. This was not surprising because it is likely that dioxin will be measurable in any urban soil at part per trillion levels (21). The highest concentration was identified in a sample collected from Mayor Sue Bauman's residence on the west side of Madison, approximately 4 miles southwest of Madison Kipp. The soil test results did not identify a hazard to human health or the environment and indicated that multiple sources over time were likely to be responsible for the dioxin present in the soil. According to their most recent permit, Madison Kipp will be required to perform dioxin emissions tests to determine if they are a source of dioxin. At this time, Madison Kipp is in the process of performing stack tests for dioxin.

*Areas lacking data, Organic Chemical Emissions*

1) Organic chemical emissions from Madison Kipp may not be completely characterized.
   a) WI DNR has required Madison Kipp to perform stack testing for the presence of dioxin as a condition of their most recent air emissions permit.
   b) Further characterization may be possible through process evaluation and sampling activities.

## Madison Kipp Odors

Madison Kipp processes generate distinctive odors. The community has reported a wide variety of odors over the last 10 years; however, chlorine odor and a "waxy/oily/burnt" chemical odor are the most frequently reported odors from the facility. Some complainants have identified both of these odors as the cause of acute illness including asthma attacks, sore throat, nausea, vomiting, etc. Research has shown that strong odors may trigger asthmatic or allergic responses in sensitive individuals (22). Other complainants are concerned because they consider these odors to be a marker of exposure to unknown emissions from Madison Kipp. While these concerns may not be directly related to illness, they should not be dismissed because they represent a decrease in quality of life for the community.

It is reasonable to assume that the reports of chlorine odors originate from the aluminum melting and drossing process (see discussion of chlorine and hydrogen chloride above). This does not exclude the possibility that additional sources of chlorine odors may exist in the community. However, emission of chlorine from this process is the most likely source of these odor complaints. Other sources of chlorine odor are suspected because a small number of chlorine odor complaints have been received during times that the facility was inactive or not using chlorine. This may also be explained by some misclassification of the odors reported.

The "waxy/oily/burnt" chemical odor is a product of the die-casting process. This has been determined through personal experience of this process and recognition of these odors in the community. WI DNR staff and others have also recognized the similarities between die casting odors and the "waxy/oily/burnt" chemical smell reported by neighbors. However, the chemical composition of this odor is unknown. Emissions causing this odor are expected to be a mixture of particulates and organic chemicals. Wisconsin State Occupational Health Lab (WSOH) chemists have suggested that organic chemicals, rather than particulates, are the compounds most likely to be responsible for the odor (23). The above discussion of particulate matter and organic chemical emissions characterize what is currently known about emissions from the die casting process. However, this data does not clearly explain the odor emitted by this process. This is not considered to be uncommon to WSOH or Madison Department of Public Health chemists. The human nose is considered to be a relatively acute sensor that current scientific air monitoring equipment is not yet able to duplicate.

During July and August 1996, WI DNR attempted to identify and quantify the VOCs present in the ambient air during a period when the "waxy/oily/burnt" chemical odor was present (24). Volatile organic compounds were collected using long-term, short-term, and instantaneous sampling methods. The long-term method measured VOCs over 31½ days at three locations down-wind and one location upwind of the Waubesa facility. These results, reported in levels of benzene and total hydrocarbons, found two of the three down-wind locations to be essentially the same as the up-wind location. The third down-wind sample found levels of these chemicals slightly higher than the upwind site. Short-term monitoring lasted for 4 hours during a strong odor event. Analysis of the 4-hour sample identified small amounts of total hydrocarbons and formaldehyde. No benzene was detected using this method. The instantaneous test involved collecting an air sample in a 1.8-liter steel, vacuum canister during a period of especially strong odor. The results of the short-term and instantaneous sample analyses identified a wide variety of volatile organic compounds; however, the concentrations of the chemicals identified were below current air quality standards and odor thresholds. Overall, WI DNR staff concluded that the types and quantities of VOCs identified by these analyses were typical of urban areas with car and truck traffic similar to that on Atwood and East Washington Avenues. For this reason, it is not possible to definitively identify the source of the VOCs measured.

