Calcium Magnesium Acetate: Comparative Toxicity Tests and an Industrial Hygiene Site Investigation

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A commercial formulation of calcium magnesium acetate (CMA), an alternative deicing agent for salt-sensitive areas, was evaluated for toxicity. A subchronic toxicity test was performed, as was a full complement of short-term toxicity tests including acute oral toxicity, acute inhalation toxicity, acute dermal toxicity, eye irritation, skin irritation, and dermal sensitization tests. Presented in this report are the results of those tests, conducted through the Chevron Environmental Health Center, Inc., which are compared to similar toxicity data on sodium chloride and some worker experience with CMA. The goal was to identify and characterize any immediate or short-term toxic effects CMA may produce in humans and compare the results with data on sodium chloride (common salt). This series of tests showed CMA to have very low mammalian toxicity. In general, the effects produced by CMA are similar to those caused by sodium chloride in similar toxicity tests. The systemic toxicity potential of CMA is similar to that of sodium chloride, as are the eye and skin irritation potentials. In the subchronic feeding study, CMA produced no toxicity at a "limit" dose of 1,000 mg/kg/day for 28 days. The acute inhalation toxicity of CMA is also low and CMA produced no evidence of immunologic reactivity in a dermal sensitization test. In spite of the low irritation potential evidenced in the acute eye and skin tests, highway workers at one field test site complained of eye and skin irritation when handling CMA. An industrial hygiene site investigation was conducted to attempt to reconcile this human experience with the laboratory data. Dust exposures at the site in question were found to greatly exceed the threshold limit value for occupational exposure to nuisance dusts; respirable dust levels were much lower. In summary, laboratory and human evidence indicate CMA to have a toxicity comparable to that of sodium chloride.

Calcium magnesium acetate (CMA) is being evaluated as an alternative road deicing agent in the United States and abroad, especially in environmentally sensitive areas. Two attractive features of CMA, as compared to traditional road salt, are that it is (a) less corrosive and (b) less damaging to the environment. CMA has been shown to be less corrosive to concrete, zinc, aluminum, and steel than has salt; it is therefore expected to produce less damage to bridges and other road structures and to automobiles. CMA contains no sodium or chloride to contribute to groundwater contamination and is expected to have less effect on salt-sensitive vegetation.

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If CMA is to play a major role as a deicing agent, other factors must also be considered; prime among these is toxicity. Toxicity is the capability of a compound to injure living organisms. The mitigating factor to toxicity is dose, the amount of the compound to which a living organism is exposed. Virtually all compounds have some toxicity; the extent of its expression depends on the level of exposure required for injury to occur (injury from a compound of low toxicity requires exposure to a larger amount).

Salt is perceived by the public as "nontoxic"; it has a low mammalian toxicity in comparison with other compounds common to society. Therefore, before the public can be expected to accept an alternative deicing agent, its toxicity should be evaluated and compared to that of salt.

CHEMICAL INFORMATION

Toxicity studies were conducted on the Chevron Ice-B-Gon™ deicer formulation of CMA. This CMA formulation has a nominal 3:7 calcium:magnesium ratio and is approximately 91 percent CMA (dry basis). Formulations of Chevron Ice-B-Gon™ deicer having different proportions of calcium and magnesium may be developed in the future. It is believed that the results of the studies described in this paper will be generally representative of the toxicity of these other formulations. Because of potential differences in manufacturing processes, physical and chemical properties, and impurities present, however, it is not known if these data will be relevant to CMA prepared by other manufacturers.

An actual commercial sample from an early production run of the CMA was used for toxicity evaluation. For testing, the normally hard, spherical pellets were ground into a fine powder, a procedure that usually increases biological reactivity and allows for precise exposure control.

Following is the structure of the commercial formulation of CMA used in the toxicity studies and the field tests that form the basis of this report:

$$CMA = Ca_xMg_y(C_2H_3O_2)_{2(x+y)}$$

where

x = 3 to 4
y = 7 to 6

TOXICITY OF CALCIUM MAGNESIUM ACETATE

The toxicity tests performed on CMA included acute oral toxicity, acute inhalation toxicity, acute dermal toxicity, eye irritation, skin irritation, and a subchronic oral test. This series of tests is appropriate for a deicing agent, a compound which is expected to be used daily, but only on a seasonal basis. The tests were performed in accordance with federal guidelines for toxicity testing, where applicable (*1*, *2*).

