



## Department of Pesticide Regulation

Gov. Gavin Newsom  
Governor

Yana Garcia  
Secretary for  
Environmental Protection

### MEMORANDUM

Julie Henderson  
Director

TO: Minh Pham  
Environmental Program Manager II  
Environmental Monitoring Branch

VIA: Shelley DuTeaux, PhD MPH, Chief  
Human Health Assessment Branch

FROM: Brandon M. Brown, PhD, Staff Toxicologist  
Pete Lohstroh, PhD, Senior Toxicologist  
Toxicology and Dose Response Assessment Section

Svetlana Koshlukova, PhD, Senior Toxicologist  
Risk Assessment Section

DATE: November 17, 2022

SUBJECT: RISKS FROM HUMAN EXPOSURE TO DIURON RESIDUES IN  
GROUNDWATER

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On August 09, 2022, the Department of Pesticide Regulation's (DPR) Human Health Assessment (HHA) Branch was notified by the Environmental Monitoring (EM) Branch that monitoring conducted by the Groundwater Protection Program (GWPP) detected diuron and two of its degradates, 3,4-Dichloroaniline (3,4-DCA) and 1-(3,4-dichlorophenyl)-3-methyl urea (DCPMU, diuron desmethyl), in California's groundwater. The highest concentrations of diuron, 3,4-DCA, and DCPMU detected in a domestic well were 5.2 ppb, 0.541 ppb, and 0.079 ppb, respectively. EM requested that HHA determine whether any of the detected pesticides are a health concern for individuals using these wells as a source of drinking water and to provide human health screening levels for diuron and its degradates (see request, Appendix 1). This memorandum is in response to that request.

#### **Conclusion**

HHA calculated Human Health Reference Levels (HHRLs) to be used when residues are detected in groundwater. Residue levels of diuron, 3,4-DCA and DCPMU equal to, or less than, the DPR HHRL of **100 ppb** are not expected to pose a risk to human health, including sensitive subpopulations, if ingested in drinking water.

