PESTICIDE REGISTRATION AND EVALUATION COMMITTEE (PREC) Meeting Minutes – September 18, 2020

Committee Members/Alternates in Attendance:

Amalia Neidhardt – Department of Industrial Relations (DIR)
Dave Tamayo – Structural Pest Control Board (SPCB)
David Ting – Office of Environmental Health Hazard Assessment (OEHHA)
Emily Zakowski – California Department of Food and Agriculture (CDFA)
Heather Williams – Department of Resources Recycling and Recovery (CalRecycle)
Jaime Rudd – Department of Fish and Wildlife (DFW)
Jeff Fowles – Department of Public Health (DPH)
Karen Morrison – Department of Pesticide Regulation (DPR)
Lynn Baker – Air Resources Board (ARB)
Matt Hengel – University of California, IR-4 Program
Ruben Arroyo – CA Agricultural Commissioners and Sealers Association (CACASA)
Valerie Hanley – Department of Toxic Substances Control (DTSC)

Visitors in Attendance:

Note: Only attendees who identified themselves using their full name are listed below

Anne Katten – California Rural Legal Assistance Foundation
Charles Valadez
Christopher Paulino
Emily Saad – Exponent
Heather Williams – Department of Resources Recycling and Recovery (CalRecycle)
Jean-Mari Peltier
Katherine Sutherland-Ashley – Office of Environmental Health Hazard Assessment (OEHHA)
Ouahiba Laribi – Office of Environmental Health Hazard Assessment (OEHHA)
Tammy Tyler

DPR Staff in Attendance:

Annette Narzynski – Environmental Monitoring Branch
Brandon Brown – Human Health Assessment Branch
Brenna McNabb – Pesticide Registration Branch
Brittanie Clendenin – Pesticide Registration Branch
Denise Alder – Pesticide Registration Branch
Dilhara Ranasinghe – Human Health Assessment Branch
Eric Kwok – Human Health Assessment Branch
Jason Carter – Environmental Monitoring Branch
Jason Eiserich – Pesticide Evaluation Branch
Jennifer Teerlink– Environmental Monitoring Branch
Jonathan Sullivan – Pesticide Evaluation Branch

DPR Staff in Attendance continued:

Kara James – Pesticide Registration Branch
Kim Truong – Human Health Assessment Branch
Laura Benn – Pesticide Registration Branch
Mitra Geier – Human Health Assessment Branch
Murray Clayton – Environmental Monitoring Branch
Nan Singhasemanon – Pesticide Programs Division
Neelima Verma – Human Health Assessment Branch
Pete Lohstroh – Human Health Assessment Branch
Puttappa Dodmane – Human Health Assessment Branch
Shelley DuTeaux – Human Health Assessment Branch
Svetlana Koshlukova – Human Health Assessment Branch
Weiying Jiang – Human Health Assessment Branch

1. Introductions and Committee Business – Karen Morrison, Chair, DPR

a. Approximately forty-four (44) people attended the meeting.
b. DPR extended the comment period on the draft regulations for mitigation of neonics and their effects on pollinators to October 11, 2020.
c. DPR published the 2019-2020 progress report, now available on the department's website.
d. DPR hosted a brown-bag lunch on Integrated Pest Management at schools. The presentation is available on the department's website.
e. The Pesticide Registration Workshop has been postponed until 2021.

2. Update on Wastewater Monitoring – Jason Carter and Jennifer Teerlink, DPR

The DPR Surface Water Protection Program (SWPP) tends to focus on aquatic organisms, as those organisms tend to be the most sensitive to pesticides in surface water. Over the years, the program has been established as a combination of regulation, prevention, monitoring, mitigation, modeling, assessment, and outreach. This model has been effective in protecting surface water in urban and agricultural environments and is now being used to look at wastewater as well.

DPR has been monitoring pesticides in surface water since the early 1990s, starting with characterizing surface water sites impacted by agricultural runoff. In 2008, the department established an urban monitoring program which takes samples from both stormwater and dry weather events, focusing on irrigation runoff. Wastewater influent and effluent sampling began in 2019.

