BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:	)	
	)	R 2022-018
PROPOSED AMENDMENTS TO	)	
GROUNDWATER QUALITY	)	
(35 ILL. ADM. CODE 620)	)	

NOTICE OF FILING

PLEASE TAKE NOTICE that I have today filed with the Office of the Clerk of the Illinois Pollution Control Board, the **ILLINOIS ENVIRONMENTAL PROTECTION AGENCY'S RESPONSES TO ADDITIONAL QUESTIONS AND COMMENTS**, a copy of which is served upon you.

Respectfully submitted,

Dated: August 9, 2024

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY,

Sara Terranova
Division of Legal Counsel
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BY: /s/ Sara Terranova

THIS FILING IS SUBMITTED ELECTRONICALLY

SERVICE LIST

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ILLINOIS ENVIRONMENTAL PROTECTION AGENCY'S RESPONSES TO ADDITIONAL QUESTIONS AND COMMENTS

NOW COMES the Illinois Environmental Protection Agency (Illinois EPA or Agency), by and through one if its attorneys, and submits Responses to the Illinois Pollution Control Board's (Board) questions and the following Comments:

RESPONSES

Board Question 1.

In PC 62, the International Molybdenum Association cites an undated letter written by the United States Environmental Protection Agency (USEPA), Region 8 regarding a site-specific Colorado molybdenum water quality standard for protection of the water supply use classification. PC 62 at 4. The letter supports the choice of the 2020 ATSDR intermediate oral minimal risk level (MRL) for the reference dose to use in the proposed molybdenum water quality standard at issue in that case.

a. *Please comment on whether the Board should consider the USEPA Region 8's finding concerning 2020 ATSDR molybdenum MRL in this rulemaking to revise the proposed molybdenum groundwater quality standards (GWQS). Id. at 5.*

b. *If so, propose revised molybdenum Class I and Class II GWQS based on the 2020 ATSDR MRL of 0.06 mg/kg-day.*

Illinois EPA Response to 1a.

The Agency reached out to the State Risk Assessor's Group, a group of risk assessors from regulatory agencies across the country, including U.S. EPA, to determine potable water quality standards from other states. Nine states responded to the Agency's request for information and are listed on the following table:

State	RfD/MRL Used (mg/kg-day)	RfD Source	RSC Used
Arizona	No Criteria		

California	0.005	IRIS	---[a]
Colorado	0.02	ATSDR with additional UF=3	0.8
Iowa	0.005	IRIS	0.2
Michigan	0.005	IRIS	0.4
Pennsylvania	0.005	IRIS	0.2
Washington	0.005	IRIS	---[a]
West Virginia	0.005	IRIS	---[a]
Wisconsin	0.009	State-Derived	1[b]

a. The State uses U.S. EPA Regional Screening Level (RSL) tapwater equations to calculate potable water standards. The tapwater equations do not consider relative source contribution (RSC) in the calculations.

b. Wisconsin regulations require the use of an RSC of 1 when calculating standards.

The email responses are included in Attachment 1. Included with Colorado's email response is an attachment dated July 3, 2024, discussing its calculation of a revised molybdenum water supply standard. Colorado selected a final standard of 0.53 mg/L based on adult exposure. Colorado also applied an additional subchronic to chronic uncertainty factor of three to the ATSDR MRL. Wisconsin's email response also includes the information used to develop its state-specific RfD. The majority of states that replied stated they use the IRIS chronic RfD for calculating potable water use standards or health advisories (Part 620 Class I potable resource groundwater quality standards).

Illinois EPA selected U.S. EPA's IRIS toxicity value for calculating a health-based potable resource concentration for multiple reasons:

- IRIS is the Tier 1 toxicity source listed in U.S. EPA's hierarchy and its chronic toxicity value is used by several states.
- The IRIS toxicity value is based on chronic exposure, which is the exposure type used in calculating health-based standards for noncancer health effects for residential populations. The ATSDR toxicity value is based on intermediate (subchronic) exposure.
- U.S. EPA uses the IRIS toxicity value for developing chronic health-based screening levels for residential populations (child and adult), including its Lifetime Health Advisory for drinking water. U.S. EPA uses the ATSDR toxicity value for developing subchronic health-based screening levels for construction worker populations.
- ATSDR's subchronic toxicity value is not derived from benchmark dose (BMD) or pharmacokinetic (PK) models using time-weighted averages. For the ATSDR intermediate molybdenum MRL, investigators estimated doses using body weight and food consumption data. As a result, it is not appropriate to use the subchronic value for evaluating chronic exposure without applying an additional uncertainty factor of 10 for subchronic to chronic extrapolation.
- IRIS molybdenum toxicity value has a critical effect of increased uric acid, based on the chronic human study selected for calculating its RfD. Increased molybdenum ingestion results in decreased copper absorption. As a result, more copper is excreted from the body as higher amounts of molybdenum are ingested. Copper assists in the excretion of uric acid. When low dietary copper levels are present, uric acid builds up.

> The Koval'skiy, et al., study selected by IRIS is a human health study conducted in a region selected specifically for its high molybdenum content in plants and its low copper content due to this inverse relationship. For ATSDR's toxicity value, an assumption was made that the average copper intake of the U.S. population exceeds dietary requirements. Therefore, animal studies involving inadequate levels of copper were not considered relevant in the derivation of its toxicity value. Although ATSDR included a modifying factor of 3 to address a concern that reproductive or developmental effects may occur in populations with marginal copper intakes, the use of the IRIS toxicity value is specifically protective for those with marginal copper intakes for increased uric acid levels.

The Agency does not agree with Region 8's assessment that chronic inhalation toxicity data supports a decision to accept the intermediate oral MRL as a chronic MRL without assigning an uncertainty factor for extrapolation. The NTP 1997 chronic inhalation study referenced by Region 8 evaluated molybdenum trioxide (CASRN 1313-27-5), not molybdenum (CASRN 7439-98-7). In addition, subsection 620.Appendix A(c)(2)(D) requires correction factors be applied to extrapolate an inappropriate route of exposure (inhalation) to oral exposure. Following Region 8's assessment, Colorado chose to apply an uncertainty factor of three to extrapolate the ATSDR chronic value from the subchronic value.

The Agency also does not agree with the use of an RSC of 0.8 for protection of groundwater for potable use. The assessment is based on a subchronic MRL and an adult body weight of 80 kg. The Agency proposes the use of child exposure factors to calculate health-based Class I groundwater quality standards. In addition, page 120 of ATSDR's molybdenum toxicological profile states, "Exposure to molybdenum to the general population is almost entirely through food." The toxicological profile is included as Attachment 1 of the Agency's Post-Hearing Comments submitted to the Board March 3, 2023 (PC 54). If exposure is almost entirely from food, an RSC value representing 80% of molybdenum human exposure via drinking water is not appropriate. An RSC value of 20% (0.2) is the more appropriate value for molybdenum's contribution to human exposure via water ingestion.

Illinois EPA Response to 1b.

The Agency requires the use of chronic oral reference doses for calculating potable resource groundwater quality standards. Depending on how the human point of departure (POD) is derived (benchmark dose, pharmacokinetic, estimation, etc.), an uncertainty factor to extrapolate from a subchronic RfD/MRL to a chronic RfD/MRL is needed. The appropriate uncertainty factor to extrapolate the chronic RfD/MRL from the intermediate MRL calculated with dose estimations is ten, per U.S. EPA's, "A Review of the Reference Dose and Reference Concentration Process," incorporated by reference at Section 620.125. When extrapolating a chronic dose from the ATSDR intermediate dose, the total uncertainty factor to be applied is 1,000:

- 10 for extrapolation from animals to humans
- 10 for variability within humans
- 10 for extrapolation from a subchronic value to a chronic value

With ATSDR's modifying factor of three, the extrapolated chronic MRL is 0.006 mg/kg-day. Although the Agency still proposes the use of the IRIS chronic RfD, if the Board opts for a health-based Class I groundwater quality standard calculated with ATSDR's extrapolated chronic MRL, the applicable Human Threshold Toxicant Advisory Concentration (HTTAC) calculation is:

$$HTTAC\ \left(\frac{mg}{L}\right) = \frac{RSC \bullet ADE}{W}$$

Where:

RSC	=	Relative Source Contribution as a unitless value. The proposed RSC for the calculation is 0.2.
ADE	=	Acceptable Daily Exposure of substance in mg/day. ADE is calculated as the chronic RfD/MRL multiplied by the body weight of a child (0-6 years of age), equal to 15 kg.
W	=	Per capita daily water consumption for a child (0-6 years of age), equal to 0.78 L/day.

$$HTTAC\ \left(\frac{mg}{L}\right) = \frac{0.2 \bullet (0.006 \bullet 15)}{0.78}$$

The calculated health-based concentration using the extrapolated chronic ATSDR MRL is 0.023 mg/L.

Board Question 2.

In PC 63, the Illinois Environmental Regulatory Group questions whether Illinois "laboratories will have the capacity to process a sudden and unprecedented influx of Illinois groundwater PFAS tests." PC 63 at 3.

a. *Please comment on whether IEPA expects a sudden increase in number of PFAS tests performed by Illinois laboratories upon the adoption of the proposed rules as well as USEPA's PFAS drinking water MCLs.*

b. *If so, is IEPA aware of whether Illinois laboratories have adequate capacity to meet the increased demand to conduct the required PFAS analyses?*

c. *If not, would it be possible for IEPA to contact Illinois laboratories regarding capacity issues for analyzing PFAS samples resulting from the potential adoption of proposed groundwater quality standards as well as the recent USEPA drinking water MCLs and report back to the Board?*

d. *Please clarify whether Part 620 requires PFAS analyses to be performed by only Illinois laboratories.*

Illinois EPA Response to 2a.

Yes, there will be an increase in the number of PFAS analyses being performed.

Illinois EPA Response to 2b.

The number of laboratories in Illinois and other states obtaining NELAC accreditation for PFAS analysis has increased over the last several years.

Illinois EPA Response to 2c.

Due to the increased number of laboratories in Illinois and other states obtaining NELAC accreditation for PFAS analysis, it is not necessary to contact individual laboratories to inquire about their capacity to analyze samples for PFAS.

Illinois EPA Response to 2d.

No, Part 620 does not require PFAS analyses to be performed only by Illinois laboratories. The requirement is to use a laboratory with NELAC accreditation for the selected PFAS method(s) and analytes. The TNI National Environmental Laboratory Accreditation Management System database https://lams.nelac-institute.org/ can be searched by matrix (Drinking Water, Non-Potable Water, Solid and Chemical Materials) and method (537.1, 533, 1633, 8327) to obtain a listing of accredited laboratories.

A TNI LAMS search on 7/31/24 yielded the following number of laboratories by matrix and method:

- Drinking Water by EPA Method 537.1 – 56 laboratories with accreditation
  - Four Illinois laboratories with Illinois ELAP primary accreditation
  - 12 laboratories in other states with Illinois ELAP secondary accreditation
- Drinking Water by EPA Method 533 – 55 laboratories with accreditation
  - Four Illinois laboratories with Illinois ELAP primary accreditation
  - 11 laboratories in other states with Illinois ELAP secondary accreditation
- Non-Potable Water by EPA Method 1633 – 34 laboratories with accreditation
  - One Illinois laboratory with Illinois ELAP primary accreditation
  - One laboratory in other state with Illinois ELAP secondary accreditation
- Solid and Chemical Materials by EPA Method 1633 – 33 laboratories with accreditation
  - One Illinois laboratory with Illinois ELAP primary accreditation
  - One laboratory in other state with Illinois ELAP secondary accreditation
- Non-Potable Water by EPA Method 8327 – 3 laboratories with accreditation
- Solid and Chemical Materials by EPA Method 8327 – 3 laboratories with accreditation

The Agency allows the use of Method 1633 for groundwater analyses from monitoring wells even though it is listed as a non-potable water method. The Method 1633 LLOQs are sufficiently low enough to meet the proposed groundwater quality standards.

Note: NELAC-accredited laboratories may analyze Part 620 samples for PFAS. NELAC-accredited laboratories analyzing drinking water for the Public Water Supply program are required

to obtain IL ELAP accreditation (primary for Illinois laboratories and secondary for laboratories in other states).

Board Question 3.