A review of the toxicology literature for similar data on sodium chloride did not identify any toxicity studies on road salt itself. Since road salt is primarily sodium chloride, the toxicity data on sodium chloride were used for the comparison to CMA; any toxicities of the additives and impurities present in road salt are not represented by these data.

Short-term toxicity tests are conducted using unrealistically high doses of the test compound, the rationale being that these high doses will exaggerate any subtle effects that might not otherwise be apparent. In addition, these tests characterize any risk associated with one-time or occasional use of the test compound.

These tests showed CMA to have low mammalian toxicity. In general, the effects produced by CMA were similar to those caused by sodium chloride (common salt) in the same tests. As evidenced by the acute and subchronic oral toxicity tests, the systemic toxicity potentials of the two compounds are very similar. Dermal and ocular testing showed the skin and eye irritation potentials of CMA to be equivalent to or less than those of sodium chloride. Few inhalation data on sodium chloride are available for comparison; however, CMA exhibited very low toxicity by this route of exposure. Signs of respiratory difficulty developed in some animals during the inhalation study, but this was in response to an exposure level 450 to 500 times that of the threshold limit value (TLV) for occupational exposure to nuisance dusts (which is 10 mg/m^3).

Acute Oral Toxicity

An acute oral toxicity test provides a basic indication of the level of toxicity of the compound being studied. This test is most relevant to single or occasional human overexposures. In addition to indicating the potential of the substance to cause harm, the test yields information about the symptoms and time course of any poisoning that may occur in humans.

This test also provides a value (the LD_{50}) for use in comparing the toxicity of different chemicals. The LD_{50} is the theoretical dose predicted to be fatal to one-half of the animals tested. Compounds with lower LD_{50}'s are more toxic than those with higher LD_{50}'s.

Calcium Magnesium Acetate

The acute oral LD_{50} for CMA was found to be 3,150 mg/kg (milligrams CMA per kilogram body weight) in rats. This LD_{50} places CMA in the "slightly toxic" category of a standard classification scheme (Table 1) for chemical toxicities (*3*). For humans, the estimated probable lethal dose by ingestion of a "slightly toxic" compound is about 250 g (slightly more than ½ lb). Table 2 (*4*) presents LD_{50} values for a series of other compounds to compare the toxicity of CMA.

TABLE 1 ACUTE LETHAL DOSES FOR REPRESENTATIVE COMPOUNDS (*3*)

Example Compound	Acute LD_{50} (mg/kg)
Ethanol	10,000
Sodium chloride	3,750
Calcium magnesium acetate	3,150
Ferrous sulfate	1,500
Morphine sulfate	900
Phenobarbital	150
Strychnine sulfate	2
d-Tubocurarine	0.5
Tetrodotoxin	0.1
Dioxin	0.001
Botulinus toxin	0.00001

Clinical signs observed in this study indicated an effect on the lungs; signs of stress and general malaise were also noted. Effects on the lung appeared related to development of edema (fluid in the air spaces) and were confirmed by a pathology examination.

Sodium Chloride

The acute oral LD_{50} of sodium chloride in rats is 3,750 mg/kg (*5*), essentially the same as the LD_{50} for CMA. (Another widely cited value for sodium chloride is 3,000 mg/kg; however, documentation for this value was not found in a search of the literature.) Sodium chloride is therefore also a "slightly toxic" compound and is often cited as the prototype for this category (*3*).

Although sodium chloride is a common household chemical and is considered exceptionally "safe" by the public, it is not benign. Serious poisonings and even deaths have occurred following ingestion of large quantities or after its use to induce vomiting (*6–8*).

Calcium Chloride

Data are also available on the acute oral toxicity of calcium chloride, a frequently used low-temperature road deicing salt. The single dose oral LD_{50} is reported by Frank (*9*) to be between 1,000 and 2,000 mg/kg in rats. This places calcium chloride also in the "slightly toxic" category (*3*).

Subchronic Oral Toxicity

Subchronic oral toxicity testing indicates whether toxicity can develop from repeated exposures. Subchronic testing mimics human exposures of moderate duration or intermittent nature. A subchronic test is especially appropriate for a deicer that is used only seasonally, but on a daily basis. Another reason for this testing is that a few compounds exhibit greater toxicity from repeated versus single exposures.