As set by DNR rules, no person or company may emit or cause to emit objectionable odors as defined by the rule. WI DNR may determine if an odor meets the definition of objectionable through staff evaluation or performance of an odor survey in the affected community (23). Prior to 1999, WI DNR staff evaluations determined that the odors identified in the community surrounding Madison Kipp did not meet all criteria for an objectionable odor. After receiving a petition from the neighborhood in 1999 concerning odors from Madison Kipp, WI DNR developed and performed an odor survey of the neighborhood surrounding Madison Kipp's Waubesa facility. In response to this survey, 374 (58%) members of the community returned their survey and 103 (28%) of these reported that odors from Madison Kipp were objectionable. For the odor to be found objectionable, 60% of the community surveyed must find the odors from Madison Kipp to be objectionable. Wisconsin DNR staff stopped actively soliciting survey responses when it was clear that the mandatory level of 60% could not be reached. While the results of this survey are not enforceable under the WI DNR code, these results do identify that a considerable portion of the community is concerned about Madison Kipp's odors.

*Areas lacking data, Odors*

1) The chemical composition of the waxy, oily odor is unknown.
    a) This may indicate a need for further characterization of die-casting organic chemical emissions.

## Exposure to Mixtures

Understanding the impact of chemical mixtures on human health has been recognized as an important public health issue. Many of Madison Kipp's emissions, specifically $Cl_2$, HCl, $SO_2$, $NO_X$, and particulate matter, are potential respiratory irritants and may act in combination to cause respiratory illness or irritation after inhalation of sufficient concentrations.

Combining the available data on these emissions to assess their potential to cause illness is difficult. One method for evaluating the potential impact of a mixture of chemicals with similar toxic effects is to calculate a hazard index. In order for a hazard index to be valid, the chemicals combined in the index must cause similar health effects and act independently of each other (26). There are some problems with using a hazard index to assess Madison Kipp's emissions. Different averaging times for each of these emissions makes it difficult to generate a valid hazard index. Ambient air concentrations for each of these emissions are based on Madison Kipp's maximum potential to emit. This means that the actual emissions of these chemicals from Madison Kipp may be lower due to variation in plant activity and any calculation of a hazard index would overestimate the potential for respiratory illness.

Without combining the exposure data for respiratory irritants emitted by Madison Kipp, it is difficult to assess the effect of this combination of chemicals. As additional data on Madison Kipp's emissions and methods for assessing chemical mixtures is made available, the potential for these chemicals to cause respiratory illness or irritation should be re-evaluated.

*Areas lacking data, Exposure to Mixtures*

1) Ambient air concentrations of $SO_2$, $NO_X$, $PM_{2.5}$ and $PM_{10}$ resulting from normal operations at Madison Kipp have not been determined.
    a) These data are necessary to calculate a hazard index that is more representative of the potential risk for respiratory illness in the community.
    b) These data should be presented as 24-hour and annual averages to allow for accurate comparison with other emissions.

## Determining Public Health Significance of the Data Gaps

As stated earlier, the purpose of this report is to support the efforts to evaluate the efficacy of a health study of the community surrounding Madison Kipp Corporation. For this reason, the data gaps identified above are evaluated here with respect to their public health significance. In this instance, public health significance refers to the potential of the missing data to identify a human health hazard that could be conclusively evaluated with a health study. The following are the criteria used by MDPH to determine the public health significance of a question or data gap.

- ✓ The chemical or group of chemicals is known to cause acute or chronic illness.
- ✓ It is likely that the public is exposed to levels of the chemical or group of chemicals that are sufficient to cause a measurable level of illness.

Repeating the limited ambient air monitoring of $Cl_2$ and HCl is not expected to provide information that will be meaningful to the performance of a health study. While it is possible that short-term levels of these chemicals in ambient air have changed since 1994, it is not expected that these levels have increased sufficiently in comparison to the AAC. The reasons for this position are that measured levels of these chemicals in 1994 were small compared to the AAC and improvements have been made in chlorine injection control over the last several years that have reduced the potential for $Cl_2$ and HCl releases. Data on the daily and yearly variation in $Cl_2$ and HCl would allow better understanding of the long-term exposures to these chemicals. However, if the available data represents ambient air conditions under maximum output, long-term average concentrations are not expected to be sufficient to cause chronic illness.

The lack of information on ambient air concentrations of respiratory irritants ($Cl_2$, HCl, $SO_2$, $NO_X$ and particulate matter) during normal operating conditions is not considered to have public health significance at this time. Combinations of these chemicals may cause illness at sufficient levels. However, there is insufficient evidence to suspect that the levels of these chemicals combined would be adequate to cause observable respiratory illness in the community.

Ambient air monitoring of $PM_{2.5}$ and $PM_{10}$ may have public health significance with respect to the community's exposure to particulates. However, this monitoring data may not sufficient to support a health study of Madison Kipp's emissions. The applicability of ambient air monitoring of these particulates to the evaluation of Madison Kipp emissions is limited by the ability to separate Madison Kipp particulates from those generated by other sources in the community. Modeling of particulate emissions is likely to be the best tool for evaluating Madison Kipp; however, monitoring is needed in the case of $PM_{2.5}$ and $PM_{10}$ to ensure the area is in agreement with NAAQS standards.

