



# Department of Pesticide Regulation



Mary-Ann Warmerdam  
Director

## MEMORANDUM

Arnold Schwarzenegger  
Governor

TO: Mr. Roger Briggs  
Central Coast Regional Water Quality Control Board  
895 Aerovista Place, Suite 101  
San Luis Obispo, California 93401

FROM: Mary-Ann Warmerdam  
Director  
916-445-4000

DATE: December 1, 2010

SUBJECT: RESPONSE TO THE CENTRAL COAST REGIONAL WATER QUALITY CONTROL BOARD COMMENTS DATED JUNE 10, 2010 REGARDING METHYL IODIDE REGISTRATION DECISION

---

### BACKGROUND

The Central Coast Regional Water Quality Control Board letter expressed opposition to the Department of Pesticide Regulation's (DPR's) decision to register methyl iodide (MeI) as a pesticide product. The opposition was based on their view that MeI poses a substantial risk to contaminate California's ground water. The following points were cited in the letter:

1. The potential risk of iodide that was proposed in the DPR's Risk Characterization Document.
2. Their view that the mitigation measures will not prevent leaching based on longer soil half-life as compared to methyl bromide (MeBr).
3. Environmental modeling results that indicated deeper soil movement for MeI than for MeBr.
4. Data from a peer-reviewed publication that indicated significant leaching of MeI several days after fumigation and aeration.

### RESPONSE

Point one reiterates that movement to ground water by iodide is the major concern for ground water contamination after soil fumigation with MeI. Iodide is a degradation product of MeI. An important aspect of iodide's fate in soil is that, although it is thought of as a stable halide anion, investigations into soil reactions indicate a more reactive nature. For example, an important study by Bowman (1984) compared the use of chemicals as surrogates for tracking the movement of water through the soil column in laboratory and field experiments. Bromide is widely used to trace water movement in soil because it is stable and it does not readily react with soil components. Bowman also attempted to use iodide as a tracer for water movement because it is a similar halide anion. Movement in soil was compared between studies conducted indoors and in the field. The indoor study used soil columns where the soil was loamy sand with 1.5 percent organic carbon content. After the columns were packed with soil, water was introduced to simulate either ponding or drip applications. Water leached through the column,



was collected, and the concentration over time compared between bromide and iodide. There was no difference in the results between bromide and iodide from the indoor column study so the initial conclusion was that iodide could potentially be used as a water tracer. In a follow-up field study, an experimental plot was subjected to flood irrigation. Soil suction lysimeters were located at approximately three and six feet deep in the soil from which soil water was sampled and analyzed for presence of bromide and iodide. Soil cores were also extracted and sampled to provide a physical measure of the exact concentration and movement of bromide and iodide throughout the soil profile. Iodide was measured in water extracted from the three foot soil depth but concentrations were greatly reduced when compared to bromide. For soil core data, iodide could not be measured in samples taken 14 days after application of the tracer, whereas bromide was evident throughout the soil core. Bowman concluded that iodide may be a useful tracer under laboratory conditions but that in the field it is rapidly lost under aerobic field conditions. Most importantly, this study illustrates that observations made in experiments conducted indoors must be confirmed with studies conducted in the field. The potential role of organic matter in transformation of iodide to other oxidized forms has been suggested in studies conducted by Sheppard and Thibault (1992) and Fuge and Johnson (1986). Santschi and Schwehr (2004) propose that microbial extra-cellular peroxidases are responsible for iodination of soil organic matter through either abiotic or biotic pathways.

The three other points provide arguments for increased concern for either MeI or iodide based on studies that have been conducted under simulated laboratory conditions. Although they provide valuable information on potential soil movement and interaction, they do not represent the full data set upon which DPR's environmental fate decision was based. The U.S. Environmental Protection Agency required the registrant to conduct terrestrial field dissipation studies (TFD) for measuring the environmental fate of MeI and iodide under actual field applications (DPR document number 52875-0008). Targeted rates of application were high at 250 lbs MeI/acre. Although tarps were used, the exact nature of the tarp was not specified. The tarps were removed after five days. More importantly irrigation applications commenced 14 days after application. In the study conducted in California, irrigation water applications followed U.S. Environmental Protection Agency guidelines where the amount was applied at 110 percent of the ten-year monthly average of evapotranspiration. Scientists from the DPR's ground water protection program do not accept this as a realistic water treatment. The requirement to limit irrigation water application to 133 percent of crop need at each irrigation is a further mitigation measure that minimizes the rate of water percolation and enhances the rate of degradation of pesticides residues in the upper layers of soil.