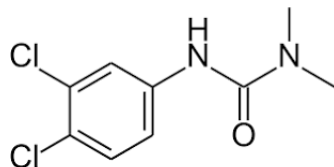
## **Background**

**Technical Name:** Diuron (DCMU)

**Chemical Name:** 3-(3,4-Dichlorophenyl)-1,1-dimethylurea

**Chemical Abstracts Service Registry Number (CASRN):** 330-54-1 (NIH, 2022c)

**Chemical Structure:**

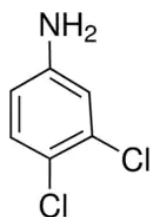


**Technical Name:** 3,4-DCA (or simply DCA)

**Chemical Name:** 3,4-Dichloroaniline

**Chemical Abstracts Service Registry Number (CASRN):** 95-76-1 (NIH, 2022b)

**Chemical Structure:**

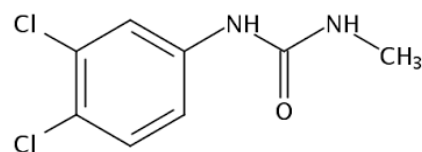


**Technical Name:** DCPMU

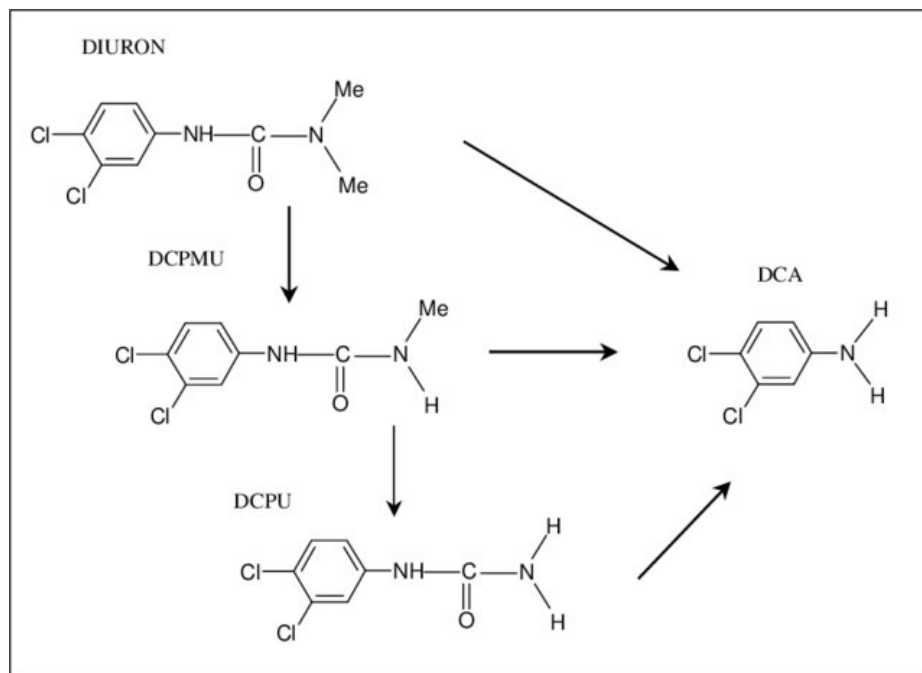
**Chemical Name:** 1-(3,4-dichlorophenyl)-3-methyl urea

**Chemical Abstracts Service Registry Number (CASRN):** 3567-62-2 (NIH, 2022a)

**Chemical Structure:**



Diuron is an herbicide that is an inhibitor of photosynthesis (USEPA, 2003). 3,4-DCA and DCPMU are metabolites and degradation and environmental transformation products of diuron (USEPA, 2020b; NIH, 2022b; NIH, 2022a). 3,4-DCA is also a metabolite of DCPMU and a biodegradation product of several phenylcarbamates, phenylurea and acylanilide herbicides, including propanil and linuron (EFSA, 2006; USEPA, 2020b). Analytical methods for residues of concern in agricultural commodities quantify diuron and its metabolites as equivalents of 3,4-DCA (USEPA, 2020b). The aerobic degradation pathway of diuron and its metabolites is depicted in Figure 1.



**Figure 1. Aerobic degradation pathway of diuron and its metabolites (Lapworth, 2005).**  
*DCPU is an abbreviation for the degradation product 3,4-dichlorophenylurea.*

Diuron is registered for use as a pre- and post-emergent herbicide to control weeds on a variety of crops and non-crop areas, as well as a mildewcide and an algacide in commercial fish production, residential ponds and aquariums (USEPA, 2003; USEPA, 2020b). In California diuron is used on alfalfa, apples, artichokes, avocado, cherries, citrus, cotton, grapes, lemon, mint, olives, oranges, pears, peas, pecans, prickly pear, pineapples, tangelo, tangerine, tomato and walnut with nearly 200,000 pounds used annually (DPR, 2022a). Diuron was first registered in California in 1981 and there are currently 39 products with active registrations (DPR, 2022b).

### ***Review of Regulatory Documents and Databases***

As part of this evaluation, a review of pertinent regulatory documents and databases was performed to ensure that the most scientifically supportable toxicological data were used for the evaluation (summarized in Table 1, below). A comprehensive systematic review was beyond the scope of this evaluation.

**Table 1. Review of Regulatory Documents and Databases**

Agency	Year	Title	Reference(s)
USEPA	2020	Diuron: Draft Human Health Risk Assessment for Registration Review	(USEPA, 2020b)
USEPA	2020	Diuron: Draft Ecological Risk Assessment for Registration Review	(USEPA, 2020a)
USEPA	2003	Reregistration Eligibility Decision (RED) for Diuron	(USEPA, 2003)
USEPA	2001	Drinking Water Assessment for Diuron and its Degradates	(USEPA, 2001)
USGS	2018	Health-Based Screening Levels (HBSL) Supporting Toxicity Data	(USEPA, 2018b)
USGS	2018	Health-Based Screening Levels (HBSL): Updated 2018 Technical Information	(USEPA, 2018c)
USGS	2018	Health-Based Screening Levels for Evaluating Water-Quality Data	(USGS, 2018a)
DPR	2019	Propanil Risk Characterization Document	(DPR, 2019)
EFSA	2006	European Union Risk Assessment Report 3,4-Dichloraniline (3,4-DCA)	(EFSA, 2006)
USEPA	1988	IRIS summary for diuron	(USEPA, 1988)
USEPA	2022	US EPA Human Health Benchmarks for Pesticides (HHBP) list	(USEPA, 2022a)
USEPA	2018	US EPA Drinking Water Health Advisories for Diuron	(USEPA, 1987; USEPA, 2018a)
USEPA	2022	US EPA CompTox Chemicals Dashboard	(USEPA, 2022c)
OEHHA	2022	Prop 65 list	(OEHHA, 2022)