At this time, the data gap concerning organic chemical emissions is not considered to have public health significance as defined in this report. Measurement of these chemicals in process emissions and ambient air have shown that organic chemicals from Madison Kipp processes are present at levels that are less than the AAC. While these chemicals are known to cause various human health effects, the levels that have been identified are not sufficient to suspect that a health risk exists for the community due to these emissions. However, this department supports further efforts by the WI DNR to characterize and measure the organic chemical emissions from Madison Kipp. As it becomes available, new data on dioxin and any other organic emissions will be reviewed to determine their impact on this exposure evaluation.

Determination of the public health significance of Madison Kipp's odors is difficult. Currently, the chemical composition of the "oily/waxy/burnt chemical" odor is unknown. The process that generates this odor has been determined to be the die casting process. As discussed earlier in this report, the organic emissions resulting from this process are not at

levels sufficient to cause adverse health effects. However, complaints received by this process clearly show that some members of the community are very concerned about the chemicals that make up this odor. Many of the complaints received associate this odor with various symptoms. However, this data does not assist us in determining the odor's potential for causing human health effects due to the wide variety of symptoms and the lack of consistency in symptom reports among callers and individual complaints. The potential exists that symptoms associated with Madison Kipp odors are due, at least in part, to an increase in anxiety about potential chemical exposures. This has been found in many health studies evaluating the effect of various odors on human health (22). From this perspective, it may be possible to conclude that Madison Kipp's odors indirectly cause adverse health effects. However, it is impractical to use a health study to evaluate this relationship. Clearly, explanation or elimination of the odors associated with Madison Kipp's processes would be beneficial to reducing the concerns of the neighborhood. However, the data gaps related to odors are not considered to have public health significance as defined in this report.

## Summary and Conclusions

Over the past several years, an increasing proportion of the community surrounding Madison Kipp has expressed concern about the operation of this facility. Neighbors are concerned for several reasons. These reasons include, but may not be limited to:

1. Neighbors are continually reminded of Madison Kipp's presence by its odorous emissions,
2. Neighbors are convinced that the majority of Madison Kipp's emissions are unknown,
3. Neighbors are convinced that Madison Kipp's emissions are causing illness in their community,
4. Neighbors are convinced that Madison Kipp's emissions are higher than necessary and need to be reduced.

Issues related to odor and unknown emissions are addressed by this report. This report also addresses the potential relationship between known emissions and human illness. However, this health study evaluation process does not attempt to address community desires for process alternatives and emissions reductions at the Madison Kipp facilities.

Wisconsin DNR staff had already determined that Madison Kipp meets ambient air quality standards. While neighbors are concerned that air quality standards are not protective enough, the data presented in this report indicate that emissions from Madison Kipp do not present an obvious human health threat to the community. Chlorine and hydrogen chloride have been periodically documented at detectable levels. However, these chemicals have not been found or estimated at levels known to result in acute human health effects. Similarly, the modeled levels of particulate matter, both total suspended particulate and the particulate smaller than 10 microns, are within acceptable air quality standards. Finally, levels of the organic chemicals, including VOC, identified in ambient air are not present at levels expected to result in human health effects. This data suggests that Madison Kipp's neighbors are exposed to low levels of chemical emissions from this facility. However, a study designed to measure

health outcomes as they relate to these known exposures is unlikely to be conclusive because low level exposures are not expected to create enough variation in health outcomes to be detectable with epidemiological methods.

While much is known about Madison Kipp emissions, this report also identifies several areas in which data is insufficient to answer the community's questions about Madison Kipp's emissions. To summarize, the knowledge gaps identified in this report include:

1. What is the variation in chlorine and hydrogen chloride levels in ambient air?
2. Have chlorine and hydrogen chloride levels in ambient air changed since 1994?
3. What are the long-term (daily and yearly) ambient air concentrations of $Cl_2$ and HCl and how does this compare with EPA's reference concentration?
4. How much of the measured particulate matter consists of $PM_{2.5}$ and $PM_{10}$?
5. Have Madison Kipp's volatile organic compound emissions been completely characterized?
6. What is the chemical composition of the "waxy/oily/burnt" chemical odor released from Madison Kipp?
7. What is the expected ambient air concentration of $SO_2$, $NO_X$, $PM_{2.5}$ and $PM_{10}$ under normal operating conditions?