Influent refers to wastewater that exits homes and other buildings through drains and enters a water treatment plant. In California, the majority of treated water, or effluent, is then discharged to surface water sites, such as river, ocean, or estuary environments. The solid materials remaining after wastewater treatment, or biosolids, include microbes and may also contain

chemicals that have been removed from the water during treatment. In California, biosolids are often land applied.

An early SWPP study, in partnership with the Bay Area Regional Monitoring Program, San Francisco Estuary Institute (SFEI), Arizona State University (ASU), and TDC Environmental, measured concentrations of fipronil, fipronil degradates, and imidacloprid in both influent and effluent at eight Bay Area wastewater treatment plants. The study found that the final wastewater effluent concentrations exceeded the U.S. EPA aquatic benchmarks, which are used by the program as a screening tool. Concentrations of imidacloprid in effluent were almost identical to the influent levels. The data shows minor levels of fipronil removal, but most of the decrease can be attributed to fipronil degradates.

California has hundreds of pesticides registered for use, however, a data search only resulted in 81 pesticides with reported data in the United States. The search was limited to the United States to maintain a consistent regulatory structure. Of those 81 pesticides, 41 were detected. The data is limited both spatially and temporally, as many of the studies were focused on a specific active ingredient or a specific area. Because of this, the number of samples and number of facilities varies across the active ingredients. Another limiting factor involves inconsistencies between treatment technologies, making it difficult to report on treated wastewater effluent. Adding to this, some cases only reported effluent data, which limits the understanding of pesticide sources coming in to influent. Varying detection limits across the studies created yet another barrier to data analysis. The permanent wastewater program was created with the goal of reducing or eliminating these issues and inconsistencies.

Pesticides enter wastewater in various ways. For example, flea and tick treatments for pets could make their way down the drain directly, through washing the animal, or indirectly as a result of washing pet bedding and other fabrics where pesticide residues were transferred. Foggers and sprays may make their way down the drain during cleaning. Some pesticide products are impregnated into fabrics, such as an insecticide in clothing, which can enter drains through laundering activities. Additionally, pesticides may be tracked into the home from outside, eventually making their way down the drain. While these types of pesticide residue sources may be common and widespread, they typically represent low concentrations. Of greater concern are more highly concentrated sources, such as those from pest control operators, laundromats, pet grooming/boarding, and nurseries.

In order to address these issues, SWPP submitted a budget change proposal, which was awarded on July 1, 2019. This allowed for the creation of a permanent wastewater program, including funding for contract and analytical support, as well as two additional staff positions. Through the pesticide registration process, SWPP routinely evaluates products with potential impact to surface water using the Pesticide Registration Evaluation Model (PREM). Staff are in the process of expanding the capabilities of PREM to include down-the-drain transfer, for products such as pet products, washable impregnated materials, and products that are applied directly to sewer lines or floor drains. Technical modeling can be challenging due to limited information on

aspects such as removal rates during treatment, patterns and frequency of pesticide use, and the fractions of pesticide residue that can wash-off and make it down the drain.

The monitoring component of the wastewater program focuses on spatial coverage and establishing temporal trends. The current study includes over 25 participating wastewater treatment plants, each with a daily capacity of at least 1 million gallons, located predominantly in urban centers. During the first phase of the study, staff sampled four influent/effluent events as 24 hour time-weighted composites. Staff also sampled one biosolids event, however that data is still pending. The second phase, which has been delayed due to Covid-19, will focus on sampling influent closer to concentrated pesticide sources.

Data from the first phase of the study shows no detections of carbamates, fungicides, insect growth regulators, or a subset of pyrethroids. Detections were found for fipronil, most degradates of fipronil, some pyrethroids, and imidacloprid. It is worth noting that the limit of detection for imidacloprid was somewhat high, and staff may expect more detections if the limit of quantification is lower. Observations less than the limit of quantification were not considered as detections.

Seasonality is also a factor in influent sampling. Samples for this study were collected in June 2019, August 2019, December 2019, and May 2020. Bifenthrin was detected in influent in all four months, with the fewest number of detections and lowest range of detections in December, and the highest range in May. Chlorpyrifos was also detected in all four months, with the broadest range occurring in December, and the highest detection occurring in May. For fipronil, the median concentration detected was similar for all four months, which indicates broad input across many sources.