The City of Springfield (CWLP) and Dynegy again raise the issue of shifting the basis of the proposed Class I and Class II standards for selenium from health-based USEPA MCL to a beneficial use criterion for irrigation of crops. PC 65 at 8-9; PC 66 at 4. The participants ask the Board to look to more recent scientific data rather than the 1972 Water Quality Criteria relied upon in this rulemaking proposal. Please comment on Dynegy's concerns (below) regarding the reliance on the 1972 Water Quality Criteria as the basis of the proposed selenium and fluoride standards.

a. *The 1972 selenium criterion is based "on studies done in areas (Oregon, Wyoming, New Zealand and Denmark) with different agricultural conditions than Illinois." PC 66 at 4 citing Ex. 24 at 9. These studies "relate to livestock foraging on range plants, which do not typically serve as forage for livestock in Illinois." Id. at 5 citing Ex. 24 at 6, 8-9. Thus, "range plants typically require higher levels of irrigation than the types of forage crops that exist in Illinois." Id. citing Ex. 30 at 3-4.*

b. *The 1972 selenium criterion is based on three acre-feet water use per acre, per year. PC 66 at 5 citing Ex. 24 at 7. The average irrigation in Illinois is estimated at 0.5 acre-foot of water use per acre, per year. Id. Dynegy argues that there is no evidence in the record or the Board's order "refuting the fact that irrigation rates in Illinois are much lower than the irrigation rate that serves as a basis for the 0.02mg/L recommendation." Id.?*

Illinois EPA Response to 3a.

Water Quality Criteria, 1972, states, "Selenium is toxic at low concentrations in nutrient solutions, and only small amounts added to the soils increase the selenium content of forages to a level toxic for livestock." Studies found that selenium concentrations at levels of 0.025 mg/L in nutrient solution decrease alfalfa yields. Alfalfa is a cover crop increasingly used in Illinois to help prevent soil breakdown and erosion. Alfalfa is also used for feed for livestock. The proposed MCL value of 0.05 mg/L could damage alfalfa. Studies listed in *Water Quality Criteria, 1972*, show bioaccumulation in forage plants and vegetables. Selenium applications of 0.2 mg/hectare produce concentrations in plants that can be toxic to animals. The excerpt from *Water Quality Criteria, 1972*, discussing the toxic effects on plants and animals is included in the Agency's Initial Filing dated December 7, 2021, on page 4,834.

The Illinois Groundwater Protection Act (IGPA), adopted in 1987, states,

> ... it is the policy of the State of Illinois to restore, protect, and enhance the groundwaters of the State, as a natural and public resource. The State recognizes the essential and pervasive role of groundwater in the social and economic well-being of the people of Illinois, and its vital importance to the general health, safety, and welfare. It is further recognized as consistent

> with this policy that the groundwater resources of the State be utilized for beneficial and legitimate purposes; that waste and degradation of the resources be prevented; and that the underground water resource be managed to allow for maximum benefit of the people of the State of Illinois.

A beneficial use of groundwater is irrigation. Agriculture is a primary industry in the State and those who grow crops using irrigation should be able to utilize the resource without concerns of reduced yields and livestock toxicity. Class I groundwater quality standards have historically included irrigation and livestock recommendations from *Water Quality Standards, 1972*.

For example, the Agency recommends maintaining the current Class I groundwater quality standard of 2.0 mg/L for boron, based on irrigation. The health-based concentration, calculated with a toxicity value derived in 2004, is less stringent than the irrigation value and would not be protective for the beneficial and legitimate purpose of irrigation. As a result, the Agency did not propose to update the Class I groundwater quality standard to the health-based value during the Board's R08-18 rulemaking. The proposal for selenium is not different.

Response to 3(b):

The Agency cannot determine the basis of Dynegy's statement that average Illinois irrigation is 0.5 acre-foot of water use per acre, per year. The Agency's Pre-Filed Answers to Follow-Up Questions, submitted to the Board May 6, 2022, provides several attachments discussing increasing irrigation rates across the state due climate change and contract changes by seed corn dealers that require assured crop yields after the 2012 drought.

This increase is illustrated by U.S. Geologic Survey (USGS) at: https://waterdata.usgs.gov/il/nwis/water_use/ . The following table is from data collected for the irrigation of crops.

Year	Irrigation Crop Self-Supplied Groundwater Withdrawals for Crops (Mgal/day)	Irrigation Crop Sprinkler Irrigation for Crops (acre-foot)
2010	196.30	435,140
2015 (most recent data)	203.52	600,650

million gallons per day (Mgal/d)--a rate of flow of water equal to 133,680.56 cubic feet per day, or 1.5472 cubic feet per second, or 3.0689 acre-feet per day. A flow of one million gallons per day for one year equals 1,120 acre-feet (365 million gallons).

acre-foot (acre-ft)—the volume of water required to cover 1 acre of land (43,560 square feet) to a depth of 1 foot. Equal to 325,851 gallons or 1,233 cubic meters.

Water Quality Criteria, 1972, states it kept the value for use up to 20 years on fine-textured soils of pH 6.0-8.5 equal to the value for waters used continuously on all soil as a factor of safety due to selenium's relative mobility in soils, bioaccumulation, and lack of information on soil reactions.

Board Question 4.

Dynegy notes that the proposed fluoride standards are intended afford protection for livestock from potential aesthetic dental impact and not any other harmful effects which are expected until concentrations are multiple times higher. PC 66 at 5.

a. Please comment on whether there are any harmful effects of fluoride on livestock other than "tooth mottling" that the Board should consider to support the proposed standards.

b. If not, comment on whether the Board should withdraw the proposed fluoride standards and maintain the current Class I and Class II standards, as suggested by Dynegy.

Illinois EPA Response to 4(a):

Both the livestock recommendation of 2.0 mg/L and the MCL of 4 mg/L for fluoride are based on dental fluorosis as the health effect, which both sources recognize is a cosmetic effect. In addition, U.S. EPA lists a fluoride value of 2.0 mg/L for its Secondary Drinking Water Regulations (SDWR). This information is located in the Agency's initial filing dated December 07, 2021, as Attachment 11, on page 4,828 of the initial filing.

Response to 4(b):

The Agency does not agree with withdrawing the proposed fluoride standards. Both the proposed livestock value and the MCL rely on the same cosmetic effect. U.S. EPA's Secondary Drinking Water Regulations (SDWRs) fluoride value of 2.0 mg/L is equal to the proposed livestock value. SDWRs are non-enforceable Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.

Board Question 5.

Dynegy claims that evidence in the record "clearly demonstrates that selenium deficiency is a problem for Illinois livestock and that supplements are recommended for livestock to protect against selenium deficiency." PC 66 at 5 citing Exh. 24, Dynegy's Post-Hearing Comment at Exh. D and E (Mar. 3, 2023) (P.C. #57). Please review the cited information and comment on whether the proposed selenium standard is necessary or detrimental for the protection of livestock.

Illinois EPA Response 5.

Water Quality Standards, 1972, recommends an upper limit value of 0.05 mg/L for livestock watering. The proposed selenium standard of 0.02 mg/L for irrigation is slightly below the recommended upper limit. As mineral supplements, including selenium, are regular practice for livestock farmers, the proposed selenium standard is not detrimental for the protection of livestock.

Board Question 6.

Following the Board's first notice order, many participants have again raised the issue of the economic reasonableness of the proposed rule amendments, specifically concerning the PFAS GWQS. Some participants have pointed to other states that have performed an economic reasonableness evaluation of their own PFAS standards. See, PC 61 at 2, pointing to a Minnesota rulemaking. Does IEPA have any additional information on economic reasonableness of the proposed PFAS GWQS that could be considered by the Board?

Illinois EPA Response 6.

While the Agency appreciates the issue regarding economic reasonableness specifically regarding the PFAS GWQS, the economic impact of the PFAS GWQS is dependent upon how the numbers are utilized under specific programs. The Agency reiterates the Board's finding that,

> For facilities that may be impacted by the groundwater standards, compliance and any potential remediation will be addressed under specific programs like Part 811 and 814 landfills, the Site Remediation Program and the Underground Storage Tank program. Following the adoption of the proposed amendments to Part 620, the Agency will identify and develop amendments needed in other rules addressing specific programs. Additionally, where appropriate, regulatory relief mechanisms such as the adjusted standard process are available. PCB R22-18, First Notice at 68 (March 7, 2024).

The Agency agrees with the Board's conclusion and reiterates that the economic impact resulting from each program's specific utilization of the PFAS GWQS will be addressed in the appropriate rulemakings as they occur over time.

COMMENTS

The Agency found a few inconsistencies with the Board's First Notice addendum regarding the 2,4-dinitrotoluene and 2,6-dintrotoluene Class I and Class II GQS in Sections 620.410(b) and 620.420(b), respectively.

2,4-Dinitrotoluene
Initial Filing proposed Class I GQS: 0.001 mg/L as the LLOQ/LCMRL (page 5017 of the initial filing), Class II GQS: 0.005 mg/L (page 5029 of the initial filing).
First Notice Addendum Class I GQS: 0.00025 mg/L as the health-based carcinogen value (page 35 of the First Notice addendum), Class II GQS: 0.00125 mg/L (page 46 of the addendum)

2,6-Dinitrotoluene
Initial Filing proposed Class I GQS: 0.001 mg/L as the LLOQ/LCMRL (page 5017 of the initial filing), Class II GQS: 0.005 mg/L (page 5029 of the initial filing).
First Notice Addendum Class I GQS: 0.0001 mg/L as the LLOQ/LCMRL (page 35 of the First Notice addendum), Class II GQS: 0.0005 mg/L (page 46 of the addendum).

In addition, the Agency identified one other constituent with different First Notice addendum GQS than proposed: 1,3-Dinitrobenzene. Please see the table below.

Section 620.410(b)

CASRN	Constituent	Initial Filing Class I GQS (mg/L)	Basis of Initial Filing Class I GQS	First Notice addendum Class I GQS (mg/L)	Basis of First Notice addendum Class I GQS
99-65-0	1,3-Dinitrobenzene	0.001	LLOQ/LCMRL	0.0007	Health-Based Value Using Methods presently in Part 620
121-14-2	2,4-Dinitrotoluene	0.001	LLOQ/LCMRL	0.00025	Health-Based Value Using Methods proposed in Part 620
606-20-2	2,6-Dinitrotoluene	0.001	LLOQ/LCMRL	0.0001	Cannot Determine the Basis of the GQS

Section 620.420(b)

CASRN	Constituent	Initial Filing Class II GQS (mg/L)	Basis of Initial Filing Class II GQS	First Notice addendum Class II GQS (mg/L)	Basis of First Notice addendum Class II GQS
99-65-0	1,3-Dinitrobenzene	0.001	No Treatability Factor Applied	0.0007	No Treatability Factor Applied

121-14-2	2,4-Dinitrotoluene	0.005	Treatability Factor 5	0.00125	Treatability Factor 5
606-20-2	2,6-Dinitrotoluene	0.005	Treatability Factor 5	0.0005	Treatability Factor 5

PFOA is also changed from IEPA's proposed LCMRL of 2 ng/L (0.000002 mg/L) to USEPA's MCL of 4 ng/L (0.000004 mg/L) for both Class I and Class II GQS. The Board discussed this change in its First Notice Summary of Actions.

WHEREFORE, the Illinois EPA asks the Board to accept these Responses and Comments.

Respectfully submitted,

Dated: August 9, 2024

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY,

BY: /s/ Sara Terranova

Sara Terranova
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CERTIFICATE OF SERVICE

I, the undersigned, on affirmation state the following:

That I have served the attached **NOTICE OF FILING** and **ILLINOIS ENVIRONMENTAL PROTECTION AGENCY'S RESPONSES AND COMMENTS** by e-mail upon the attached service list.

That my e-mail address is: Sara.Terranova@illinois.gov.

That the e-mail transmission took place before 4:30 p.m. on the date of August 9, 2024.

/s/ Sara Terranova

August 9, 2024

Attachment 1

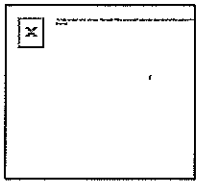
Hawbaker, Carol

From: Debi Goodwin <goodwin.debi@azdeq.gov>
Sent: Thursday, July 25, 2024 11:34 AM
To: Hawbaker, Carol
Subject: [External] Molybdenum groundwater or drinking water stands question

Hi Carol;

Arizona does not have a standard for molybdenum in groundwater or surface water.

Debi Goodwin, MS
Senior Environmental Scientist
602-771-4453



azdeq.gov
Your feedback matters to ADEQ. Visit azdeq.gov/feedback

Arizona Point of Contact
ITRC States Engagement Program
https://itrcweb.org/home

Hawbaker, Carol

From: Hristov, Hristo@OEHHA <Hristo.Hristov@oehha.ca.gov>
Sent: Thursday, July 25, 2024 6:21 PM
To: Hawbaker, Carol
Cc: Gettmann, Kimberly@DTSC
Subject: [External] RE: Molybdenum groundwater or drinking water stands question

California does not have a health based standard, such as PHG for molybdenum in drinking water. I am not aware of MCL for molybdenum. One may use the molybdenum health-based US EPA RSL screening level for drinking water or modify it to site-specific conditions. Please refer to the website below:

https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/MCLsandPHGs.html

Please note: OEHHA is subject to the California Public Records Act. E-mail communications with OEHHA staff are not confidential and may be produced to members of the public upon request.