### **Summary of Toxicology**

Diuron has an acute Toxicity Category<sup>a</sup> value of III for oral toxicity, dermal toxicity (based on the median lethal doses), and primary eye irritation (based on the median lethal concentration), and acute Toxicity Category IV for inhalation (median lethal concentration) and primary skin irritation (based on all irritation being cleared by 72 hours) (USEPA, 2003; USEPA, 2020a). Diuron is not a skin sensitizer. In 1996, the US Environmental Protection Agency (US EPA) classified diuron as a “known/likely” human carcinogen, based on urinary bladder carcinomas, and kidney carcinomas in the rat and mammary gland carcinomas in the mouse (USEPA, 2003; USEPA, 2020a). Diuron was placed on the Proposition 65 list for cancer in 2002 (OEHHA, 2022).

<sup>a</sup> Acute Toxicity Categories. US EPA Label Review Manual Chapter 7: Precautionary Statements. US Environmental Protection Agency, Office of Pesticide Programs, Registration Division. Revised March 2018. <https://www.epa.gov/sites/production/files/2018-04/documents/chap-07-mar-2018.pdf>

HHA has not conducted a human health risk assessment for diuron but has evaluated all required toxicity data that were submitted as part of registration in California. For the purpose of this evaluation, HHA adopted the toxicological endpoints and points of departure (PODs) established by US EPA (USEPA, 2020b). The acute POD was a no observed adverse effect level (NOAEL) of 20 mg/kg/day based on reduced motor activity and rearing seen at the lowest observed adverse effect level (LOAEL) (100 mg/kg/day) in an acute neurotoxicity study in rats (USEPA, 2020b). The acute NOAEL was divided by a total uncertainty factor ( $UF_{TOTAL}$ ) of 100 to calculate an acute RfD (aRfD) of 0.2 mg/kg/day for females (13 to 49 years), infants and children. The  $UF_{TOTAL}$  included a 10x for interspecies extrapolation ( $UF_A$ ) and a 10x for intraspecies variation ( $UF_H$ ). The chronic POD for estimating the chronic dietary risks to all populations was a NOAEL of 1 mg/kg/day based on hematologic effects, increased incidence of blood in urine, increased spleen weights in females and spleen, bone marrow, and urinary bladder histopathologies seen at the LOAEL (10 mg/kg/day) in a combined chronic toxicity/carcinogenicity study in rats (USEPA, 2020b). The chronic RfD (cRfD) of 0.01 mg/kg/day was calculated by dividing the NOAEL by a  $UF_{TOTAL}$  of 100 that included a 10X  $UF_A$  and a 10X  $UF_H$ .

The databases for 3,4-DCA and DCPMU are limited. Because of this, US EPA assumed that diuron, 3,4-DCA and DCPMU had equivalent toxicity based on similar chemical structures (USEPA, 2020b). DPR accepted this assumption for DCPMU because there were no relevant data to establish a POD or to evaluate the validity of the equivalence. DPR also supports the assumption that the PODs selected for diuron will be protective for 3,4-DCA toxicity based on its own evaluation of this chemical as the active metabolite of the herbicide propanil (DPR, 2019). DPR concluded that critical acute and chronic PODs (14.1 mg/kg/day and 1.5 mg/kg/day, respectively) for propanil based on hematologic toxicity would be protective of acute and chronic dietary exposures to propanil residues convertible to 3,4-DCA. Because the critical PODs for diuron (20 mg/kg/day and 1 mg/kg/day, respectively) are similar to those for propanil, they will also be protective for 3,4-DCA effects (DPR, 2019).