Phase two sampling in fall 2020 will focus on specialty sites, to help staff gain a better understanding of whether total loading to influent is more influenced by small ubiquitous inputs or sites that have the potential for higher pesticide concentrations. SWPP is collaborating with a wastewater partner to identify sites that would represent inputs from treated textiles, pest control operators, pet grooming/boarding, nursery operations, indoor products, and industrial laundry. The analytical methods for these samples will include screening for a targeted list of pesticides, as well as non-target techniques that will identify pesticides that were not already on the targeted list.

SWPP is also collaborating with several other entities on this work. Dr. Choe at UC Riverside and his team are researching indoor depositional patterns of pesticides from fogger products to estimate wash-off fraction for down-the-drain modeling. Dr. Jacelyn Rice at the University of North Carolina at Charlotte and her team are looking at the fraction of California surface water that is comprised of treated wastewater effluent. This research will help identify the most sensitive streams and creeks to ensure there are representative wastewater treatment plants in those areas. Dr. Rice is also looking at the impact of extreme weather events due to climate change on the fraction of treated effluent in streams. Now that the wastewater program is

permanent at DPR, the lab work will be migrating from Tom Young's lab at UC Davis to the state lab run by the Department of Toxic Substances Control (DTSC) in Southern California.

Next steps include establishing analytical methods with DTSC as a partner, with a focus on lowered reporting limits to ensure toxicologically relevant values. The program is also interested in selecting additional wastewater treatment plants for future monitoring that are smaller, serve agricultural regions, or utilize diverse treatment technologies. As the program continues, a key priority will be establishing and developing sustainable relationships with long-term monitoring sites.

Committee Comment

Karen Morrison asked about the general location of the wastewater treatment plants where samples are collected. Jennifer Teerlink replied that the exact locations are not being disclosed at this time, but they are generally located in urban centers of Sacramento, Los Angeles, and the San Francisco Bay area.

Dave Tamayo asked why chlorpyrifos is showing up in urban wastewater effluent and why there were high spikes of concentration. Jennifer Teerlink replied that there is a registered chlorpyrifos product that is intended for use in sewer lines that is likely the cause of the high concentrations. Jennifer further clarified that the referenced concentrations were for influent, and that chlorpyrifos was detected in much lower concentrations in effluent, likely because it is hydrophobic and therefore mostly removed from the aqueous phase during treatment. Dave then asked if the program has reviewed the biosolids data. Jennifer replied that they have not yet received the biosolids results.

Lynn Baker asked if biosolids are tested for pesticide residues prior to land applications. Jennifer Teerlink replied that biosolids application is regulated by CalRecycle, who would have more information on potential testing.

Matt Hengel asked for clarification on whether the chlorpyrifos oxone was included in the detected concentration of chlorpyrifos. Jennifer Teerlink replied that the detected concentration was chlorpyrifos alone, and not the oxone.

Jeff Fowles asked why chlorpyrifos concentrations are so much higher in December and May, and whether the program has any concerns about potential environmental impacts. Jennifer Teerlink replied that the chlorpyrifos concentrations likely came from a product registered for use in sewer lines and that the particularly high spike in May could be the result of sampling shortly after product application. Jennifer clarified that because chlorpyrifos was found in much lower concentrations in effluent, it is not currently cause for concern for introduction into the environment.

Public Comment

Emily Saad asked if the expansion of PREM to include down-the-drain use patterns will ultimately result in the application of this modeling for products beyond the initial scope of this study. Emily also asked for more information on an anticipated process and timeline for implementation if this is the case. Jennifer replied that at this time the focus is on the specific types of products mentioned in this presentation.