Sincerely,

Hristo T. Hristov, MD, Ph.D., M.Env. Sc.
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From: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Sent: Thursday, July 25, 2024 8:19 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Cc: Cole.Elizabeth@epa.gov; Berry, David <Berry.David@epa.gov>; Carol.Hawbaker@illinois.gov
Subject: FW: Molybdenum groundwater or drinking water stands question

EXTERNAL:

Good morning,

Please see the email below requesting information on regulation of molybdenum in groundwater, drinking water or both. Please respond to Carol Hawbaker, she is cc'ed on this email.

Thank you,
Kim

Kimberly C. Gettmann, Ph.D.
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kimberly.gettmann@dtsc.ca.gov
Department of Toxic Substances Control
8800 Cal Center Drive, Sacramento,
California 95826-3200
California Environmental Protection
Agency

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Sent: Thursday, July 25, 2024 7:58 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Subject: Molybdenum groundwater or drinking water stands question

Hi Kim,

Would you please distribute the following question to the Risk Assessors Group?

I'm taking a poll of states that regulate molybdenum in either groundwater, drinking water, or both. If your state regulates it, would you please provide the basis of the standard and the toxicity value used if the value is a health-based standard?

You may respond to my email below. I appreciate all responses!

Thank You,

Carol

Carol Hawbaker
Manager
Office of Toxicity Assessment
Illinois Environmental Protection Agency
Telephone: 217-558-3351
Email: Carol.Hawbaker@illinois.gov

Hawbaker, Carol

From: Williams - CDPHE She Her, Meghan <meghan.williams@state.co.us>
Sent: Thursday, July 25, 2024 11:50 AM
To: Hawbaker, Carol
Cc: Andrea Kingcade - CDPHE She Her Ella; Kelsey Ruehling - CDPHE; Stephanie Baker - CDPHE She Her
Subject: [External] Molybdenum standards from Colorado
Attachments: Regulation #31 and #33 (Molybdenum)_PFA memo_with attachments.pdf

Hi Carol,

We recently completed a rulemaking effort to revise Colorado's human health water supply standards for molybdenum. A standard of 530 ug/L was derived after reviewing available toxicity and exposure data and considering input from stakeholders. The draft final action document is attached - you can find the rationale for the standard, including toxicological information, beginning on the 9th page of the document (numbered page 7).

Please feel free to reach out to me or my colleagues cc'd on this email if you have any questions.

Thanks,
Meghan

Meghan Williams (she/her)
Toxicologist
Toxicology and Environmental Epidemiology Office
4300 Cherry Creek Drive South, Denver, CO 80246
303-692-2606
meghan.williams@state.co.us | https://cdphe.colorado.gov/TEEO

COLORADO
Water Quality
Control Commission
Department of Public Health & Environment

Memorandum

To: Parties to the June 10-12, 2024 Molybdenum Rulemaking Hearing on the Basic Standards and Methodologies for Surface Water, Regulation #31 (5 CCR 1002-31), and Classifications and Numeric Standards for Upper Colorado River Basin and North Platte River (Planning Region 12), Regulation #33 (5 CCR 1002-33)

From: Jojo La, Director, Administrator for the Water Quality Control Commission
Maureen Mulcahy, Deputy Director, Environmental Boards and Commissions

Date: July 3, 2024

Subject: Review of Preliminary Final Action - Molybdenum Rulemaking Hearing on the Basic Standards and Methodologies for Surface Water, Regulation #31 (5 CCR 1002-31), and Classifications and Numeric Standards for Upper Colorado River Basin and North Platte River (Planning Region 12), Regulation #33 (5 CCR 1002-33)

The hearing record for the Molybdenum Rulemaking Hearing on the Basic Standards and Methodologies for Surface Water, Regulation #31 (5 CCR 1002-31), and Classifications and Numeric Standards for Upper Colorado River Basin and North Platte River (Planning Region 12), Regulation #33 (5 CCR 1002-33), was closed on June 12, 2024. I attach for your information and review the final drafts of the proposed revisions to the Basic Standards and Methodologies for Surface Water, Regulation #31 (5 CCR 1002-31), and Classifications and Numeric Standards for Upper Colorado River Basin and North Platte River (Planning Region 12), Regulation #33 (5 CCR 1002-33).

These documents reflect the commission's preliminary final approval decisions, along with the final drafts of the accompanying Statements of Basis, Specific Statutory Authority, and Purpose as discussed during the commission's deliberations. Please note the following during your review of the draft documents:

- The attached draft regulations show redlines for all changes as compared to the existing effective regulations and as approved by the commission at the rulemaking hearing. The statements of basis and purpose show redlines only for changes drafted during deliberations for ease of stakeholder review.
- The draft regulation and statement of basis and purpose for the Classifications and Numeric Standards for Upper Colorado River Basin and North Platte River (Planning Region 12), Regulation #33 (5 CCR 1002-33) also reflect changes from the concurrent rulemaking hearing that included the Regulation #33 triennial basin review, biennial temporary modifications review, and review of discharger-specific variances in Regulation #33. Draft documents for the concurrent rulemaking hearing were provided to parties to that rulemaking hearing with a separate draft final action memorandum.

If you believe that the enclosed documents do not accurately reflect the commission's preliminary decisions, please let me know at your earliest convenience, but no later than **July 17, 2024**. Also, **please copy the other parties to the hearing on any proposed corrections that you submit.** The commission anticipates taking final action regarding these rulemaking hearings at its meeting on **August 21, 2024**.

Should you have any questions, please feel free to contact me by email at jojo.la@state.co.us or 720-277-9262.

COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

Water Quality Control Commission

REGULATION NO. 31 - THE BASIC STANDARDS AND METHODOLOGIES FOR SURFACE WATER

5 CCR 1002-31

[Editor's Notes follow the text of the rules at the end of this CCR Document.]

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31.16 TABLES

(1) INTRODUCTION

The numeric levels for parameters listed in Tables I, II, III shall be considered and applied as appropriate by the Commission in establishing site-specific numeric standards, in accordance with section 31.7.

For the purposes of integrating these parameters into NPDES discharge permits, the duration of the averaging period for the numeric level is designated in the tables. Chronic levels and 30-day levels are to be averaged as defined in section 31.5(7). Acute levels and 1-day levels are to be averaged as defined in section 31.5(2).

Certain toxic metals for Aquatic Life have different numeric levels for different levels of water hardness. Water hardness is being used here as an indication of differences in the complexing capacity of natural waters and the corresponding variation of metal toxicity. Other factors such as organic and inorganic ligands, pH, and other factors affecting the complexing capacity of the waters may be considered in setting site-specific numeric standards in accordance with section 31.7. Metals listed in Table III for aquatic life uses are stated in the dissolved form unless otherwise indicated.

(2) TESTING PROCEDURES

Various testing procedures to determine that numeric values for water quality parameters may be appropriate to present to the Water Quality Control Commission at stream classification hearings. (See section 31.6(3)). These include:

(a) Standard Test Procedures

(i) Code of Federal Regulations, Title 40, Part 136;

(ii) The latest approved EPA Methods for Chemical Analysis of Water and Wastes;

(iii) Standard Methods for the Examination of Water and Wastewater (current edition), American Public Health Association;

(iv) ASTM Standards, Part 31, Water;

(v) EPA Biological Field and Laboratory Methods.

(b) Toxicity testing and Criteria Development Procedures:

(i) The latest EPA Methods for Chemical Analysis of Water and Wastewater; ASTM, Standard Methods for Examination of Water, Wastewater;

(ii) Interim Guidance on Determination and Use of Water-Effect Ratio for Metals, EPA-823-B-94-001, U.S. Environmental Protection Agency, February, 1994.

(iii) Other approved EPA methods.

(c) Other Procedures:

Other procedures may be deemed appropriate by either the Water Quality Control Commission and/or the Water Quality Control Division.

(3) REFERENCES

Capital letters following levels in the tables indicate the sources of the level; they are referenced below.

(A) EPA Quality Criteria for Water, July 1976, U.S. Environmental Protection Agency, U.S. Government Printing Office: 1977 0-222-904, Washington, D.C. 256 p.

(B) EPA Water Quality Criteria 1972, Ecological Research Series, National Academy of Sciences, National Academy of Engineering, EPA-R3-73-033, March 1973, Washington, D.C. 594 p.

(C) Davies, P.H. and Goettl, J.P., Jr., July 1976, Aquatic Life - Water Quality Recommendations for Heavy Metal and Other Inorganics.

(D) Parametrix Inc., Attachment II, Parametrix Reports - Toxicology Assessments of As, Cu, Fe, Mn, Se, and Zn, May 1976, Bellevue, Washington, 98005. submitted to Water Quality Control Commission by Gulf Oil Corp., Inc., 161 p.

(E) EPA National Interim Primary Drinking Water Regulations, 40 Code of Federal Regulations, Part 141.

(F) EPA, March 1977, Proposed National Secondary Drinking Water Regulation, Federal Register, Vol. 42 No. 62, pp 17143-17147.

(G) Recommendations based on review of all available information by the Committee on Water Quality Standards and Stream Classification.

(H) American Fishery Society, June 1978, A Review of the EPA Red Book Quality Criteria for Water, (Preliminary Edition).

(I) Section 307 of the Clean Water Act, regulations promulgated pursuant to Section 307.

(J) Final Report of the Water Quality Standards and Methodologies Committee to the Colorado Water Quality Control Commission, June 1986.

(K) Proposed Nitrogenous Water Quality Standards for the State of Colorado, by the Nitrogen Cycle Committee of the Basic Standards Review Task Force, March 12, 1986 (Final Draft).

(L) Quality Criteria for Water, 1986, and Updates Through 1989, U.S. Environmental Protection Agency, U.S. Government Printing Office, EPA 440/5-86-001, Washington, D.C. 20460.

(M) Level modified by Commission

(N) 1999 Update of Ambient Water Quality Criteria for Ammonia (1999 Ammonia Update), U.S. Environmental Protection Agency, Office of Water, EPA-823-F-99-024, Washington, D.C. 20460.

(O) Raisbeck, M.F., S. L. Riker, C. M. Tate, R. Jackson, M. A. Smith, K. J. Reddy and J. R. Zygmunt. 2008. Water quality for Wyoming livestock and wildlife. University of Wyoming AES Bulletin B-1183.

(P) Agency for Toxic Substances and Disease Registry. Toxicological Profile for Molybdenum, May 2020

. . . .