The test compound is given by mouth for 28 consecutive days. Although the doses are lower than for the acute test (nonlethal doses are used), they are still high relative to anticipated human exposures. The animals are observed daily for any signs of illness. In addition, food consumption and body weight are monitored (decreases in either can indicate toxicity).

TABLE 2 TOXICITY CLASSIFICATION BASED ON LETHAL DOSE (*4*)

Category	Oral LD_{50} (Rat) (mg/kg)	Dermal LD_{50} (Rabbit) (mg/kg)	Probable Human Lethal Dose	Example
Extremely toxic	≤1	≤5	Taste	Nicotine
Highly toxic	1–5	5–45	Teaspoon	Parathion
Moderately toxic	50–500	45–350	Ounce	DDT
Slightly toxic	500–5,000	350–2,800	Pint	Salt
Practically nontoxic	5,000–15,000	2,800–22,600	Quart	Ethanol
Relatively harmless	>15,000	>22,600	>1 quart	Mineral oil

Calcium Magnesium Acetate

For subchronic oral testing, an upper "limit" dose of 1,000 mg/kg/day is recommended for compounds that exhibit low acute toxicity. This dose was used in the CMA study. For a human being this corresponds to ingestion of approximately 2½ oz of CMA per day.

No signs of toxicity developed in any of these animals. All of the animals maintained normal food consumption and growth patterns. Following the 28 days of CMA dosing, the animals were sacrificed and a complete autopsy was performed; no effect of CMA was observed.

Sodium Chloride

No subchronic oral toxicity studies on sodium chloride are available for comparison. A chronic toxicity study in rats, however, was performed by Boyd et al. (*10*). This study identified the LD_{50} for a 100-day repeated administration to be 2,690 mg/kg/day for sodium chloride.

It appears that sodium chloride and CMA are of comparable toxicity following repeated administration. Since no deaths resulted from administration of CMA at 100 mg/kg/day and the single dose LD_{50} was 3,150 mg/kg, it is reasonable to project that a 100-day LD_{50} would be in the range similar to that found for sodium chloride.

Acute Inhalation Toxicity

In the acute inhalation toxicity study, exposure to the test compound is through breathing rather than by mouth. Animals are exposed for 4 hours to very high airborne levels of the compound and then observed over 14 days for toxicity. Concentrations used in this test are often many times greater than the TLV for occupational exposure to nuisance dusts.

Calcium Magnesium Acetate

The 4-hour inhalation exposure to extremely high airborne levels of CMA produced no deaths in the exposed laboratory rats. The primary clinical sign observed following the exposure to CMA was respiratory difficulty; all affected animals returned to normal within 3 to 5 days. No other signs of toxicity attributable to CMA developed and all animals appeared normal until sacrifice at 14 days; no pathology was evident upon autopsy.

Sodium Chloride

Aerosolized saline (0.9 mg/100 ml sodium chloride in water) has been used for control exposures in some laboratory inhalation studies. There is some evidence from one of these studies to indicate that sodium chloride levels in the range of 90 to 100 mg/m^3 may produce minor lung irritation during an acute exposure (2 hours); all signs of irritation cleared within 2 days in these animals (*11*).

Eye Irritation

The primary eye irritation test measures irritation or damage as a result of direct eye contact. The test compound is deposited directly onto the eye and any reactions occurring during the next 21 days are evaluated by a standard scoring system (*12*). Both rinsed and unrinsed eyes were tested for their response to CMA.

Mechanical irritation, in addition to any chemical irritation, may occur when the compound is a solid. Therefore, granular or crystalline compounds often produce some irritation in this test.

Calcium Magnesium Acetate

Eyes treated with CMA and then washed developed only mild irritation, including moderate redness and discharge with some swelling of the iris. There was no effect on the clarity of the lens or its protective surface. By 24 hours only minor irritation remained, which cleared by 72 hours. Mild to moderate irritation occurred in the unwashed eyes. All showed slight redness and moderate to severe swelling or discharge initially, with some swelling of the iris. Slight clouding of the cornea was present initially, but cleared by 24 to 48 hours. This mild effect is not considered a "positive" response under the Federal Hazardous Substance Act guidelines (*13*). No effect on the lens was noted. Most irritation cleared by 48 hours and all eyes were completely normal within 3 to 10 days.