Additional observations on the conclusions made for each of the points based on the supporting references are:

- **In point #2, the half-life estimate for MeI is taken only from an indoor experiment.**  
The estimate of the soil-life for MeI is taken from Gan et al. (1996), which was an indoor study. Since the study attempted to isolate the effect of soil on the degradation rate of MeI, soil was held in sealed vials and either MeBr or MeI was injected into the soil. The results did indicate a slower rate of degradation for MeI on the coarse-textured Greenfield sandy loam soil, but loss of MeI from soil by volatilization was minimized because of the sealed vials. In contrast, half-lives for MeI determined from the TFD studies conducted in the field in California and Florida indicated a dissipation half-life of around five days for both sites. Soil in the California study was a sandy loam with 1.3 percent organic carbon and in Florida it was loamy fine sand with 1.2 percent organic carbon. Volatilization from the soil was an important route of dissipation in both field studies. Imposition of a 14 day reentry interval would allow longer time for dissipation of soil residues, especially for continued off-gassing rather than by degradation.
- **Point #3 relies upon a modeling procedure that has not been validated.**  
The assertion in point number 3 that MeI is likely to move deeper in soil than MeBr relies upon data generated in the Yates (1996) citation. This study was an initial attempt to determine fate of MeI using only a modeling procedure. The publication is extremely short (about one page) where the author cautions in the last paragraph “Although this gives a first glimpse into the behavior of MeI in soils, the effect of numerous model simplifications need to be investigated before making any conclusions using the figures above.” We are not aware if the author has revisited these modeling results in light of the environmental fate data that has been generated since the publication of this short article in 1996.
- **Point #4 indicates greater MeI leaching after fumigation and aeration in an indoor study but it does not integrate data generated from actual field use and agricultural practices.**  
Evidence to support the statement that MeI leaches even several days after fumigation and aeration was based on the Guo et al. (2004) citation. This study was conducted in a laboratory where soil movement was measured in packed soil columns. The total length of the soil column was 2.2 feet (70 cm). The study measured soil distribution of MeI under experimental conditions designed to simulate shank-injection or drip application methods. Water was applied to the soil 7 days after the application of MeI to the soil column where the water was added under a constant head of 1.2 inches (3 cm) in depth. This would represent a ponded soil condition for 19 consecutive days. Leaching was not directly measured during the first seven days but the distribution in the soil profile was monitored. Residues of MeI were measured throughout the soil profile. This result was expected because a gaseous soil

fumigant easily permeates throughout a 2.2 foot length of soil in the gaseous phase. Actual leaching of MeI was not measured until the addition of water to the soil columns on day 7, but a constant ponded condition for 19 consecutive days is not reflective of actual irrigation practices that would occur after applications to crops. DPR has implemented a 14-day reentry interval where the soil will remain tarped. As indicated previously, TFD data indicating rapid dissipation of MeI and the potentially rapid transformation of iodide degradation product to other oxidized forms should mitigate potential for leaching of MeI or iodide to ground water in vulnerable soils. The restriction of irrigations to 133 percent of crop need after removal of the tarp will provide further restriction to the residues out of the upper layers of soil. This restriction is designed to decrease the amount of percolation water produced and to maximize retention of residues in the upper layers of soil. Troiano et al. (1993) illustrated the effectiveness of limiting percolating water on the movement of atrazine in a coarse sandy soil with very low organic carbon content. Limiting downward soil movement resulted in faster degradation of atrazine residues.

In summary, the conditions of use and mitigation measures for MeI developed by DPR incorporated data from all available studies. Emphasis was placed on information that was generated from field studies because they are most reflective of environmental fate under actual agricultural use. When viewing all available data, the ground water protection staff's conclusion is that the potential for movement to ground water appears low. The condition of a 14-day moratorium between the time of application and the initiation of agricultural activity should provide for rapid dissipation of MeI by volatilization and degradation and rapid reaction of iodide with soil components. As part of its obligation to continuously evaluate all registered pesticides, DPR will conduct well monitoring for both MeI and iodide anion breakdown product. Additionally, based on the recommendation of the State Water Resources Control Board, DPR will conduct a field dissipation study to address its concerns.

cc: Dr. Lisa Ross, DPR Environmental Program Manager

## REFERENCES

- Bowman, R.S. 1984. Evaluation of some new tracers for soil water studies. *Soil Sci. Soc. Am. J.* 48:987-993.
- Fuge, R. and C.C. Johnson. 1986. The geochemistry of iodine—a review. *Environ. Geochem. Health* 8:31-54.
- Gan, J., and S.R. Yates, S.R. 1996. Degradation and phase-partitioning of methyl iodide in soil. *Jouranal Agricultural and Food Chemistry.* 44:4001-4008.
- Guo, M., W. Zeng, S.K. Papiernic, and S.R. Yates. 2004. Distribution and leaching of methyl iodide in soil following emulated shank and drip application. *Journal of Environmental Quality* 33:2149-2156.
- Santschi, P.H. and K.A. Schwehr. 2004. <sup>129</sup>I/<sup>127</sup>I as a new environmental tracer or geochronometer for biogeochemical or hydrodynamic processes in the hydrosphere and geosphere: the central role of organo-iodine. *Sci. Tot. Environ.* 321:257-271.
- Sheppard, M.I. and D.H. Thibault. 1992. Chemical behaviour of iodine in organic and inorganic soils. *Appl. Geochem.* 7:265-272.
- Troiano, J., C. Garretson, C. Krauter, J. Brownell, and J. Hutson. 1993. Influence of Amount and Method of Irrigation Water Application on Leaching of Atrazine. *J. Environ. Qual.* 22: 290-298. Available at: <<http://www.cdpr.ca.gov/docs/emon/pubs/ehapref/atrzne.pdf>>. (verified July 6, 2010).
- Yates, S.R. 1996. Methyl iodide as a replacement for methyl bromide: Environmental implications. Agricultural Research Service, U.S. Department of Agriculture, October 15, 1996.