TABLE III - METAL PARAMETERS

TABLE III METAL PARAMETERS (concentration in µg/L)						
Metal[1]	Aquatic Life[1][3][4][J]		Agriculture[2]	Domestic Water Supply[2]	Water + Fish[7]	Fish Ingestion[10]
	ACUTE	CHRONIC	CHRONIC		CHRONIC	CHRONIC
Aluminum	$e^{(1.3695*\ln(\text{hardness})+1.8308)}$ (total recoverable)	87 or $e^{(1.3695*\ln(\text{hardness})-0.1158)}$ (total recoverable)[11]			---	---
Antimony[18]				6.0 (chronic)	5.6	640
Arsenic	340	150	100[A]	0.02 – 10[3] (chronic)	0.02	7.6
Barium[18]				1,000[E] (acute) 490 (chronic)	---	---
Beryllium[18]			100[A,B]	4.0 (chronic)	---	---
Cadmium	Warm[17] = (1.136672-(ln(hardness)* 0.041838))*$e^{(0.9789*\ln(\text{hardness})-3.443)}$ Cold[17] = (1.136672-(ln(hardness)* 0.041838))*$e^{(0.9789*\ln(\text{hardness})-3.866)}$	(1.101672-(ln(hardness)*0.041838))* $e^{(0.7977*\ln(\text{hardness})-3.909)}$	10[B]	5.0[E] (acute)	---	---
Chromium III[5]	$e^{(0.819*\ln(\text{hardness})+2.5736)}$	$e^{(0.819*\ln(\text{hardness})+0.5340)}$	100[B]	50[E] (acute)	---	---
Chromium VI[5]	16	11	100[B]	50[E] (acute)	100	---
Copper	$e^{(0.9422*\ln(\text{hardness})-1.7408)}$	$e^{(0.8545*\ln(\text{hardness})-1.7428)}$	200[B]	1,000[F] (chronic)	1,300	---
Iron		1,000 (total recoverable)[A,C]		300 (dissolved)[F] (chronic)	---	---
Lead	(1.46203-(ln(hardness)* 0.145712))*$e^{(1.273*\ln(\text{hardness})-1.46)}$	(1.46203-(ln(hardness)* 0.145712))*$e^{(1.273*\ln(\text{hardness})-4.705)}$	100[B]	50[E] (acute)	—	---
Manganese	$e^{(0.3331*\ln(\text{hardness})+6.4676)}$	$e^{(0.3331*\ln(\text{hardness})+5.8743)}$	200[B][12]	50 (dissolved)[F] (chronic)	—	---
Mercury		FRV(fish)[6] = 0.01 (total recoverable)		2.0[E] (acute)	—	---

TABLE III METAL PARAMETERS (concentration in µg/L)						
Metal[1]	Aquatic Life[1][3][4][J]		Agriculture[2]	Domestic Water Supply[2]	Water + Fish[7]	Fish Ingestion[10]
	ACUTE	CHRONIC	CHRONIC		CHRONIC	CHRONIC
Molybdenum			300[O,15]	~~210530~~[P] (chronic)		
Nickel	$e^{(0.846*ln(hardness)+2.253)}$	$e^{(0.846*ln(hardness)+0.0554)}$	200[B]	100[E] (chronic)	610	4,600
Selenium[9]	18.4	4.6	20[B,D]	50[E] (chronic)	170	4,200
Silver	$0.5*e^{(1.72*ln(hardness)-6.52)}$	$e^{(1.72*ln(hardness)-9.06)}$ Trout[19] = $e^{(1.72*ln(hardness)-10.51)}$		100[F] (acute)	—	---
Thallium[18]		15[C]		0.5 (chronic)	0.24	0.47
Uranium[16]	$e^{(1.1021*ln(hardness)+2.7088)}$	$e^{(1.1021*ln(hardness)+2.2382)}$		16.8 – 30[13] (chronic)	---	---
Zinc	$0.978*e^{(0.9094*ln(hardness)+0.9095)}$	$0.986*e^{(0.9094*ln(hardness)+0.6235)}$ Sculpin[14] = $e^{(2.140*ln(hardness)-5.084)}$	2000[B]	5,000[F] (chronic)	7,400	26,000
Note: Capital letters in parentheses refer to references listed in section 31.16(3); numbers in parentheses refer to Table III footnotes.						

Table III – Footnotes

(1) Metals for aquatic life use are stated as dissolved unless otherwise specified.

Where the hardness-based equations in Table III are applied as table value water quality standards for individual water segments, those equations define the applicable numerical standards. As an aid to persons using this regulation, Table IV provides illustrative examples of approximate metals values associated with a range of hardness levels. This table is provided for informational purposes only.

(2) Metals for agricultural and domestic uses are stated as total recoverable unless otherwise specified.

. . . .

31.61 STATEMENT OF BASIS, SPECIFIC STATUTORY AUTHORITY AND PURPOSE; JUNE 10, 2024 RULEMAKING; FINAL ACTION AUGUST 21, 2024; EFFECTIVE DATE DECEMBER 31, 2024

The provisions of C.R.S. 25-8-202(1)(a), (b) and (2); 25-8-203; 25-8-204; and 25-8-402; provide the specific statutory authority for adoption of these regulatory amendments. The commission also adopted, in compliance with 24-4-103(4) C.R.S., the following statement of basis and purpose.

BASIS AND PURPOSE

I. Molybdenum Water Supply Standard

The commission adopted a revised chronic Water Supply standard for total recoverable molybdenum of 530 µg/L. The standard was calculated using the non-cancer equation and some of the default exposure assumptions from Policy 96-2. The molybdenum Water Supply standard uses the Agency for Toxic Substances and Disease Registry's (ATSDR) minimal risk level (MRL; ATSDR's alternative to a reference dose (RfD)) of 0.06 mg/kg/day (ATSDR 2020), a relative source contribution (RSC) of 0.8, a subchronic to chronic uncertainty factor of 3, and the U.S. Environmental Protection Agency (EPA) updated exposure factors, as discussed below. Climax Molybdenum Company (Climax) proposed a Water Supply standard of 1,600 µg/L in this hearing, using an RSC of 0.8 and no subchronic to chronic uncertainty factor, however, the commission found that a standard of 1,600 µg/L would not be adequately protective of human health, given the available data and information.

A. Calculation of Revised Molybdenum Standard

In adopting the revised molybdenum standard, the commission relied on its past policy decisions and precedence documented in Commission Policy 96-2, along with the EPA *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (2000).

1. Reference Dose

As per Departmental policy, the commission relied on toxicity information from ATSDR's 2020 Toxicological Profile for Molybdenum as its source of toxicological data to derive an updated Water Supply standard for molybdenum.

The commission declined to use EPA's 1992 Integrated Risk Information System (IRIS) assessment for molybdenum, because it is based on an outdated, discredited study by Koval'skiy et al. (1961). The commission previously departed from the EPA IRIS assessment for molybdenum when it first adopted the Water Supply standard of 210 µg/l for molybdenum in 2010 based on Fungwe et al. (1990). See Section 31.48(l)(H). The commission at that time acknowledged there were ongoing studies on molybdenum, and urged that the standard be reviewed and revised in the future.

Since the 2010 rulemaking, significant advances have been made in the development of molybdenum toxicological information, including three peer-reviewed and published studies in 2014 and 2019 that were conducted according to the Organization for Economic Cooperation and Development (OECD) guidelines and Good Laboratory Practice. ATSDR considered these studies in its 2020 Toxicological Profile for Molybdenum and in calculating its intermediate oral MRL of 0.06 mg/kg/day. ATSDR calculated this MRL using the no observed adverse effect level (NOAEL) of 17 mg/kg/day (based on kidney effects in rats), and by applying an uncertainty factor of 100 (10 for interspecies, 10 for intraspecies). ATSDR also applied a modifying factor of 3 to address concerns that reproductive/developmental effects may be a more sensitive endpoint than kidney effects in populations with marginal copper intakes. This resulted in a total uncertainty factor of 300.

In its testimony, Climax suggested that more recent peer-reviewed and published studies suggest a lack of support for ATSDR's application of the modifying factor of 3 and call into question the results of Fungwe et al. (1990). However, at this time, the commission did not make any modifications to ATSDR's intermediate oral MRL of 0.06 mg/kg/day. The commission may consider reviewing the molybdenum standard in the future, if EPA or ATSDR publish new assessments or toxicological profiles.

Thus, the commission used the ATSDR MRL of 0.06 mg/kg/day as the RfD-like value in calculating the revised Water Supply standard for molybdenum.

2. Uncertainty Factor to Account for Chronic Exposure

Because sufficient data to calculate a chronic MRL were not available, the ATSDR Toxicological Profile for Molybdenum developed an intermediate (i.e., subchronic) duration MRL of 0.06 mg/kg/day. However, Colorado's Water Supply standards are intended to provide adequate protection for the general population from a substance over a lifetime of exposure.

Climax proposed a chronic Water Supply standard of 1,600 µg/L in this hearing, using no subchronic to chronic uncertainty factor. Climax's position that an additional uncertainty factor to account for chronic exposure was unnecessary was primarily based on two arguments. First, Climax cited a 1997 National Toxicity Program (NTP) inhalation study in which rats were exposed to molybdenum over a two-year (chronic) period. While the rats were exposed to molybdenum in air, not water, Climax argued that the results of the NTP study could be compared to the results of the ingestion study selected by ATSDR as the critical study to derive its intermediate oral MRL and that this comparison provides sufficient evidence to understand chronic toxicity, thereby making an additional uncertainty factor accounting for chronic exposures unnecessary. However, to conclude the chronic inhalation study provides sufficient evidence to fully characterize chronic ingestion exposure would be contrary to ATSDR's conclusions. ATSDR evaluated this chronic inhalation study as part of its Toxicological Profile for Molybdenum and only used the study to assess inhalation toxicity, concluding that there was insufficient evidence to derive a chronic oral MRL. Second, Climax stated that because molybdenum is an essential element, homeostatic regulation prevents overexposure and it is therefore unnecessary to apply an additional uncertainty factor to account for chronic impacts. However, other essential elements can cause toxic impacts on humans, such as iron, selenium, and copper (e.g., see Denver Water Responsive Prehearing Statement Exhibits 2 and 3). In addition, essential elements have both a recommended daily intake to maintain health, as well as a tolerable upper limit intended to prevent adverse health effects, and this range can be narrow (e.g., National Institutes of Health; see division Responsive Prehearing Statement). Therefore, the commission concluded that homeostatic regulation of essential elements is not always a reliable process to prevent toxic effects in humans.

Therefore, because limited evidence is available to understand potential health impacts from chronic molybdenum exposure, and ATSDR found insufficient evidence to derive a chronic MRL, the commission determined that an additional uncertainty factor of 3 to account for extrapolation from a subchronic study to chronic exposure conditions was appropriate. This factor addresses the increased risk associated with lifetime of exposure to elevated molybdenum in drinking water. To calculate the revised chronic Water Supply standard, ATSDR's subchronic MRL was used as the non-carcinogenic reference dose (RfD) in Commission Policy 96-2 equation 1-1 and the additional uncertainty factor of 3 was included in the denominator of equation 1-1.

3. Relative Source Contribution

The RSC is the percentage of the total daily exposure to molybdenum contributed by drinking water. Climax presented information to support departure from the default RSC of 0.2, as provided for in Commission Policy 96-2. This information included a detailed analysis using the Exposure Decision Tree from EPA's *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (2000), demonstrating that intake from the diet and other potential exposure pathways (air, soil, etc.) is a small percentage of the calculated MRL for molybdenum for the general public.

To reach an RSC of 0.8, the critical step in the EPA decision tree requires answering "Yes" to Step 3: "Are adequate data available to describe central tendencies and high-ends for relevant exposure sources/pathways?" Climax provided data and calculations on molybdenum concentrations in food to demonstrate that it is unlikely that a typical adult diet would contain more than 20% (320 µg/day) of the amount of theoretical molybdenum intake based on ATSDR's intermediate MRL and an additional uncertainty factor of 3 to account for chronic exposure (0.06 mg/kg/day * 80 kg = 4.8 mg/day or 4,800 µg/day ÷ 3 = 1,600 µg/day). Therefore, an RSC of 80% (0.8) is acceptable for drinking water. Inhalation, dermal contact, and soil ingestion were determined to not be significant exposure pathways for the general population.

Based on this information, the commission applied an RSC of 0.8 in calculating the revised Water Supply standard for molybdenum.

4. Body Weight and Daily Drinking Water Consumption

In 2015, EPA updated its exposure factors for adults. The body weight factor was increased from 70 kilograms to 80 kilograms, and the drinking water ingestion rate was increased from 2 liters per day to 2.4 liters per day. The commission applied the EPA updated exposure factors, as they rely on more recent exposure data than those used to derive the exposure factors in Commission Policy 96-2. This decision is also consistent with recent commission actions on other human health standards (e.g., 31.58(l)).

Therefore, the commission applied the average body weight of 80 kg and daily drinking water consumption rate of 2.4 liters per day in calculating the revised Water Supply standard for molybdenum.

5. Other Considerations

The commission also heard evidence that there are sensitive subpopulations that may experience adverse effects from molybdenum exposure at lower levels than the general population, including individuals with kidney impairment, formula-fed infants, and others. For example, data from one study (Hosokawa and Yoshida, 1994; e.g., see Denver Water Responsive Prehearing Statement Exhibit 2) indicate that patients on kidney dialysis have substantially more molybdenum in their blood than healthy adults, likely because kidneys control molybdenum removal from the blood. Reduced kidney function is a common occurrence and the result of many factors. Also, infants fed formula made with water containing a molybdenum concentration of 530 µg/L would be ingesting about 60 to 250 times more molybdenum than is typically contained in breast milk (breast milk values from Bougle et al., 1988; e.g., see Denver Water Rebuttal Exhibit 17; infant exposure values from EPA Responsive Prehearing Statement). The lack of scientific data on how individuals with reduced kidney function and infants will respond to a large increase in molybdenum in their water supply and the lack of studies on more subtle outcomes of molybdenum toxicity, such as neurological effects, are compelling reasons to be conservative in setting a new statewide molybdenum standard.