### ***Calculation of DPR Human Health Reference Levels for Diuron***

HHA calculated acute and chronic screening levels (human health reference levels or HHRLs) for diuron and proposes that the lower of the two values (the chronic HHRL of 100 ppb) be used by EM as a guide when residues of diuron and its degradates 3,4-DCA and DCPMU are detected in groundwater. This HHRL should be used for screening maximum detected residue levels in groundwater and should be compared to the sum of diuron, 3,4-DCA and DCPMU if they are present in the same sample (i.e., from the same well).

An HHRL is the threshold pesticide residue for a maximum water intake that results in the maximum safe oral exposure. The reference levels were calculated using the acute and chronic RfDs for diuron as the maximum safe exposure and the acute (95<sup>th</sup> percentile) and chronic (mean) drinking water intake rates for non-nursing infants as the maximum water intake. Non-nursing infants are the population identified as having the highest consumption of drinking water among the standard populations that HHA evaluates, including the general US population and sensitive subpopulations such as infants, children aged 1 – 2, and women of childbearing age (13 – 49 years old). The water consumption rates were from the Dietary Exposure Evaluation Model - Food Commodity Intake Database (DEEM-FCID, version 4.02, 5-10c) and the What We Eat in America (WWEIA) database. WWEIA is the dietary intake interview component of the National Health and Nutrition Examination Survey (NHANES). It is a collection of two-day dietary survey data (including drinking water consumption) from 2005 to 2010 for the US population and select subgroups (USEPA, 2014). HHA uses the 95<sup>th</sup> percentile of the exposure levels for non-nursing infants as the default upper bound for acute exposures, while two-day nonconsecutive food intake for non-nursing infants is used as a surrogate for chronic consumption patterns (DPR, 2009). HHA does not calculate lifetime HHRLs to screen for cancer risk. This is because HHRLs are intended to be compared with maximum residue levels; lifetime exposure to a maximum residue level is highly improbable.

The HHRLs for diuron in drinking water are summarized below (Table 2). The lowest reference value (chronic level 100 ppb) was selected as the HHRL for residues of diuron, 3,4-DCA and DCPMU in groundwater and is intended to be used for screening maximum detected residue levels. Diuron, 3,4-DCA, and DCPMU do not have Human Health Benchmarks for Pesticides (HHBP) as of 2021 (USEPA, 2022a). However, diuron does have US EPA Health Advisories and US Geological Survey (USGS) Health Based Screening Levels (HBSLs) for drinking water (USEPA, 2018a; USGS, 2018a) (Appendices 2 and 3). The DPR HHRLs, US EPA Health Advisories, and USGS HBSLs differ in that they are calculated using different parameters and assumptions. The chronic RfD used to establish the HBSLs and Health Advisories was updated by US EPA in 2020 (USEPA, 1987; USEPA, 2003; USEPA, 2018a; USGS, 2018b; USEPA, 2020b). Further, the DPR HHRL of 100 ppb is the only reference level that is specifically intended to be used for screening maximum detected residue levels in groundwater. There are no US EPA maximum contaminant levels (MCLs) for diuron, 3,4-DCA and DCPMU as of 2022 (USEPA, 2022b). US EPA MCLs are used for the protection of public drinking water systems and do not apply to privately owned wells or any other individual water system.

**Table 2. Acute and Chronic DPR HHRLs for Diuron, 3,4-DCA and DCPMU in Drinking Water**

Residue	Acute or Chronic	Water Consumption for Non-Nursing Infants <sup>a</sup> (kg water/kg BW)	RfD <sup>b</sup> (mg/kg/day)	Human Health Reference Levels <sup>c</sup> (ppb)
Diuron, 3,4-DCA, and DCPMU	Acute	0.194566	0.2	1028
	Chronic	0.099559	0.01	<b>100</b>

<sup>a</sup> 95<sup>th</sup> percentile water consumption for non-nursing infants from NHANES database (2005-2010). Acute and chronic water consumption data were extracted using the Dietary Exposure Evaluation Model - Food Commodity Intake Database (DEEM-FCID, version 4.02, 5-10c); a 1 ppm residue level was used so that resulting exposure levels would be numerically equal to corresponding consumptions.

<sup>b</sup> Acute and chronic reference doses (RfDs) for diuron. Acute and chronic RfDs were calculated using corresponding acute and chronic points of departure (PODs) and total uncertainty factors (UFs).