The reactions to CMA yielded mean irritation scores of 11 (out of a possible 110) in the washed eyes and 23 in the unwashed eyes. These results classify CMA as a mild-to-moderate eye irritant. It is likely that at least part of the irritation observed was mechanical, due to the granular nature of the CMA. As expected for a granular material, this test demonstrated that prompt washing can reduce the mild irritation produced by CMA.

Sodium Chloride

In a similar test, granular sodium chloride was found to be slightly more irritating than CMA and was classified as a moderate eye irritant (*14*).

Skin Irritation

The skin irritation test assesses the test compound's ability to irritate or damage the skin upon direct contact. Irritation is due to a direct chemical reaction on the skin; it does not include activation of the immune system (allergic reactions).

A paste is made from the test compound and applied to the shaved skin of rabbits under an occlusive patch. Following an exposure of 4 to 6 hours, the paste is removed and any reactions are graded according to a standardized scale (*12*).

Calcium Magnesium Acetate

In the CMA study, the only sign of any reaction was mild redness, which was barely perceptible at 1 hour and cleared within 24 hours. These results classify CMA as nonirritating to the skin.

Sodium Chloride

Sodium chloride has been reported to be mildly irritating; this report is a Czechoslovakian publication and details are lacking (*15*).

Acute Dermal Toxicity

Acute dermal toxicity testing determines if the test compound can be absorbed across the skin in amounts sufficient to produce systemic effects. It is most relevant to a single, prolonged skin exposure.

A concentrated paste of the test compound is applied to the shaved skin of rabbits for 24 hours and the animals are observed for 14 days. The dermal exposure in this test is devised to maximize penetration of the compound through the skin for uptake into the body; it is not predictive of skin reactions.

Calcium Magnesium Acetate

In this study, a dose of 5,000 mg/kg CMA was tested for the ability to cross the skin and produce systemic toxicity. None of the test animals exhibited any systemic signs of toxicity. Some developed mild-to-moderate irritation of the exposed skin, which cleared after the first day. Therefore, following a single exposure, there is insufficient absorption of CMA across normal skin to be a health hazard.

Sodium Chloride

Although results on a similar study on sodium chloride are not available, it is unlikely that systemic toxicity would occur from dermal contact.

Dermal Sensitization

Dermal sensitization testing predicts the test compound's ability to elicit allergic skin reactions. Guinea pigs are the preferred animal for sensitization testing because they are the most sensitive laboratory animals (*16*).

Relatively large amounts of the test compound are repeatedly applied to the skin of guinea pigs over the course of 3 weeks; repeated exposure allows the animal sufficient opportunity to develop immunologic responsiveness. Following this induction phase, a single challenge dose is applied and any skin reaction is evaluated. Since the challenge dose is much smaller, the response is dictated by the animals' immunologic reactivity, not by any chemical irritancy of the test compound. The reaction, if any, is compared to that of a known sensitizer and the percentage of animals responding determines the strength of the sensitizer.

Calcium Magnesium Acetate

Calcium magnesium acetate produced no reaction in dermal sensitization testing. There was no evidence of any ability to elicit allergic responsiveness.

Sodium Chloride

Sodium chloride is not believed to have any sensitization potential.

Interpretation of CMA Toxicity Tests

The acute toxicities of CMA and sodium chloride are compared in Table 3. CMA exhibited a toxicity similar to that of sodium chloride for acute oral toxicity as well as skin and eye irritation potential. No inhalation or dermal toxicity data are available on sodium chloride for comparison; CMA exhibited low toxicity by both of these routes of exposure. In the subchronic oral toxicity test, CMA produced no toxicity at a "limit" testing dose, thus indicating low toxicity upon repeated exposure.

TABLE 3 COMPARATIVE ACUTE TOXICITY OF CALCIUM MAGNESIUM ACETATE AND SODIUM CHLORIDE

	Calcium Magnesium Acetate	Sodium Chloride
Rat oral LD_{50}	3,150 mg/kg[a]	3,750 mg/kg[a]
Eye irritation	11/110[b]	13/110[b]
Skin irritation	Nonirritating	Mildly irritating
Acute inhalation LC_{50}	>5,000 mg/m^3	NA[c]
Acute dermal LD_{50}	>5,000 mg/kg	NA

[a] "Slightly toxic" category (*4*).
[b] "Nonirritating" (*11*).
[c] Not available.