B. Summary

Applying the MRL from ATSDR (2020) of 0.06 mg/kg/day, subchronic to chronic uncertainty factor of 3, RSC of 0.8, and updated exposure factors of 80 kg body weight and 2.4 L/day drinking water consumption rate, the commission calculated a revised Water Supply molybdenum standard of 530 µg/L using the following equation:

$$\frac{\underset{\text{Body Weight (kg)}}{80} \times \underset{\text{MRL (mg/kg/day)}}{0.06} \times \underset{\text{Conversion Factor (µg/mg)}}{1{,}000} \times \underset{\text{RSC}}{0.8}}{\underset{\text{Drinking Water Consumption (liters/day)}}{2.4} \times \underset{\text{Uncertainty Factor: Group C Chemicals}}{1} \times \underset{\text{Uncertainty Factor: Subchronic to Chronic}}{3}} = \underset{\text{Mo TVS}}{530\ \mu g/L}$$

This revised standard was adopted in Section 31.16, Table III.

C. Consideration of Statutory Requirements

In adopting the revised Water Supply molybdenum standard, the commission has considered the factors enumerated in Section 25-8-204(4), C.R.S. The commission has considered evidence regarding: the need for standards to regulate molybdenum, the existing low levels of molybdenum in most of the state, and the fact that molybdenum is naturally occurring in certain areas of Colorado. The commission has also considered the technical evidence regarding treatment techniques to achieve the revised standard of 530 µg/L. Pursuant to Section 25-8-102(5), C.R.S., the commission also found that the revised standard is economically reasonable and consistent with a water quality program in which the water quality benefits of pollution control measures utilized have a reasonable relationship to the economic, environmental, energy, and public health costs and impacts of those measures. Based on the evidence presented, the commission believes that the revised standard will support the beneficial uses of State waters, including drinking water, and that the standard adopted is appropriate and scientifically supported by the record.

D. Other Changes

The commission added a new reference at Section 31.16(3)(P) for the ATSDR Toxicological Profile for Molybdenum. A notation was added to the 530 µg/L standard to refer to this profile.

The commission also adopted the revised 530 µg/L standard on one water quality segment in Regulation No. 33 (Blue River Segment 14). No other segments received this updated value at this time. Before adopting this standard on other segments, it will be necessary to conduct outreach to stakeholders that may be impacted by the change.

Hawbaker, Carol

From: Nellesen, Shelly <shelly.nellesen@dnr.iowa.gov>
Sent: Thursday, July 25, 2024 10:31 AM
To: Hawbaker, Carol
Subject: [External] Molybdenum in Groundwater

Hi Carol,
The Iowa DNR Contaminated Sites Section uses the EPA's Lifetime Health Advisory level of 0.04 mg/L Molybdenum when regulating groundwater assessment/clean-up.
Thanks,

Shelly Nellesen
Environmental Specialist Sr.
Solid Waste and Contaminated Sites Section
Iowa Department of Natural Resources
6200 Park Ave, Des Moines, IA 50321
515-669-5494 (m)
shelly.nellesen@dnr.iowa.gov
www.iowadnr.gov

Hawbaker, Carol

From: Wildfang, Eric (EGLE) <WILDFANGE@michigan.gov>
Sent: Thursday, July 25, 2024 3:10 PM
To: Hawbaker, Carol
Subject: [External] RE: Molybdenum groundwater or drinking water stands question

Hi Carol,

Molybdenum is not regulated as an inorganic contaminant for public drinking water supplies in Michigan.

Molybdenum is regulated as an inorganic hazardous substance for groundwater used as a drinking water source (private well). Michigan determines separate health-based environmental drinking water criteria for residential and nonresidential receptors. These and the relevant toxicity information are presented in the following table.

Criteria		
Residential drinking water criterion	73 (µg/L)	
Nonresidential drinking water criterion	210 (µg/L)	
Toxicity Reference Value		
Oral reference dose	5E-3 (mg/kg-day)	Based on Koval'skiy et al., 1961; see EPA IRIS
Relative Source Contribution	0.4	Dietary contribution to Mo RfD was calculated to be 0.6

Please reach out if you have any questions.

Good luck with your state survey.

Eric

wEric Wildfang | Toxicology Unit Manager
Remediation & Redevelopment Division
Michigan Department of Environment, Great Lakes, and Energy
Lansing, MI 48909-7926
Office: 517-284-5170
wildfange@michigan.gov
Michigan.gov/EGLE

From: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Sent: Thursday, July 25, 2024 11:19 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Cc: Cole.Elizabeth@epa.gov; Berry, David <Berry.David@epa.gov>; Carol.Hawbaker@illinois.gov
Subject: FW: Molybdenum groundwater or drinking water stands question

Good morning,

Please see the email below requesting information on regulation of molybdenum in groundwater, drinking water or both. Please respond to Carol Hawbaker, she is cc'ed on this email.

Thank you,
Kim

Kimberly C. Gettmann, Ph.D.
Supervising Toxicologist, Branch Chief
Human and Ecological Risk Office
Site Mitigation and Restoration Program
916-255-6685
kimberly.gettmann@dtsc.ca.gov
Department of Toxic Substances Control
8800 Cal Center Drive, Sacramento,
California 95826-3200
California Environmental Protection
Agency

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Sent: Thursday, July 25, 2024 7:58 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Subject: Molybdenum groundwater or drinking water stands question

Hi Kim,

Would you please distribute the following question to the Risk Assessors Group?

I'm taking a poll of states that regulate molybdenum in either groundwater, drinking water, or both. If your state regulates it, would you please provide the basis of the standard and the toxicity value used if the value is a health-based standard?

You may respond to my email below. I appreciate all responses!

Thank You,

Carol

Carol Hawbaker
Manager
Office of Toxicity Assessment
Illinois Environmental Protection Agency
Telephone: 217-558-3351
Email: Carol.Hawbaker@illinois.gov

Hawbaker, Carol

From: Marshall, Dana T <dmarshall@pa.gov>
Sent: Thursday, July 25, 2024 12:10 PM
To: Hawbaker, Carol
Subject: Re: [External] FW: Molybdenum groundwater or drinking water stands question
Attachments: image001.jpg; image002.png; image003.png; image004.png

Hello Carol,

For the purposes of demonstrating attainment to the Statewide Health Standard in the PA DEP's Act 2 program, the medium specific concentrations (MSCs) for molybdenum are below. The MSCs are based on the US EPA's lifetime health advisory level for molybdenum. The details of the selection/calculation of the MSCs can be found in 25 PA Code Chapter 250.304 (link below). Thank you.

25 Pa. Code Chapter 250. Administration Of Land Recycling Program (pacodeandbulletin.gov)<https://secure-web.cisco.com/1Sdv38OgxljbUMP8_CyPZG6Fu2tQiM2aR6OSfcv_psyZlV2ZXCnO4YW4XAwzYRkNwA3AeCpnKZKj2mKthzok4jzbessuDiUgNWe1gO6xKB0HgzEHcH5OknO78GHJzGC1W2JeKUC75fdns81WWsIxlUS19d-k_gQPrikKeRaY35bSNelrT52I5U3ICCOks7_gGsm5U36KRwCjjNoL_AS5GsvPL80CL6j0XxlrD2kEJclkRW6zII1NgxedrNaFU303UTsroreCg2WjMZc4LNgmvzq76A9j_vum7HtHrdm0HeqOLJollDHjZC-Qt82D6SZeeiojWnDnWPRnwhwipZzpWoFbJ84vcenNp_V2YKwrl1gS9BFVfTcuKz1QrL0LLI2yWhZOn2hH1wzlRuMpoJHwyG9sk9asCEaRLk714AHYkhm5qGY/https%3A%2F%2Fwww.pacodeandbulletin.gov%2FDisplay%2Fpacode%3Ffile%3D%2Fsecure%2Fpacode%2Fdata%2F025%2Fchapter250%2Fchap250toc.html%26d%3D>

Excerpt from Table 2 - Medium-Specific Concentrations (MSCs) for Inorganic Regulated Substances in Groundwater

Regulated Substance
CASRN
Used Aquifers
Nonuse Aquifers
TDS ≤ 2500
TDS > 2500
R
NR
R
NR
R
NR
MOLYBDENUM
7439-98-7

40
H
40
H
4000
H
4000
H
40000

H
40000
H

concentrations in ug/L
R - Residential
NR - Nonresidential
TDS - Total dissolved solids
H - Lifetime health advisory level

Excerpt from Table 5B - Physical and Toxicological Properties for Inorganic Regulated Substances

Regulated Substance
CAS
RfDo (mg/kg-d)
CSFo (mg/kg-d)-1
RfC (mg/m3)
IUR (ug/m3)-1
Kd
MOLYBDENUM
7439-98-7
0.005
I

20

I - Integrated Risk Information System

Dana T. Marshall | Environmental Chemist 1 Department of Environmental Protection | Bureau of Environmental Cleanup and Brownfields Rachel Carson State Office Building
400 Market Street | Harrisburg, PA 17105-8471
Phone: 717.772.5642 | Fax: 717.772.5598
http://secure-web.cisco.com/1CmNonnf71T5TGmLBWHpi_a6tQNJ2p_D3nud6iSCV6vRtjWvr1o8V-qSe2kJACxeG0VxDBKlfAhJZQ7JC3hTfv_VXbFiN0Lp05bA4c0viK1GnDBJQjUs6Y-zwz3mxzXNsK4MlnHUyHbD26eDHw8yOeUcRWrTElqGN8NB4ImWsu-ydnvm3vVUA8sdz9J4VNBxSkNrZBb7Hq6TRLEe6ZgNKy_rXALGnqm9EcXdCFKueeJXXpTD5ZX6XBQRTy0QCvgwiqlDmc_sQ340Rj3k59WZ3FhC3o3_fC8wt7OxkLDp8zQN2rTvPX5GeVGH24rOgyPZIFOhxqp0Bt859EZLjBJZcAqw9fFHYvu8w4_Qbsf1seMfQnWn_N6o5GPlDkv3OZqhnlM3EfXANOfwu81yJzwjl-E8B3VHCS_zGD7VisyI7RECI/http%3A%2F%2Fwww.dep.pa.gov<http://secure-web.cisco.com/13lHlYATl8uDS_Cr7j5Z1i0Nj1UfIYCEGcapyhGeRNksK0uT9M0ovKAFiXNmrC6OO16ny24syf7P4MxSI5eSbKutrJ-El2PKFT6xodB_p3N11ZrMwDVVAjsA-LaoLpWFHSMb8iqz6C2piceDeZ5CvxBH3LZs9iEahl9pBhxeH17cGtx9q_iofmLHOc3LrOzRIWgRK91xsfLWTqiDDomyDRcHmNOB2VDsoeTShU721GX5Qdp25VGT2Iyf_0wyMgFM1Y38YK7gKbdG20J8kU5pNQDKgbGS283_MeDSMXya98us1kpUeOM6-y9ncMt05N6FuzvSDjtP3LPVREil0g40_xQWTUE5uu9NumVaSjF69MrSQkl-9Alv49CiB-ggENxs_9UpztomIP9F1NG-9Cpf6EyVC4KNQqOBTLhCMXytYRg0/http%3A%2F%2Fwww.dep.pa.gov%2F>

From: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Sent: Thursday, July 25, 2024 11:19 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Cc: Cole.Elizabeth@epa.gov; Berry, David <Berry.David@epa.gov>; Carol.Hawbaker@illinois.gov
Subject: [External] FW: Molybdenum groundwater or drinking water stands question

Good morning,

Please see the email below requesting information on regulation of molybdenum in groundwater, drinking water or both. Please respond to Carol Hawbaker, she is cc'ed on this email.

Thank you,

Kim

Kimberly C. Gettmann, Ph.D.
Supervising Toxicologist, Branch Chief

Human and Ecological Risk Office

Site Mitigation and Restoration Program

916-255-6685

kimberly.gettmann@dtsc.ca.gov<mailto:kimberly.gettmann@dtsc.ca.gov>

Department of Toxic Substances Control

8800 Cal Center Drive, Sacramento, California 95826-3200

California Environmental Protection Agency

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov<mailto:Carol.Hawbaker@Illinois.gov>>
Sent: Thursday, July 25, 2024 7:58 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov<mailto:Kimberly.Gettmann@dtsc.ca.gov>>
Subject: Molybdenum groundwater or drinking water stands question

Hi Kim, Would you please distribute the following question to the Risk Assessors Group? I'm taking a poll of states that regulate molybdenum in either groundwater, drinking water, or both. If your state regulates it, would you please provide

Hi Kim,

Would you please distribute the following question to the Risk Assessors Group?

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You may respond to my email below. I appreciate all responses!