3. **Draft Risk Assessment for Allyl Isothiocyanate (AITC) – Puttappa Dodmane and Weiying Jiang, DPR**

The scope of this Risk Characterization Document (RCD) was limited to inhalation exposure to allyl isothiocyanate (AITC). Based on the exposure assessment, the key groups affected by AITC exposure via inhalation were agricultural handlers, re-entry workers, occupational bystanders, and residential bystanders. Agricultural handler and re-entry worker exposures were assessed for short-, intermediate- (seasonal), and long-term (annual) exposure periods, whereas bystanders were assessed only for short-term exposure. Among workers, the handlers and re-entry workers were the primary subgroups for AITC exposure. Subgroups for occupational bystanders focused on adult risks and residential bystanders focused on risk to both adults and children. AITC is a naturally occurring compound, present in many brassica plants. It is an enzymatic byproduct of the breakdown sinigrin, a glucosinolate. When released, AITC acts as a defense mechanism for the plant. AITC can also be synthesized in the laboratory by combining propargyl chloride and potassium thiocyanate. AITC's pesticidal mode of action is not well understood, but likely includes multiple cellular effects. In humans, AITC is a known to be an irritant and sensitizer, and induces pain sensation.

DPR staff evaluated and discussed the available studies on AITC exposure by the inhalation and oral routes. However the information was limited. A systematic review of the open literature screened 2,134 references, including 25 related to genotoxicity, 13 to toxicokinetics, and one relevant to chronic toxicity. Effects observed by inhalation exposure to low doses in animal models included degeneration of the olfactory epithelium, metaplasia of the respiratory epithelium, decreased motor activity, and decreased rearing counts. Higher doses resulted in decreased respiratory rate, body temperature, and body weight, as well as mortality, tremors, and olfactory bulb atrophy. The most sensitive effect following oral exposure was epithelial hyperplasia in the urinary bladder. Other effects were documented in the stomach, eye, liver, and thyroid.

DPR used the inhalation studies to calculate the critical point of departure (POD), because inhalation was the relevant exposure route. For acute exposure, the critical endpoint was decreased motor activity and rearing counts, with a lowest observed effect level (LOEL) of 25 ppm. Using a dose extrapolation factor of 10, the POD was set at 2.5 ppm. At the subchronic level of exposure, the critical endpoint was degenerative change in the nasal olfactory epithelium, metaplastic lesions in the nasal respiratory epithelium, and decreased motor activity,

resulting in a LOEL of 10 ppm and a POD of 5 ppm. There were no inhalation studies for chronic exposure, so the POD was set by using a subchronic-to-chronic extrapolation factor of 10, resulting in a POD of 0.5 ppm.

The proposed PODs were derived from animal studies. Therefore, DPR applied default uncertainty factors (3x for interspecies and 10x for intraspecies extrapolation resulting in a total uncertainty factor of 30) to a human equivalent concentration (POD_{HEC}) to calculate reference concentrations (RfC) using the U.S. EPA dosimetric guidelines. Using the equation $RfC=POD_{HEC}/UF_{TOTAL}$, DPR calculated acute, subchronic, and chronic inhalation reference concentrations for the various subgroups.

Risks were expressed as margins of exposure (MOEs). MOEs are calculated by dividing the critical POD_{HEC} by the estimate for human exposure for each scenario. The resulting MOE is then compared against a target MOE to determine if there is a risk or no risk for the given scenario. A target MOE of 30 (3x interspecies, 10x intraspecies) was applied for protection of humans. When the calculated MOE is less than 30, that scenario is considered a risk to humans, while an MOE equal or greater than 30 is considered unlikely to present a risk. The exposure assessment takes into account several factors, including restricted entry interval (REI), mandated personal protective equipment (PPE), application method, exposure periods, and whether the exposure occurs during application or sometime after application.

For each assessed exposure scenario, short-term exposure was used to represent the highest exposure an individual may realistically experience while performing a label-permitted activity. To calculate this exposure, staff multiplied the breathing-height air concentration by inhalation rate, dividing the result by body weight. In this calculation, both inhalation rate and body weight were represented by constants, with air concentration acting as the only variable. Staff also calculated intermediate and long-term exposures. This calculation adds in variable adjustment factors to account for different application rates and number of applications for different averaging periods.

Due to a lack of AITC-specific data, 1,3-dichloropropene (1,3-D) and chloropicrin were used as surrogates in estimating air concentrations for handlers and re-entry workers. Use patterns were based on other soil fumigants currently registered in California. For bystanders, the air concentrations were derived from computer modeling that estimated AITC air dispersions around a treated field. Again, with limited AITC-specific data available, 1,3-D and chloropicrin soil emission rates were used as surrogates in the computer model. These surrogates were chosen based on the assumption that at the same application rate and with the same application method, worker exposures would be approximately equal and soil emission rates comparable. These assumptions were validated by comparing the soil emission rates and breathing-height air concentrations using all of the available AITC data. Staff determined that using the surrogate data is less likely to underestimate AITC exposures, considering the data gaps. Further details of those discussions can be found in the appraisal section of the exposure assessment document.