While each of these questions identifies an area where information about Madison Kipp's emissions is lacking, the importance of answering each of the questions will vary depending the purpose of answering the question. If the purpose of filling these data gaps is to gather as much information as possible about Madison Kipp's environmental impact, then all of these questions should to be answered.

However, the purpose of this exposure evaluation was to determine if Madison Kipp's emissions are sufficient to cause human health effects that can be evaluated with a health study. While seven data gaps are identified in this report, none of these gaps meet both of the criteria for public health significance. Questions with public health significance are those that meet the following criteria.

- ✓ The chemical or group of chemicals is known to cause acute or chronic illness.
- ✓ It is likely that the public is exposed to levels of the chemical or group of chemicals that are sufficient to cause a measurable level of illness.

This report finds that the available emissions and monitoring data does not support the performance of a health study based on environmental exposures. The available data suggests that the surrounding community is exposed to low levels of Madison Kipp's emissions. However, the levels identified are in compliance with health-based air quality standards and not expected to cause human health effects that are observable with an epidemiological health study. Additional emissions data that would be useful in this evaluation has been identified. As additional data becomes available, this exposure evaluation will be revised and re-evaluated to determine if the potential for adverse human health effects has changed.

## Citations


1. Guidelines for Investigating Clusters of Health Events. 1990. MMDW, Centers for Disease Control and Prevention. Vol. 39 / No. RR-11.
2. Public Health Evaluation of Health Concerns Related to Madison Kipp Corporation. 2001. Unpublished report from Madison Department of Public Health.
3. Analysis, preliminary determination and draft permit for Madison-Kipp Corporation. 2000. Unpublished draft permit from Wisconsin Department of Natural Resources. Permit #99-BSP-912.
4. Chlorine search in the Hazardous Substances Data Bank. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
5. Hydrogen chloride search in the Hazardous Substances Data Bank. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
6. Analysis and preliminary determination for the construction and operation permits for the proposed modification of the RCI 2 furnace to allow chlorine usage. 2000. Unpublished draft permit from Wisconsin Department of Natural Resources. Permit #00-BSP-944 and 00-BSP-944-OP.
7. Personal communication with John Roth, WI DNR. Feb. 14, 2001.
8. Air monitoring near the Madison-Kipp Corporation, Madison. Feb. 7, 1995. Memorandum from Mark Allen, WI DNR, to Tom Sheffy, WI DNR.
9. Evaluation of chlorine ambient monitoring results. Jan 14, 1997. Memorandum from Brian Barbieur, WI DNR, to WI DNR Madison Kipp File.
10. Chlorine. US Environmental Protection Agency Air Toxics Website. http://www.epa.gov/ttnatw01/hlthef/chlorine.html.
11. Chlorine search in the Integrated Risk Information System. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
12. Hydrogen chloride search in the Integrated Risk Information System. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
13. Air Dispersion Analysis for Madison Kipp Corporation – Madison. Jul. 12, 2000. Memorandum from John Roth, WI DNR, to Brad Pyle, WI DNR.
14. Personal communication with Lynda Knobeloch, WI DHFS. May 3, 2001.
15. Sulfur dioxide search in the Hazardous Substances Data Bank. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
16. Nitrogen dioxide search in the Hazardous Substances Data Bank. 2001. Toxnet, National Library of Medicine Website. http://toxnet.nlm.nih.gov/.
17. Personal communication with Tom Roushar, WI DNR. Jun. 1, 2001
18. Dockery, DW and CA Pope III. Outdoor Air I: Particulates. 1997. Topics in Environmental Epidemiology. Oxford University Press. pp 119-166.
19. Air Emissions Management System. Data provided by Tom Roushar on Jan. 17, 2001.
20. Analysis of emissions from die-casting operation. Feb. 17, 1997. Letter from James S Rickun, RMT, Inc, to Tom Roushar, WI DNR.
21. Soil dioxin results. Nov. 27, 2000. Memorandum from Chuck Warzecha, WI DHFS, to John Hausbeck, MDPH.

22. Shusterman, D. Critical review: The health significance of environmental odor pollution. 1992. Archives of Environmental Health, Vol. 47(1):76-87.
23. Personal communication with Dr. Jamie Schauer, WI State Laboratory of Hygiene, Jan. 20, 2001.
24. Results from air monitoring near Madison Kipp.. Oct. 10, 1996. Memorandum from Mark Allen, WI DNR, to Tom Sheffy, WI DNR.
25. Odor survey summary. 1999. Unpublished report from WI Department of Natural Resources.
26. Pratt, GC, K Palmer, CY Wu, F Oliaei, C Hollarbach, MJ Fenske. An assessment of air toxics in Minnesota. 2000. Environmental Health Perspectives, Vol 108(9).