Thank You,

Carol

Carol Hawbaker

Manager

Office of Toxicity Assessment

Illinois Environmental Protection Agency

Telephone: 217-558-3351

Email: Carol.Hawbaker@illinois.gov<mailto:Carol.Hawbaker@illinois.gov>

Hawbaker, Carol

From: Kallus, Andrew (ECY) <akal461@ECY.WA.GOV>
Sent: Monday, July 29, 2024 10:55 AM
To: Hawbaker, Carol
Subject: [External] RE: Molybdenum groundwater or drinking water stands question

Hi Carol

Washington State Ecology has derived a drinking water standard of 80 ug/L for molybdenum (based on an HQ of 1). This standard is based on its IRIS oral RfD of 0.005 mg/kg day.

Thanks, Andy

From: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Sent: Thursday, July 25, 2024 8:19 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Cc: Cole.Elizabeth@epa.gov; Berry, David <Berry.David@epa.gov>; Carol.Hawbaker@illinois.gov
Subject: FW: Molybdenum groundwater or drinking water stands question

External Email

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Kim

Kimberly C. Gettmann, Ph.D.
Supervising Toxicologist, Branch Chief
Human and Ecological Risk Office
Site Mitigation and Restoration Program
916-255-6685
kimberly.gettmann@dtsc.ca.gov
Department of Toxic Substances Control
8800 Cal Center Drive, Sacramento,
California 95826-3200
California Environmental Protection
Agency

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Sent: Thursday, July 25, 2024 7:58 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Subject: Molybdenum groundwater or drinking water stands question

Hi Kim,

Would you please distribute the following question to the Risk Assessors Group?

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Carol Hawbaker
Manager
Office of Toxicity Assessment
Illinois Environmental Protection Agency
Telephone: 217-558-3351
Email: Carol.Hawbaker@illinois.gov

Hawbaker, Carol

From: Brittain, Ross A <ross.a.brittain@wv.gov>
Sent: Thursday, August 1, 2024 9:40 AM
To: Hawbaker, Carol
Subject: Re: [External] Re: FW: Molybdenum groundwater or drinking water stands question

Hi Carol,
When we are calculating risk-based standards for groundwater that do not have a promulgated MCL, we use the RSL tapwater equations to establish the De Minimis Standard. Any chemical that has a promulgated MCL at either the federal or state level will default to the MCL as our De Minimis Standard. So, for Molybdenum we used the RSL tapwater equation.

Hope this helps...
Ross Brittain, PhD
Environmental Toxicologist
WVDEP-OER
Phone: 304-926-0499, ext. 30202
Cell: 304-918-7456

On Thu, Aug 1, 2024 at 10:02 AM Hawbaker, Carol <Carol.Hawbaker@illinois.gov> wrote:

Thank you for your response, Ross!

Do you use the RSL tapwater equation or the drinking water equation which includes an RSC?

Thanks again,

Carol

Carol Hawbaker

Manager

Office of Toxicity Assessment

Illinois Environmental Protection Agency

Telephone. 217-558-3351

Email: Carol.Hawbaker@illinois.gov

From: Brittain, Ross A <ross.a.brittain@wv.gov>
Sent: Thursday, July 25, 2024 3:54 PM
To: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Subject: [External] Re: FW: Molybdenum groundwater or drinking water stands question

Hi Carol,

In WV we have not promulgated formal Water Quality Standards for surface water or groundwater for Molybdenum. However, we have promulgated risk based De Minimis Standards for Molybdenum in groundwater based on the IRIS RfD of 0.005 mg/kg*d, and standard EPA exposure parameters for residents drinking water use. The De Minimis Standard is not enforceable in general sense, but it is enforceable from the standpoint of remediation activities and/or groundwater use restrictions are required when the value is exceeded.

I hope this helps. Please let me know if you have any questions.

Good luck!

Ross Brittain, PhD

Environmental Toxicologist

WVDEP-OER

Phone: 304-926-0499, ext. 30202

Cell. 304-918-7456

On Thu, Jul 25, 2024 at 11:19 AM Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov> wrote:

Good morning,

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Thank you,

Kim

Kimberly C. Gettmann, Ph.D.
Supervising Toxicologist, Branch Chief

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916-255-6685

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Department of Toxic Substances Control

8800 Cal Center Drive, Sacramento,
California 95826-3200

California Environmental Protection
Agency

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Sent: Thursday, July 25, 2024 7:58 AM
To: Gettmann, Kimberly@DTSC <Kimberly.Gettmann@dtsc.ca.gov>
Subject: Molybdenum groundwater or drinking water stands question

Hi Kim,

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You may respond to my email below. I appreciate all responses!

Thank You,

Carol

Carol Hawbaker

Manager

Office of Toxicity Assessment

Illinois Environmental Protection Agency

Telephone: 217-558-3351

Email: Carol.Hawbaker@illinois.gov

Hawbaker, Carol

From: Yang, Sarah P - DHS <SarahP.Yang@dhs.wisconsin.gov>
Sent: Thursday, August 1, 2024 9:27 AM
To: Hawbaker, Carol
Subject: [External] RE: Molybdenum
Attachments: Molybdenum_DHS Support Document_Cycle 8.pdf; 2013_DHS_Memo - Review of Molybdenum Toxicity Information.pdf

Hi Carol,
Are you asking for groundwater standards or drinking water? We do not have a drinking water standard for molybdenum, but we do have public health groundwater standards.

Our general protocol for establishing these standards is found here:
https://www.dhs.wisconsin.gov/publications/p02816.pdf

Long story short – we have an official groundwater standard of 40 ug/L for molybdenum set in 2006. In 2013, we established an interim health advisory of 90 ug/L. I have attached the scientific support documents for these values.

The groundwater standard is used for regulatory purposes – setting permitting limits for discharges to groundwater, monitoring requirements at contamination sites, etc – while the health advisory is used to provide public health advise to private well users.

I hope this helps. I am available this afternoon if you want to chat!

Sarah

Sarah Yang, Ph.D.
Toxicologist
Bureau of Environmental and Occupational Health
Wisconsin Division of Public Health
Phone: 608-266-9337
SarahP.Yang@dhs.wisconsin.gov

From: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Sent: Thursday, August 1, 2024 8:42 AM
To: Yang, Sarah P - DHS <SarahP.Yang@dhs.wisconsin.gov>
Subject: RE: Molybdenum

Hi Sarah,

My comments are due tomorrow.
My questions are pretty simple (I hope)
What equation do you use to calculate a health-based standard for drinking water?
What RfD do you use, and what is the source?

What relative source contribution do you use (if applicable), and if it's > 0.2, what it the basis of the RSC?

Thanks for your assistance, I really appreciate it!

Carol

Carol Hawbaker
Manager
Office of Toxicity Assessment
Illinois Environmental Protection Agency
Telephone: 217-558-3351
Email: Carol.Hawbaker@illinois.gov

From: Yang, Sarah P - DHS <SarahP.Yang@dhs.wisconsin.gov>
Sent: Thursday, August 1, 2024 8:32 AM
To: Hawbaker, Carol <Carol.Hawbaker@Illinois.gov>
Subject: [External] Molybdenum

Hi Carol,
Wisconsin has a groundwater standard for molybdenum.

It would probably be best to set up a time to discuss as our history is a bit complex. What is your schedule like next week?

Sarah

Sarah Yang, Ph.D.
Toxicologist
Bureau of Environmental and Occupational Health
Wisconsin Division of Public Health
Phone: 608-266-9337
SarahP.Yang@dhs.wisconsin.gov

Scott Walker
Governor

Kitty Rhoades
Secretary

State of Wisconsin

Department of Health Services

DIVISION OF PUBLIC HEALTH

1 WEST WILSON STREET
P O BOX 2659
MADISON WI 53701-2659

608-266-1251
FAX: 608-267-2832
TTY: 888-701-1253
dhs.wisconsin.gov

August 2, 2013

Jill D. Jonas, Director
Bureau of Drinking Water and Groundwater
Department of Natural Resources
101 S Webster Street, Box 7921
Madison, WI 53703-7921

Subject: Response to Request for Review of Molybdenum Toxicity Information

Dear Ms. Jonas:

This letter is in response to the Wisconsin Department of Natural Resources' (DNR) March 1, 2013 request that the Wisconsin Department of Health Services (DHS) review molybdenum toxicity information and provide a recommendation whether any action on current molybdenum NR140 Public Health Groundwater Quality Standards should be considered at this time. We have reviewed the correspondence attached to your letter as well as published information on molybdenum toxicity in light of the requirements for establishing Groundwater Quality Enforcement Standards under Wis. Stat. Chapter 160. Based on our review of the toxicological studies and since the "Federal Number" is under active review, we recommend that an interim health advisory level of 90 micrograms per liter (µg/L) of molybdenum be used when advising about the safety of private drinking water supplies. The interim health advisory level for molybdenum was developed using methods consistent with Wisconsin law.

The current Wisconsin Groundwater Quality Enforcement Standard for molybdenum of 40 µg/L was adopted in 2006. Pursuant to Wis. Stat. sec. 160.07, the molybdenum Groundwater Quality Enforcement Standard is based on a Federal Number: the Lifetime Health Advisory Level (LHA) for molybdenum that was developed by the United States Environmental Protection Agency (EPA). This LHA is derived from a study that describes an increased incidence of gout-like symptoms and increased blood uric acid levels in villagers in Soviet Armenia who had a high dietary intake of molybdenum (Koval'skiy et al. 1961).

In response to your March 1, 2013 letter we reviewed the NR140 Public Health Groundwater Quality Standard Support Document for molybdenum as well as the currently published literature. We found published reviews of molybdenum toxicity that noted several concerns regarding the methods used in the Koval'skiy study. The small number of controls (n = 5) compared to the number of exposed subjects (n = 52) in the clinical data (blood and urine molybdenum, copper, and uric acid) does not permit high statistical confidence in the evidence of a cause-effect relationship between molybdenum exposure and increased blood uric acid. In

addition, it is unclear how exposed and control subjects were chosen, and detailed data on the subjects were not provided. The information on the analytical methods used in the study to estimate dietary molybdenum and copper intake and measure blood molybdenum and copper levels is very limited. As a result, it is difficult to confirm the scientific validity of these protocols. Reviews, including ones by the U.S. National Research Council, the Food and Nutrition Board of the Institute of Medicine, and the European Commission's Scientific Committee on Food, concluded that these concerns were significant weaknesses in this study. Ultimately, the Food and Nutrition Board of the Institute of Medicine and the European Commission's Scientific Committee on Food decided not to use the Koval'skiy study as a critical study for establishing health-based guidelines.

Although the association between molybdenum exposure and human gout-like symptoms or increased serum uric acid levels is biologically plausible, after our literature review, we found that the concerns with the analytical protocols used in the Koval'skiy study significantly reduced our confidence in the reliability of using it as the critical study for establishing health guidelines.

In light of these concerns, we evaluated the published scientific literature to determine whether there are studies that could be used to assess molybdenum toxicity with greater confidence than the critical study used by the EPA when deriving the LHA. Although there are no human exposure studies that could be used other than the Koval'skiy study, there are animal exposure studies. Of those reviewed, we determined that the study from Fungwe et al. (1990), which describes reproductive and developmental effects of molybdenum in Sprague-Dawley rats, is best suited for use as the critical study to calculate a molybdenum advisory level with the greatest level of confidence. Using the data from this study and methods consistent with Wis. Stat. sec. 160.13, we calculated a molybdenum advisory level of 90 µg/L. It is our opinion that drinking water containing molybdenum at this level for an entire lifetime would not result in increased risk of adverse health effects. DHS has prepared a support document (attached) describing our analysis and calculations of this advisory level.

Given the lack of confidence in the reliability of the Koval'skiy study, if DHS were to propose revision of the current Enforcement Standard, our recommendation would probably result in a new Enforcement Standard that is different than the current Federal Number. However, it is our understanding that DHS and DNR legal counsel have determined that, under Wis. Stat. sec. 160.07 (4) (e), in order for DHS to recommend adopting a new Enforcement Standard that is different than the Federal Number, the new standard must be justified on the basis of "significant technical information which is scientifically valid and which was not considered when the federal number was established." In our review of published toxicity information, we found EPA documents published in 1975 (Friberg et al., EPA-600/1-75-004) and 1979 (Chappell et al., EPA-600/1-79-006) that clearly state the concerns with the Koval'skiy study described above. As such, it can be reasonably concluded that EPA was aware of the critiques of this study, but still chose it as the critical study driving the LHA. Given this, we cannot conclude that there is "significant technical information" that was not considered by EPA when the LHA was established. Therefore, DHS cannot at this time recommend proceeding to propose an Enforcement Standard different than the current federal LHA.