AITC is not currently registered for use as a soil fumigant, therefore use information is not available. This assessment proposed to analyze the use information from currently registered soil fumigants to predict AITC use regions and patterns in California. With that, the current assessment considered AITC use in all major soil fumigant use regions, including the central valley, central coast, inland empire, south coast and the northern region. This assessment also considered the possible use of different application methods in different regions, such as shallow shank injection or drip injection for strawberries in Monterey County, and deep injection for grapes in Tulare County.

Based on the two submitted product labels, DPR assessed human inhalation exposures to AITC for 88 scenarios, which covered agricultural handlers, re-entry workers, occupational bystanders, and residential bystanders for short-, intermediate-, and long-term exposure periods. As a pre-registration assessment, available data were limited and surrogate data from other soil fumigants were used to derive exposure estimates and use pattern information. With the assumptions and methods used, this assessment is not expected to underestimate AITC exposures. The full list of proposed exposure estimate values is available in the exposure assessment document.

MOE ranges were calculated for different scenarios involving workers, occupational bystanders, and residential bystanders. All subgroups and durations resulted in MOEs less than 30, with the exception of seasonal exposure for re-entry workers. All bystander MOEs were under 30, representing a risk to these populations.

The Draft Risk Characterization of Allyl Isothiocyanate (AITC) is currently undergoing external review. DPR anticipates revising the document based on comments and any new data received during this period. DPR is also continuing to refine the exposure assessment and potential mitigation steps that consider the identified risks. A copy of the draft document can be requested through DPR's public records process.

Committee Comment

Jeff Fowles asked if methyl isothiocyanate (MITC) had been considered as a surrogate instead of Telone (1,3-D) to determine exposure estimates. Weiying Jiang replied that MITC was not an acceptable surrogate because it is not an applied compound, but rather is generated in the field after the application of either metam sodium or metam potassium. Weiying added that the registered application methods for MITC-generating compounds are incompatible with proposed AITC application methods, and that due to these application methods, worker exposure data for MITC are limited. Karen Morrison added that DPR is exploring the use of modeling using specific chemical properties of AITC to be able to consider exposures that are not captured as part of this work.

Jeff Fowles asked if the assessment was based only on open literature or if there were also industry-performed studies for AITC. Puttappa Dodmane replied that the open literature supplemented the industry-submitted studies.

David Ting commented that OEHHA is currently conducting peer review on the draft risk characterization document and exposure assessment document.

Lynn Baker asked for clarification on whether AITC has been registered. Karen Morrison replied that it has not been registered. Lynn then asked whether AITC has the potential to break down into hydrogen sulfide when applied by aerial sprinklers, as is the case with MITC. Weiying Jiang clarified that AITC may not be applied by aerial sprinklers, only by shank or drip application.

Lynn Baker asked if bystander exposures were limited to short-term durations due to a lack of available studies and whether studies were being conducted to determine if chronic exposures could cause potential problems. Puttappa Dodmane replied that there are three chronic studies to evaluate cancer risk by oral exposure, but none by the inhalation route. Puttappa elaborated that mode of action analysis determined that the urinary bladder epithelial hyperplasia was the requisite step leading to tumors by the oral route, but no bladder effects were evident through the inhalation route. Puttappa added that chronic exposure values were calculated based on sub-chronic study levels and did not anticipate urinary bladder tumors through the inhalation route. Karen Morrison commented that evaluating chronic impacts for a product where use and distribution are based on assumptions can be extremely challenging. Karen added that the balance between the assumptions and evaluation of the toxicology data are factored into the ongoing evaluation of all pesticide products, with many points along the way to take into account new data and change course if needed.