<sup>c</sup> A Human Health Reference Level (HHRL) is calculated as the RfD divided by water intake (95<sup>th</sup> percentile for acute and mean value for chronic for non-nursing infants) and multiplied by 1000 to convert to parts-per-billion (ppb).

The HHRL recommended for evaluating screening corresponding residues in drinking water is **bolded**.

**Conclusion**

HHA calculated Human Health Reference Levels (HHRLs) to be used when residues are detected in groundwater. Residue levels of diuron, 3,4-DCA and DCPMU equal to, or less than, the DPR HHRL of **100 ppb** are not expected to pose a risk to human health, including sensitive subpopulations, if ingested in drinking water.

*Brandon M. Brown*

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**Appendices**

**Appendix 1. DPR Memo: Potential Health Effects of Diuron and Two Degradates in Groundwater 9 August 2022 (2 pages)**



Julie Henderson  
Director

Jared Blumenfeld  
Secretary for  
Environmental Protection

MEMORANDUM

TO: Shelley DuTeaux  
Environmental Program Manager II  
Human Health Assessment Branch

VIA: Minh Pham  
Environmental Program Manager II  
Environmental Monitoring Branch

*Original Signed By 8/9/22*

FROM: Joy Dias  
Environmental Program Manager I  
Environmental Monitoring Branch

*Original Signed By 8/9/22*

DATE: August 9, 2022

SUBJECT: POTENTIAL HEALTH EFFECTS OF DIURON AND TWO DEGRADATES IN GROUNDWATER

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The Environmental Monitoring Branch (EMB) monitors the environment to determine the fate of pesticides, protecting the public and the environment from pesticide contamination through analyzing hazards and developing pollution prevention strategies. Consistent with EMB's mission, the Groundwater Protection Program (GWPP) routinely monitors for diuron due to its occurrence in groundwater and diuron's status as a 3CCR 6800(a) pesticide. The GWPP also gathers data from all public agencies that report groundwater monitoring data of pesticides and their degradates and compiles the data into the Well Inventory Database. Based on these records, diuron and two of its degradates, 3,4-Dichloroaniline<sup>1</sup> (3,4-DCA) and 1-(3,4-dichlorophenyl)-3-methyl urea (DCPMU, diuron desmethyl), have been detected in California's groundwater.

The highest reported detections of diuron, 3,4-DCA, and DCPMU are listed in Table 1. The United States Geological Survey (USGS) and the California State Water Resources Control Board are the only agencies to sample for 3,4-DCA. The USGS is the only agency to sample for DCPMU.

EMB requests the assistance of the Human Health Assessment Branch in determining whether these detections pose a significant risk to human health and to provide human health reference levels for diuron, 3,4-DCA, and DCPMU to use for screening detections.

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<sup>1</sup> 3,4-DCA is also a degradate of linuron, propanil, and iprodione

**Table 1.** Summary of highest reported detections of diuron, 3,4-DCA, and DCPMU from the Well Inventory Database.

Chemical	DPR Chemical Code	CAS Number	Maximum Concentration Reported (ppb)	Year
Diuron	231	330-54-1	5.2 <sup>2</sup>	1999
3,4-DCA	3138	95-76-1	0.541	2006
DCPMU	6371	3567-62-2	0.079	2020

cc: Carissa Ganapathy, Senior Environmental Scientist (Supervisory)

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<sup>2</sup> Diuron was not detected in follow-up sampling of this well. The highest confirmed detection of diuron was 3.95 ppb by DPR in 1989.

**Appendix 2.**

**Table 3. US EPA Health Advisories<sup>a</sup> for Diuron**

<b>Chronic RfD<sup>b</sup> (mg/kg/day)</b>	<b>1-day<sup>c</sup> HA (mg/L)</b>	<b>10-Day<sup>d</sup> HA (mg/L)</b>	<b>DWEL<sup>e</sup> HA (mg/L)</b>	<b>Life-Time (mg/L)</b>	<b>Cancer Risk<sup>f</sup> HA (mg/L at 10<sup>-4</sup>)</b>
0.003	1 (1000 ppb)	1 (1000 ppb)	0.1 (100 ppb)	N/A	0.2 (200 ppb)

<sup>a</sup>Health Advisory: An estimate of acceptable drinking water levels for a chemical substance based on health effects information; an HA is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, and local officials (USEPA, 2018a).