The toxicity tests conducted (acute oral, acute inhalation, acute dermal, dermal irritation, ocular irritation, skin

sensitization, and subchronic oral toxicity) provide a good overall evaluation of the potential toxicity of CMA. These tests, as a whole, assess the local and systemic effects of the compound via a number of different routes of exposure. However, laboratory toxicity tests cannot guarantee that human exposure will always have the same results. Occasionally there are differences, mostly unexplained or incompletely defined, between the ways different species respond to chemicals. In addition, there may be more individual diversity in the human population than can be tested in laboratory animals. Therefore, laboratory tests may not completely predict the response of all individuals in the human population to all conceivable chemical exposures.

SITE INVESTIGATION

Some information is available on human exposure to CMA. Chevron Ice-B-Gon™ underwent field tests at a number of highway sites during the winters of 1986 and 1987: three sites were in the California Sierra Nevada Mountains and the others were Madison, Wisconsin; Neenah, Wisconsin; Charlotte, Michigan; and Ontario, Canada. With only one exception, there were no health-related complaints from workers at these sites.

The health complaints were received from a site testing CMA in 50-lb bags. This site normally handled deicing agents in bulk form; therefore, it neither had the dust control equipment nor followed the procedures typical of a facility accustomed to handling bags of this size. The use of CMA in bags was selected by this site because of concerns that they would be unable to store bulk material in a dry area. Six highway maintenance employees reported minor injuries—mainly skin, eye, and nasal irritation—while handling CMA. These complaints were unexpected, based on the laboratory animal data and the experience at the other field sites, and this site was investigated. A Chevron Chemical Company industrial hygienist visited the site during a February 1987 storm. Based on sampling results, observations, and discussions with employees, it appeared that dust levels during the bag dumping operation exceeded the TLV for occupational exposure to nuisance dusts (dust levels during road application were low). Thus the minor health effects appeared to be caused by overexposure to CMA as a result of the high dust levels during this operation. A recommendation was made to discontinue use of the 50-lb bags under the prevailing conditions; no further complaints were received from the workers.

Observations

Sand at this site was stored in bulk and CMA was stored on pallets in 50-lb bags. There were six employees in the crew, working a 12-hr shift; each wore coveralls, a dust mask, and goggles. During bag dumping, three employees moved bags from the pallets onto the floor; the other three cut through the middle of the bags and dumped them at their feet. The operation lasted 35 to 40 minutes and approximately two pallets of bags were cut. A dust haze was present in the room and the dust concentrations appeared to be higher near the floor where the bags were dumped. A slight acetic acid odor was noticeable and contact with the CMA left skin feeling sticky.

After the bags were dumped, a payloader was used to load sand and CMA into sanding trucks to produce a 20-percent-CMA mixture. This operation lasted approximately 5 minutes. One employee then drove the sanding truck along a 3-mi section of the highway. It took approximately 2 hours to spread one truckload (5 tons) of the sand/CMA mixture. The truck had an enclosed cab and the employee did not wear respiratory protection. Because of heavy snowfall, the employee opened his window at times to check the load.

Sampling and Results

Seven total and respirable dust samples were collected at the site. Total dust includes all dust particles collected on the sampling filter; respirable dust includes only those particles that are small enough to penetrate to the gas exchange areas of the lung.

Samples were collected on preweighed polyvinylchloride filters using Gilian HFS 113A pumps at a rate of 1.7 l/min. Respirable dust samples were collected using a cyclone. Samples were collected in the breathing zone of the employees and were analyzed gravimetrically.

Results are shown in Tables 4 and 5. Six of the samples were collected during bag dumping: four samples for total dust and two for respirable dust. The results for the bag moving operation ranged from 26.2 to 32.2 mg/m^3 total dust and 0.75 mg/m^3 respirable dust. The results for the bag cutting operation were 72.5 mg/m^3 total dust and 1.68 mg/m^3 respirable dust. (A second total dust sample result was invalid because the pump became disconnected and the sampling time is unknown.)