Public Comment

Jean-Mari Peltier provided the following statement for the record (edited for clarity):

> I appreciate all the work that the staff of DPR have undertaken over the past five years that AITC has been pending, first as a regular registration where nearly all of the reviews that were conducted, including the review from Human Health Assessment (HHA), concluded that the data supported registration. But this product for the past two years has undergone a full risk assessment because of a blanket policy that DPR has that all fumigants have to go through a full risk assessment prior to use. As we said before, allyl isothiocyanate is a naturally occurring compound found in plants like broccoli, Brussels sprouts, mustard, and wasabi. As a human being eating sushi, wasabi has about three micromoles of AITC per gram, a ten gram serving of brown mustard contains about 4,500 micrograms of AITC. In nature, AITC has a major ecological function, serving as a feeding deterrent against insects. For decades, people have plowed down brassica plants (Brussels sprouts, kale, broccoli, mustard) into the soil to try to control diseases, nematodes, and fungal plant pathogens. The difference between delivering AITC into the soil through crop production versus direct application is the quantity of the material that's needed to achieve consistent pest control. This material has been registered since the 1960s. It has been used in organic production when derived from natural plant sources. This case of putting this material through a risk assessment, despite the great work that has been done by DPR scientists to try to cobble things together, has been very difficult. This product was considered a bio-fumigant by the Obama administration, and a full set

of data was not required for registration when it was approved by the U.S. EPA in 2014. Since then, Isagro has generated additional data requested by DPR, totaling about one million dollars of additional cost. But there is still a thin traditional database to review, so that has meant that DPR has relied on the use of surrogate data. I appreciated the question raised earlier about whether the right surrogate data was used – I think that's a question that we have. I'd like to focus on one or two things that are unusual about the way this risk assessment came out. It's unusual that the acute level is set at a level that is lower than a chronic exposure (2.5 ppm compared to 5 ppm), and that is one of the artifacts of using the surrogate data. I also want to point out that by using Telone (1,3-D) as a surrogate for this material, there are some unusual assumptions, like for re-entry workers for shank application, they are assuming they will be reentering the field 157 days out of the year, which is absolutely impossible. Data from the air breathing zone, which was also based on Telone (1,3-D), used the worst-case scenario where most of the breathing zone levels were at about 1,000 micrograms. There was one outlier that was over 18,000 micrograms for Telone (1,3-D), and that was plugged in to get the 95th percentile for what we're looking at for AITC. So, we appreciate the opportunity to continue to work with DPR to refine this risk assessment, to revise some of the uncertainty factors, and hopefully get this product - which is a bio-fumigant across the rest of the United States - to have mitigations in place that will protect the people and the environment, while preserving the viability of the use of this product as an alternative fumigant in California. Thank you so much.

Anne Katten expressed appreciation that DPR is conducting a full risk assessment and commented that it is very appropriate for worker and public health protection. Anne asked if studies of degradation or environmental fate were included in the evaluation, from a worker and public exposure standpoint and possible groundwater contamination concerns. Puttappa Dodmane replied that they relied on how the exposure assessment was done. Weiying Jiang replied that the exposure assessment was based on the active ingredient, not degradates, as it is assessed for exposure immediately after the active ingredient is applied.

4. **Progress on Specific Numeric Values for Groundwater – Murray Clayton, DPR**

In the late 1970s, there were widespread detections of soil fumigants in California groundwater, particularly 1,2-dibromo-3-chloropropane (DBCP), ethylene dibromide (EDB), and 1,2-dichloropropene (1,2-D). After such detections, these products were quickly banned from use in the state. At the same time, aldicarb degradates were detected in groundwater in the north coast. In response, the California legislature passed the Pesticide Contamination Prevention Act in 1985. This legislation mandates that DPR identify pesticides with potential to impact groundwater and conduct monitoring for these pesticides. The pesticides that were identified as potential groundwater contaminates were placed on the Groundwater Protection List (GWPL). There are currently 105 pesticides on GWPL – seven are regulated pesticides that have been found in groundwater (atrazine, simazine, diuron, bromacil, bentazon, norflurazon, and prometon) and 98 others are potential groundwater contaminants that are not currently identified

as contaminants. The process to identify a pesticide's potential to impact groundwater relies on pesticide use patterns and a methodology called specific numerical values (SNV).