We understand that EPA is currently reviewing the LHA for molybdenum (J Donohue, US EPA, personal communication, March 2013). We are unable to predict when EPA will finish its review and what level EPA may establish as a result of that review. The federal process for this review has been underway for some time and may take years to complete. The result of that review could be a value other than the 90 µg/L that DHS would recommend for use to advise well owners. In addition, the NR140 rule revision process would take approximately two years to complete.

For the many homeowners making decisions about their drinking water today, it is neither practical nor necessary to wait for the issuance of a new Enforcement Standard. Although there is less confusion when the Enforcement Standard is the same as the level used for advising individual homeowners, we are not required to use the Enforcement Standard when issuing individual drinking water advisories. Therefore, although legal counsel for the agencies have concluded that a revision of the current Public Health Groundwater Quality Enforcement Standard for molybdenum is not appropriate, DHS recommends that, until EPA concludes its review, the agencies begin using a 90 µg/L value for molybdenum in individual drinking water advisories.

Please do not hesitate to contact me if you have any questions regarding this review.

Sincerely,

Charles J. Warzecha, Director
Bureau of Environmental and Occupational Health

References:

Chappell WR, Meglen RR, Moure-Eraso R, Solomons CC, Tsongas TA, Walravens PA, Winston PW. 1979. Human health effects of molybdenum in drinking water. EPA-600/1-79-006, U.S. Environmental Protection Agency, Cincinnati, OH.

Friberg L, Boston P, Nordberg G, Piscator M and Robert KH. 1975. Molybdenum – A Toxicological Appraisal. EPA-600/1-75-004, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Food and Nutrition Board. 2001. Molybdenum. *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc.* Institute of Medicine, National Academy of Sciences, Washington, DC

Koval'skiy VV, Yarovaya GA and Shmavonyan DM. 1961. Changes of purine metabolism in man and animals under conditions of molybdenum biogeochemical provinces. Zh. Obshch. Biol. 22: 179-191. (Russian trans.)

National Research Council. 1977. *Drinking Water and Health.* Safe Drinking Water Committee, Advisory Center on Toxicology, National Academy of Sciences, Washington, DC.

Scientific Committee on Food. 2000. Opinion of the scientific committee on food on the tolerable upper intake level of molybdenum. SCF/CS/NUT/UPPLEV/22 Final, European Commission Health and Consumer Protection Directorate-General, Brussels, Belgium.

MOLYBDENUM

Toxicity Information Review and Interim Health Advisory Support Document
Issued: August 2, 2013

Introduction

The Wisconsin Department of Health Services (DHS) received a request from the Wisconsin Department of Natural Resources (DNR) to review molybdenum toxicity information and provide recommendations as to whether any action on current molybdenum groundwater quality standards should be considered at this time (Correspondence from Jill D. Jonas to Charles J. Warzecha, March 1, 2013). The following document is a brief analysis conducted to answer this request.

As a result of this analysis, DHS has concluded that it lacks legal authority to recommend revising the NR140 Public Health Groundwater Quality Enforcement Standard for molybdenum at this time. However, based on the DHS review of the toxicity information on molybdenum and given that the current "Federal Number" is under active review, an interim health advisory level for molybdenum of 90 micrograms per liter (µg/L) is warranted for use with individual drinking water advisories.

DHS Analysis

Toxicity Information Review – Molybdenum Publications since 2011

The NR140 Public Health Groundwater Quality Standard Support Document for molybdenum was produced in 2006 (Appendix 1), but the most recent DHS review of the literature occurred in 2011. Therefore, the current toxicity information review primarily focused on scientific studies published since this review. A search on the National Institutes of Health's PubMed resource for relevant molybdenum articles published since 2011 was carried out.

A large number of publications (1251) were returned by the search engine using the search term "molybdenum." The results were screened against the following criteria: (1) the study investigated molybdenum toxicity or molybdenum effects on a disease state and (2) information on molybdenum exposure or dose was included as part of the study. Ideally, relevant studies used *in vivo* models and provided data for multiple doses. Four papers that fit these criteria were located. As is detailed below, none of these four studies were strong enough to be used as a critical study forming the basis for health guidelines

Publication 1: Michelis et al. (2011)

Summary: This study investigated effects of molybdate on lymphocyte activation using human peripheral blood lymphocytes (hPBLs) *ex vivo*. Treatment of hPBLs with molybdenum resulted in concentration-dependent decreases in lymphocyte activation, which reached statistical significance at the highest concentration tested (10 mM sodium molybdate). In addition, molybdenum (as 0.1 mM sodium molybdate) appeared to enhance the immunosuppressive effects of high concentrations of cyclosporin A (30 mM), a commonly used immunosuppressant.

DHS Analysis: It is difficult, if not impossible, to accurately estimate *in vivo* doses from *in vitro* (or *ex vivo*) data. As a result, the molybdenum concentrations used in this study cannot be converted into useful estimated dose information, and this study cannot be used as the basis for health guidelines.

Publication 2: Bi et al. (2012)

Summary: This study investigated effects of molybdenum exposure on preimplantation development of mouse embryos cultured *in vitro*. At very high concentrations (≥ 40 µg/mL) significant decreases in cleavage, blastocyst birth rate, average cell number and increases in the proportion of degenerative blastocysts were observed. At even higher molybdenum concentrations, effects were more drastic, ranging from inhibition of blastocyst development (at 120 µg/mL) to developmental arrest and massive degeneration of embryos (at 160 µg/mL). The results are supportive of the hypothesis that molybdenum may be able to cause effects on embryonic development.

DHS Analysis: The difficulty in estimating *in vivo* doses from *in vitro* data keeps this study from being considered for use as the basis for health guidelines.

Publication 3: Sherkhov et al. (2012)

Summary: This study is an investigation of the effects of molybdenum in rats under hypoxic conditions (Sherkhov et al., 2012). The results from this study suggest that excessive doses of molybdenum may be associated with cardiotoxicity and impaired cardiac function under hypoxic conditions in rats. The no observable adverse effect level (NOAEL) and lowest observable adverse effect level (LOAEL) from this study (0.425 mg/kg and 1.25 mg/kg, respectively) are similar to NOAELs and LOAELs from other animal studies on molybdenum. No supporting studies investigating cardiac effects of molybdenum exposure were located.

DHS Analysis: DHS notes an absence of other studies supporting a cardiotoxic mode of action for molybdenum and that the NOAEL and LOAEL values from this are similar to animal studies on reproductive and developmental effects induced by molybdenum. Given that there is more supporting evidence for molybdenum to potentially induce reproductive and developmental effects, DHS concludes that other candidate critical studies are preferred to this study.

Publication 4: Zhai et al. (2013)

Summary: This study investigated the effects of molybdenum on sperm quality and testis oxidative stress in mice. Mice were given unlimited access to drinking water containing varying concentrations of molybdenum. At low doses, molybdenum appeared to improve sperm quality as measured by epididymis index, sperm motility, sperm count, and morphology. At higher doses, sperm quality parameters were negatively affected. In addition, at these high doses decreased superoxide dismutase and glutathione peroxidase activities accompanied by increased malondialdehyde levels in the testes were observed suggesting that molybdenum may be inducing testicular oxidative stress. The authors hypothesized that oxidative stress might play a

role in the negative reproductive effects in the animals. Information was provided on the concentrations of molybdenum in the drinking water, but there was no information presented on the oral doses received. For the present DHS analysis, doses were calculated using estimated drinking water intake (U.S. Environmental Protection Agency, 1988) and body weight for the mice (Harlan Laboratories, Madison, WI). The estimated doses in this study which would represent a NOAEL and LOAEL are approximately 12.5 and 25 mg/kg/day, respectively.

DHS Analysis: Since the NOAEL and LOAEL in this study are higher than NOAELs and LOAELs from other published animal studies on reproductive/developmental effects of molybdenum, this study will not be used by DHS as a critical study forming the basis for health guidelines.

Review of the Current Critical Study

The current Wisconsin Groundwater Quality Enforcement Standard for molybdenum is based on a Federal Number: the United States Environmental Protection Agency's (EPA) Lifetime Health Advisory (LHA) (see Appendix 1 NR140 Public Health Groundwater Quality Standard Support Document for Molybdenum). The molybdenum LHA is derived from a cross-sectional investigation of a human population in Soviet Armenia (Koval'skiy et al., 1961) that was exposed to high levels of molybdenum in their diet (U.S. Environmental Protection Agency, 1993; 2012). This study provides evidence for an association between molybdenum exposure and increased incidence of gout-like symptoms and increased serum uric acid levels. The connection between molybdenum and effects on serum uric acid or incidence of gout-like symptoms is biologically plausible. Molybdenum is incorporated into an enzymatic cofactor that is necessary for the function of a number of oxidases. One of these enzymes, xanthine oxidase, is involved in breaking down purines to uric acid. High levels of uric acid in blood can result in uric acid crystallization and gout.

Reviews of molybdenum toxicity note several concerns regarding the methods used in the Koval'skiy study. The small number of controls (n = 5) compared to the number of exposed subjects (n = 52) in the clinical endpoint assessment (blood and urine analysis for molybdenum, copper, and uric acid) does not permit high statistical confidence in the evidence of a cause-effect relationship between molybdenum exposure and increased blood uric acid. In addition, it is unclear how exposed and control subjects were chosen, and detailed data on the subjects were not provided. The information on the analytical methods used in the study to estimate dietary molybdenum and copper intake and measure blood molybdenum and copper levels is very limited. As a result, it is difficult to confirm the scientific validity of these protocols. A few reviews have noted that although decreased blood copper level was observed in sick subjects compared to controls, blood copper levels in the controls seemed higher than expected (Vyskocil and Viau, 1999; Scientific Committee on Food, 2000; Food and Nutrition Board, 2001). Without details on analytical methods it is impossible to determine whether assays were conducted in a manner that minimized external contamination. These concerns have led multiple scientific reviews on molybdenum to question the value of the data from this study. The Food and Nutrition Board of the Institute of Medicine (2001) and the European Commission's Scientific Committee on Food (2000) decided that these concerns were significant enough that they did not

consider the Koval'skiy study as suitable for use as a critical study for establishing health-based guidelines for molybdenum.

Although the study describes a toxicological mechanism for molybdenum that may be biologically relevant, due to low confidence in the methodology and reported data this study cannot yield the necessary information required for development of health-based guidelines. *Therefore, DHS concludes that the Koval'skiy study is not reliable enough to be used as the critical study for establishing health guidelines for molybdenum.*

Interpretation of Wis. Stat. Chapter 160 and Application to Molybdenum Review

Wis. Stat. Chapter 160 prescribes how DHS is to develop a recommendation for Groundwater Quality Enforcement Standards. If a Federal Number exists, then DHS is required to recommend that the Federal Number shall be the Enforcement Standard unless there is significant technical information that is scientifically valid, but was not considered when the Federal Number was established, in which case DHS may recommend an Enforcement Standard different than the Federal Number (Wis. Stat. sec. 160.07 (4) (a) & (e)).

Since the current Enforcement Standard for molybdenum is based on a Federal Number (the current EPA LHA), in order for DHS to recommend a different enforcement standard, it must comply with the criteria outlined in Wis. Stat. sec. 160.07 (4) (e).

Discussions between legal counsel at DNR and DHS identified the following questions that need to be addressed for DHS to recommend an Enforcement Standard different than the Federal Number (E Wendorff, Wisconsin Department of Health Services, personal communication, May 2013):

1) Is there significant technical information regarding the toxicity of molybdenum which is scientifically valid and was not considered when EPA established the Federal Number?
2) If the answer to question 1 is "yes," can DHS conclude with reasonable scientific certainty that a different standard is justified?

If the answers to questions 1 and 2 are "yes," DHS has discretion to recommend a different Enforcement Standard for molybdenum.

The DHS review of published toxicity information found EPA documents published in 1975 (Friberg et al. EPA-600/1-75-004) and 1979 (Chappell et al. EPA-600/1-79-006) that clearly state the concerns with the Koval'skiy study described in the previous section. It can be reasonably concluded that EPA was aware of the critiques of this study but still chose it as the critical study forming the basis for the LHA. Thus, DHS cannot conclude that there is "significant technical information" that was not considered by EPA when the LHA was established. As a result, DHS cannot at this time proceed to propose an Enforcement Standard different than the current Federal Number.