TABLE 4 TOTAL DUST AIR SAMPLING RESULTS

Sample Number	Duration (min)	Total Dust (mg/m^3)	Operation
1	36	72.5	Cutting and dumping bags
2	36[a]	32.3[a]	Cutting and dumping bags
3	38	32.2	Moving bags to dumping area
4	38	26.2	Moving bags to dumping area
5	119	0.23	Driving sanding truck

[a]Pump became disconnected—sampling duration may have been less, resulting in a proportionately higher concentration.

TABLE 5 RESPIRABLE DUST AIR SAMPLING RESULTS

Sample Number	Duration (min)	Respirable Dust (mg/m^3)	Operation
6	39	1.68	Cutting and dumping bags
7	36	0.75	Moving bags to dumping area

A total dust sample was also collected during the spreading of one load of sand/CMA mixture on the highway. The driver felt that he could not wear a pump while driving, so the industrial hygienist rode in the cab and wore the pump; exposure in the cab was 0.23 mg/m^3 total dust.

Samples were not collected on the payloader operator during loading of the sanding truck because the operator felt that he could not operate the payloader while wearing a pump.

Discussion of Site Investigation

Total dust results for bag dumping exceeded the TLV for occupational exposure to nuisance dusts of 10 mg/m^3.

However, a time-weighted average for the shift would not be expected to have exceeded the limit since dust exposures during the remainder of the shift appeared to be low. The low respirable dust level indicates that most of the dust does not reach the gas exchange areas of the lung, and therefore would not be expected to produce pulmonary symptoms.

The total dust result for road application using a sanding truck was below the TLV for occupational exposure to nuisance dusts. Current practices appear to be adequate to limit dust exposures over a full shift during this activity.

Dust levels were not measured during the payloader loading of the sanding truck. Loading generates dust but because the employee is in an enclosed cab, levels are not expected to be high. The operation takes 5 to 10 minutes per truck and could occur once an hour during a shift, for a maximum exposure time of 90 minutes. It appeared that the enclosed cab adequately controls the dust; however, industrial hygiene monitoring would be needed to verify this.

Recommendations

Appropriate industrial hygiene procedures for working with nuisance dusts should be instituted whenever working with CMA, sodium chloride, or sand; these include

- Approved respiratory protection if operating conditions create high airborne dust concentrations,
- Dust reduction techniques such as local exhaust ventilation and dumping material through chutes,
- Eye-wash units capable of providing 15 minutes of tempered water as a precaution against granular irritation of the eye, and
- Use of adequate bag-handling facilities when nuisance dusts packaged in 50-lb bags are used.

CONCLUSION

When a new chemical product is introduced, two concerns must be addressed: are there potential effects on (a) humans and (b) the environment? For a road deicing agent, the environmental question should consider both natural and man-made environments. Consideration of the man-made environment is made necessary by the negative impact that traditional road deicers have had on roads, bridges, and automobiles. CMA has a low environmental impact relative to water quality, aquatic toxicity, and terrestrial ecology (*17*); in these respects the effects of CMA are similar to or less severe than the main component of traditional road salt, sodium chloride. Corrosivity data show CMA to be less damaging to the man-made environment than traditional road salt; it is much less corrosive than salt to concrete, zinc, aluminum, and steel (*18*).

This report focused on the potential effects of CMA on humans. Two types of data were reviewed: (a) laboratory toxicity studies on the toxicity of CMA and (b) a report of an industrial hygiene investigation into complaints of minor injury from handling CMA.

The acute and subchronic toxicities of CMA are low, as are the skin and eye irritation potentials. In these respects, CMA is similar to sodium chloride. Inhalation exposure does not appear to pose a hazard greater than any nuisance dust. Dermal exposure appears also to present a low hazard of adverse effect. CMA appears to have a low potential, if any, to induce allergic skin reactions.

Occupational experience with CMA during field testing bears out the conclusions from the laboratory animal studies. Health-related complaints were received from only one of the field test sites. An industrial hygiene investigation showed that exposure conditions at this site exceeded the TLV for occupational exposure to nuisance dusts. Although exposure levels were high, the complaints related only minor skin and eye irritation. Industrial hygiene practices appropriate for occupational exposure to any nuisance dust are expected to eliminate these health-related complaints.

In summary, the results reviewed in this report indicate that CMA's potential to adversely affect human health is no greater than that of sodium chloride.

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