The SNV process was prescribed by the Pesticide Contamination Prevention Act as a method to prioritize sampling for pesticides in groundwater throughout the state. The objective was to determine potential for movement of an active ingredient to groundwater based on physical/chemical properties data. The methodology involved developing a list of known leaching and known non-leaching chemicals, and then comparing distribution between the lists for each physical/chemical property. The chemical properties were broken down into two groups: soil mobility properties, such as solubility and soil absorption potential (Koc), and environmental persistence properties, such as aerobic, anaerobic, and hydrolysis half-lives. With each of these distributions, a threshold value was developed. These threshold levels were termed the Specific Numerical Values. If a pesticide exceeded a threshold from any mobility property and any persistence property, it was categorized as a potential leacher added to the GWPL.

The previous process to identify potential leacher chemicals compared the logged distribution between leacher and non-leacher chemicals and established threshold values to discriminate between the two groups. The SNV thresholds were set at the 90^{th} percentile of the leacher distributions. This approach had a high misclassification rate - 52% of chemicals listed as non-leachers were identified as leachers, and 36% of chemicals overall were misclassified. Misclassification adds pesticides to the GWPL that likely have no or only little potential to leach to groundwater. This creates potential inefficiencies related to the monitoring program through the utilization of additional sampling resources and laboratory analytical method development resources. It also results in difficulty meeting monitoring mandates because of the large number of pesticides on the GWPL. Misclassified pesticides with potential to impact groundwater may not have been identified as potential leachers to be added to the GWPL. This also results in inefficiencies in the registration process, as some new active ingredients may be routed to the groundwater protection program for evaluation in error, and some new active ingredients with the potential to impact groundwater may be misclassified as non-leachers and not routed for evaluation.

The first step in updating the SNV approach is to update the list of known leacher and non-leacher chemicals. Since the current procedure was published in 1991, additional well sampling data has been made available to expand the leacher and non-leacher lists. Improvements in chemical analytical methodologies have also allowed for the identification of breakdown products and the ability to distinguish between the breakdown products and the parent chemical. The second component is to expand the use of pesticide-specific properties that are effective in discriminating between leachers and non-leachers, beyond the original five physical/chemical properties utilized in the current SNV process. The final step is to update statistical methodology to explore a multivariate approach for improved discrimination between leacher and non-leacher chemicals.

The SNV approach utilized nationwide well sampling data. Quality assurance (QA) and quality control (QC) data indicated potential problems with some detections using this approach. Most

of the wells outside of California were not resampled to verify detections and the types or conditions of the wells were not reported. To counteract these issues, the current approach was changed to utilize only California data. DPR's GWPP conducts targeted well studies, allowing staff to search for pesticides in areas of reported use. GWPP also preferentially samples in geographically vulnerable areas, including areas where pesticides are known to reach groundwater due to soil conditions and water inputs. Domestic single family wells are preferred because they are located in rural areas where groundwater is shallow, as opposed to typically deeper municipal wells. GWPP also verifies detections reported by other state, local, and federal agencies. The program analyzes associated QA/QC data, conducts landscape analysis around detection sites for use of the detected pesticide, and resamples wells to validate the detections when warranted.

Thus far, the leacher and non-leacher lists have been updated in several ways. Due to additional monitoring and chemistry analytical improvements, the following parent chemicals and degradation products have been added to the leacher list: norflurazon, hexazinone, imidacloprid, tebuthiuron, aldicarb sulfone, aldicarb sulfoxide, alachlor ESA, metolachlor ESA, metolachlor oxime, deethyl atrazine, deethyl simazine, di-dealkylated triazine, desmethyl norflurazon, and terephthalic acid (TPA). Chemistry analytical improvements and additional well sampling have moved the following chemicals from leacher to non-leacher status: chlorthal dimethyl, alachlor, carbofuran, cyanazine, fonofos, and oxamyl. Additional monitoring has added the following chemicals to the non-leacher list: iprodione, methomyl, napropamide, oryzalin, oxyflurofen, and thiobencarb. Detections reported from other agencies have prompted further investigation of the following chemicals: 2,4-dichlorophenoxyacetic acid (2,4-D), S-ethyl dipropylthiocarbamate (EPTC), metribuzin, metolachlor, diazinon, malathion, and chlorpyrifos.