<sup>b</sup>The reference dose (RfD) used for the Health Advisories and the DWEL was based on a POD for blood effects (0.625 mg/kg/day) from a 2-year study in dogs divided by a total UF of 300. The RfD was reported as 2E<sup>-3</sup> mg/kg/day in the source document (USEPA, 1988; USEPA, 2018a). Note, in its most recent risk assessment, US EPA calculated a new cRfD of 0.01mg/kg/day for diuron (USEPA, 2020b).

<sup>c</sup>1-Day Health Advisory: The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to one day of exposure. The One-Day HA is intended to protect a 10-kg child consuming 1 liter of water per day (USEPA, 2018a).

<sup>d</sup>10-Day Health Advisory: The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to ten days of exposure. The Ten-Day HA is also intended to protect a 10-kg child consuming 1 liter of water per day (USEPA, 2018a).

<sup>e</sup>Drinking Water Equivalent Level (DWEL) Health Advisory: A DWEL is a drinking water lifetime exposure level, assuming 100% exposure from that medium, at which adverse, noncarcinogenic health effects would not be expected to occur (USEPA, 2018a).

<sup>f</sup>Cancer Risk Health Advisory (10<sup>-4</sup>): The concentration of a chemical in drinking water corresponding to an excess estimated lifetime cancer risk of 1 in 10,000 (USEPA, 2018a). The slope factor used for the Cancer HA (Q<sub>1</sub>\* = 1.91 x 10<sup>-2</sup> (mg/kg/day)<sup>-1</sup>) was based on carcinomas of the urinary bladder in male rats and mammary gland in female mice (USEPA, 2003; USEPA, 2018b; USGS, 2018a)

**Appendix 3.**

**Table 4. USGS Health Based Screening Levels (HBSLs)<sup>a</sup> for Diuron**

<b>Chronic RfD<sup>b</sup> (mg/kg/day)</b>	<b>Non-Cancer HBSL<sup>c</sup> (µg/L or ppb)</b>	<b>Cancer Slope Factor<sup>d</sup> ((mg/kg/day)<sup>-1</sup>)</b>	<b>Cancer HBSL<sup>e</sup> (µg/L or ppb at 10<sup>-4</sup>)</b>	<b>Cancer HBSL<sup>e</sup> (µ/L of ppb at 10<sup>-6</sup>)</b>
0.003	20	1.91 x 10 <sup>-2</sup>	200	2

<sup>a</sup> Health Based Screening Levels (HBSLs): Non-enforceable water-quality benchmark concentrations of contaminants in water that were developed using (1) the latest USEPA Office of Water methods for establishing drinking-water guidelines and (2) the most recent USEPA peer-reviewed publicly available toxicity information (USGS, 2018a).

<sup>b</sup>The chronic reference dose (cRfD) used for the non-cancer HBSL was calculated by dividing the LOAEL (1 mg/kg/day) based on hematological effects in rats by a total UF of 300 that included a 3X LOAEL-to-NOAEL extrapolation factor (USEPA, 2003; USEPA, 2018b; USGS, 2018a). In its most recent risk assessment, US EPA calculated a new cRfD of 0.01 mg/kg/day for diuron (USEPA, 2020b).

<sup>c</sup>Non-Cancer HBSLs: Non-enforceable concentrations of contaminants in water below which adverse noncarcinogenic health effects are not expected over a lifetime of exposure (USGS, 2018a).

<sup>d</sup>The slope factor used for the Cancer HBSLs ( $Q_1^* = 1.91 \times 10^{-2} \text{ (mg/kg/day)}^{-1}$ ) was based on carcinomas of the urinary bladder in male rats and mammary gland in female mice (USEPA, 2003; USEPA, 2018b; USGS, 2018a).

<sup>e</sup>Cancer HBSLs: Non-enforceable concentrations of contaminants in water that correspond to a range in excess estimated lifetime cancer risk of one-in-one million (10<sup>-6</sup>) to one-in-ten thousand (10<sup>-4</sup>) (USGS, 2018a).