Seven physical chemical properties are being considered for the updated procedure, including water solubility, soil sorption coefficient, aerobic degradation, terrestrial field dissipation, Henry's law constant, vapor pressure, and octanol-water partition coefficient. Due to incomplete data, anaerobic degradation, aqueous photolysis degradation, soil photolysis degradation, and hydrolysis are not being considered in the updated procedure. These properties have been sourced through registrant-submitted studies in DPR's database, the University of Hertfordshire's Pesticide Properties Database, U.S. EPA, and various scientific publications. Medians were used where there were multiple values for these physical/chemical properties. GWPP also looked at quantitative structure activity relationships (QSARs), in collaboration with Jonathan Sullivan, a scientist in the chemistry group of DPR's Evaluation Branch. QSARs are calculated properties using computer modeling software (Spartan '16), and they provide a physical description of molecular properties such as size or charge distribution. The updated procedure included 22 separate QSAR properties.

In updating the statistical methodology, steps were taken to reduce the large number of chemical properties into a manageable number for entering into multivariate analysis. Part of this process involved testing each property for distribution of normality. Properties that did not exhibit a normal distribution were either transformed to meet a normal distribution or rejected. Then, a t-test was applied to each chemical property to analyze for differences between leacher and non-

leacher pesticide groups. Properties with a probability level ≤ 0.15 were retained for further analysis, otherwise the property was rejected. Finally, staff conducted a correlation analysis to identify highly correlated chemical properties. To reduce chemical redundancy, only one property of a group of highly correlated properties was selected. Overall, the number of chemical-specific properties was reduced from 29 to 11 – 3 empirical physical/chemical properties and 8 QSAR properties.

Multivariate analysis can determine if a combination of chemical properties are effective at producing a statistically significant separation between leacher and non-leacher chemical groups. Similar to the SNV methodology, the updated procedure sets a threshold value to distinguish the leachers from the non-leachers. Since the procedure will be applied to a new chemical independent of those use to develop the model, the value at a 95% probability level was calculated as the prediction limit for the addition of one more member into the leacher group. This approach provides the benefit of a single multivariate leaching threshold value, as opposed to a separate SNV for each parameter. The process was further refined by sequentially removing properties that have the smallest influence on the multivariate model as indicated by Total-Sample Standardized Canonical Coefficients. This allowed staff to pare down the number of chemical parameters from 11 to 5 without loss in model performance and with an overall miscalculation rate of only 4.6%.

The multivariate analysis model classifies chemicals much more accurately than the SNV or previous Groundwater Ubiquity Score (GUS) models. It is likely to significantly reduce the overall number of chemicals on the GWPL and more easily allow the GWPP to meet state-mandated groundwater monitoring requirements. It can identify chemicals that potentially threaten groundwater that are not currently on the GWPL. It can also improve the use of resources in groundwater monitoring studies and refocus resources used for chemical analytical method development. The multivariate approach can also improve efficiencies related to GWPP registration evaluations.

Committee Comment

Karen Morrison commented that implementation of these methods would require a rule-making change.

Public Comment

Annette Narzynski asked what dataset was used to validate the different methods. Murray Clayton replied that GWPP used a procedure called leave-one-out analysis, which involves removing a pesticide from the analysis, rebuilding the model, and evaluating all pesticides, including the chemical that was removed. Murray added that there were no additional misclassifications in the leave-one-out analysis and this validation method is commonly used for small datasets. Annette then asked if the data was California-specific or nationwide. Murray replied that the data was California-specific and included data monitored by DPR and other agencies.

Emily Saad asked if chemistry will still be doing the first analysis to determine whether a product should route to GWPP for evaluation during the registration process, if the new procedure is adopted. Murray Clayton replied that, if approved, this procedure would replace the current SNV procedure.

5. Agenda Items for Next Meeting

The next meeting is scheduled for December 11, 2020 at 10:00 a.m. This meeting will be held virtually on the Zoom platform and broadcast live on the CalEPA webcast page. <https://video.calepa.ca.gov/>

Karen Morrison confirmed that the next meeting will include an update on the 1,3-dichloropropene (1,3-D) pilot study.

6. Adjourn