Calculating an Interim Health Advisory Level for Molybdenum

Summarizing the conclusions of the previous sections of this analysis, DHS has determined:

1) The current molybdenum Groundwater Public Health Quality Enforcement Standard is based on a Federal Number: the EPA LHA.
2) There are significant concerns regarding the reliability of the study that EPA used to derive the current LHA that suggest it may not be appropriate to use the study as the basis for health guidelines.
3) DHS cannot conclude that there is "significant technical information" that was not considered by EPA when the LHA was established. Therefore, legal counsel has determined that a revision of the current Public Health Quality Groundwater Standard is not appropriate at this time.

EPA is currently reviewing the LHA for molybdenum (J Donohue, US EPA, personal communication, March 2013). DHS is unable to predict when EPA will finish its review and what level EPA may establish as a result of that review. The federal process for this review has been underway for some time and may take years to complete. In addition, the State's NR140 rule revision process for establishing a new Enforcement Standard would take approximately two years to complete.

For future molybdenum individual drinking water advisories, it is neither practical nor necessary to wait for the issuance of a new Enforcement Standard. Although there is less confusion when the Enforcement Standard is the same as the level used for advising individual homeowners, the agencies are not required to use the Enforcement Standard when issuing individual drinking water advisories. Therefore, as part of its analysis, DHS reviewed the toxicity information on molybdenum to determine whether an interim health advisory level could be calculated to be used until EPA's review is complete.

Critical Study Selection

Given the DHS conclusion that the Koval'skiy study is not reliable enough for use as the critical study driving health-based guidelines, other possible molybdenum toxicity studies were considered. After reviewing the toxicity information on molybdenum, the study by Fungwe et al. (1990), which describes reproductive and developmental effects of molybdenum in Sprague-Dawley rats, was identified by DHS as the best candidate for a molybdenum critical study. Prolonged estrous cycle, reduced litter weight gain, and increased fetal resorption were observed in rats given $\geq$ 10 mg/L molybdenum in drinking water (approximately 1.6 mg/kg/day). The NOAEL in this study was 0.9 mg/kg/day. The methods used in this publication are clearly described. Furthermore, the size of each treatment group (12 - 14 pregnant dams in each group) was sufficient to ensure that the results were statistically sound (C Tomasallo, Wisconsin Department of Health Services, personal communication, March 2013; N Drinkwater, University of Wisconsin - Madison, personal communication, March 2013). A weakness of this study is that molybdenum intake is presented as mg molybdenum per week; doses have been estimated using

the assumption that average rat body weight was 0.1 kg (U.S. Environmental Protection Agency, 1988).

There are a number of other studies that have investigated the possibility of reproductive and developmental effects from molybdenum exposure. Schroeder and Mitchener (1971) observed increased fetal mortality, dead litters, maternal deaths, and infertility in mice receiving a dose of 1.5 mg/kg/day. Jeter and Davis (1954) found increased male infertility in rats receiving 8 mg/kg/day molybdenum. Titenko-Holland et al. (1998) carried out a dominant lethal assay in mice and found that dosing with molybdenum resulted in postimplantation loss (represented by early resorptions) and decreased pregnancy rate. The results of this study suggested that molybdenum may be associated with a postmeiotic effect on male germ cells in mice. Pandey and Singh (2002) orally administered molybdenum to adult male rats. They observed decreases in male reproductive organ weight, sperm abnormalities, alteration of various testicular enzyme activities, and molybdenum accumulation in testes, epididymides, and seminal vesicles. As described above, Bi et al. (2012) found that exposure to molybdenum at high enough concentrations interfered with mouse preimplantation embryo development *in vitro*. Zhai et al. (2013) describe negative effects on sperm quality and increased testicular oxidative stress in male mice given molybdenum in drinking water. Collectively, these other studies support the Fungwe study (1990) in suggesting that the reproductive system and the developing embryo may represent targets for adverse effects of orally ingested molybdenum.

Calculations

The methodology that DHS is required to use for establishing a new recommendation of a Public Health Groundwater Quality Enforcement Standard is clearly outlined in Wis. Stat. sec. 160.13. The following calculations to determine a recommended interim health advisory level for molybdenum for use with individual drinking water advisory follow these guidelines:

$$\text{Acceptable daily intake} = \frac{\text{NOAEL}}{\text{Uncertainty Factor}}$$

Uncertainty factor = 100 (10 for interspecies variability; 10 for human interindividual variability)

The Food and Nutrition Board recommended an uncertainty factor of 3 for molybdenum for human interindividual variability on account of (1) the rarity of copper deficiency, (2) evidence that the antagonistic relationship between molybdenum and copper may not exist in humans, and (3) the argument that molybdenum pharmacokinetics are similar in humans (Food and Nutrition Board, 2001). The pharmacokinetic studies cited in the Food and Nutrition Board report primarily examined kinetics in young adult males (early-mid 20's to early 40's) and in one study, young adult females (mid 20's to early 40's) as well. Furthermore, other studies demonstrated that absorption from oral intake may range from 28 – 77 % in humans and excretion may range from 17 – 80% (reviewed in Vyskocil and Viau, 1999). Based on the lack of pharmacokinetic information in humans of other ages and the high variability in reported absorption and excretion in human studies, *DHS concludes that there is not sufficient evidence to justify using a reduced uncertainty factor of 3 for human interindividual variability.*

With this uncertainty factor in mind, and a NOAEL of 0.9 mg/kg/day (Fungwe et al, 1990), an acceptable daily intake can be calculated as follows:

$$\text{Acceptable daily intake} = \frac{0.9 \text{ mg/kg/day}}{100} = 0.009 \text{ mg/kg/day}$$

$$\text{Advisory Level} = \frac{\text{Acceptable Daily Intake} \times \text{Body Weight}}{\text{Intake Rate}} \times \text{Relative Source Contribution}$$

Based on method in Wis. Stat. s. 160.13 (2) (c), body weight = 10 kg (young child), intake rate = 1 L/day, and relative source contribution = 1, resulting in:

$$\text{Advisory Level} = \frac{0.009 \text{ mg/kg/day} \times 10 \text{ kg}}{1 \text{ L/day}} \times 1 = 0.09 \text{ mg/L or } 90 \text{ µg/L}$$

From these calculations, DHS has derived a recommended interim health advisory level for molybdenum of 90 µg/L for use with individual drinking water advisories.

Molybdenum is an essential element for humans; therefore, minimum nutritional intake requirements should be considered when evaluating the practicality of the recommended interim health advisory. The Food and Nutrition Board has provided an Estimated Average Requirement (EAR) and Recommended Daily Average (RDA) for molybdenum in adults and children (Food and Nutrition Board, 2001). The EAR and RDA are based on total molybdenum intake (i.e. from food and water combined). Both the Food and Nutrition Board and the European Commission's Scientific Committee on Food have previously calculated their own recommendations of Tolerable Upper Limits (TUL) for molybdenum (Food and Nutrition Board, 2001; Scientific Committee on Food, 2000) based on results in the Fungwe et al. study (1990). DHS compared the molybdenum interim health advisory level to the EAR, RDA, and TUL for adults (Table 1) and children (Table 2) to determine whether the recommended interim health advisory level of 90 µg/L represents a reasonable value. Adult water intake was assumed to be 2 L/day and child water intake was assumed to be 1 L/day to derive daily molybdenum intake values at the interim health advisory level.

Table 1. Comparison of estimated adult daily molybdenum intake from drinking water containing 90 µg/L molybdenum against current nutritional and toxicity values.

Daily Intake (µg/day)	Comparison Value Basis
34	Estimated Average Requirement (EAR)
45	Recommended Daily Average (RDA)
50	Recommended Daily Average (RDA) for Pregnant Women
80	Estimated intake from water at current Enforcement Standard
180	Estimated intake from water at interim health advisory level
600	Tolerable Upper Limit (TUL) (Scientific Committee on Food)
1200	TUL (Food and Nutrition Board)

Table 2. Comparison of estimated child daily molybdenum intake from drinking water containing 90 µg/L molybdenum against current nutritional and toxicity values.

Daily Intake (µg/day)	Comparison Value Basis
13 – 33	Estimated Average Requirements (EARs)
17 – 43	Recommended Daily Averages (RDAs)
40	Estimated intake from water at current Enforcement Standard
90	Estimated intake from water at interim health advisory level
100	TUL for ages 1 – 3 (Scientific Committee on Food)
200	TUL for ages 4 – 6 (Scientific Committee on Food)
250	TUL for ages 7 – 10 (Scientific Committee on Food)
300	TUL for ages 1 – 3 (Food and Nutrition Board)
400	TUL for ages 11 – 14 (Scientific Committee on Food)
500	TUL for ages 15 – 17 (Scientific Committee on Food)
600	TUL for ages 4 – 8 (Food and Nutrition Board)
1100	TUL for ages 9 – 13 (Food and Nutrition Board)
1700	TUL for ages 14 – 18 (Food and Nutrition Board)

The methods outlined in Wis. Stat. Chapter 160 utilize a child exposure scenario for calculating the advisory level. The interim health advisory level of 90 µg/L would likely result in molybdenum intakes less than the Food and Nutrition Board's tolerable upper limit for children 1 to 3 years old of 300 µg/day but would be similar to the upper limit (100 µg/d) set by the European Commission's Scientific Committee on Food for children of this age. At the same time, the estimated intake of a child consuming water containing 90 µg/L molybdenum is greater than the EAR or RDA. Overall, these comparisons suggest that a molybdenum interim health advisory level of 90 µg/L is not so stringent as to be below current EARS and RDAs for molybdenum, but still would be at an adequate level to be protective of human health.

Recommended Interim Health Advisory Level: 90 µg/L

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Appendix 1
NR140 Public Health Groundwater Quality Enforcement Standard Support Document for Molybdenum

MOLYBDENUM

Introduction

Molybdenum is a metallic element used in the manufacture of alloys, in aeronautical engineering, in pigments and in metal-ceramic composites. In nature, molybdenum is found most commonly as molybdenite (MoS_2).

Chemical Profile

Chemical Name:	Molybdenum
CAS Number:	7439-98-7
Atomic Weight:	95.9
Atomic Symbol:	Mo
Physical State:	Silver-white metal or grey-black powder
Water Solubility:	Virtually insoluble
Specific Gravity:	10.2 g/cm^3

Occurrence

According to results from the Wisconsin Groundwater Retrieval Network, 13 of 29 potable wells and 22 of 99 non-potable wells tested had detectable levels of molybdenum.[1]

Results of the National Uranium Resource Evaluation (NURE) survey in Wisconsin found 613 of 2753 groundwater samples with a molybdenum concentration above the detection limit of 4 µg/L. The mean concentration was 7.5 µg/L and the highest reported concentration was 3500 µg/L.[2]

Human Exposure

Occupational exposure to molybdenum dusts and fumes has been reported in industries involved in production and fabrication of molybdenum products. Molybdenum is an essential element in the mammalian diet as a constituent of the enzymes xanthine oxidase, aldehyde oxidase and sulfite oxidase. The National Research Council (NRC) has established a recommended daily allowance of 45 µg for molybdenum.[3]

Toxicity

Acute

In rats and guinea pigs, oral doses of 1.2 to 6 g/kg of three molybdenum-containing compounds (molybdenum trioxide, calcium molybdate and ammonium molybdate) were fatal in all animals. Parenteral injection of guinea pigs of 800 mg/kg ammonium molybdate was fatal for all animals within hours. Similar treatment with a dose of 80 mg/kg was nonfatal up to four months following injection.[4]

Molybdenum-containing dietary supplements were implicated in a reported case in which a patient developed psychotic and hallucinatory symptoms.[5] The patient exhibited signs of anxiety and agitation after seven days on the supplement and delusions and hallucinations after fourteen days. The patient had taken seven to eight 100 mg tablets per day (700-800 mg per day).

Subchronic

Four adult males were given diets containing sorghum with varying molybdenum content for ten days to examine the effect of dietary molybdenum on uric acid and copper excretion. Urinary excretion of copper increased with increasing dietary molybdenum, with a daily intake of 22 μg/kg/day resulting in excretion of copper at twice the normal level. No effect of dietary molybdenum on uric acid excretion was observed.[6]

Chronic

In a comparative oral feeding study, white rats were fed 10-500 mg of molybdenum sulfide, molybdenum trioxide, calcium molybdate or ammonium molybdate for periods up to 232 days. Animals fed molybdenum sulfide displayed no adverse effects at any dose, while animals fed the other three compounds exhibited rough coat, loss of appetite, and unusually listless and quiet behavior.[4]

The relationship between dietary intake of molybdenum, serum uric acid levels and gout-like symptoms was examined in an Armenian village with high soil concentrations of molybdenum.[7] Villagers from Ankava were estimated to have daily molybdenum intakes ranging from 10 to 15 mg/day, corresponding to doses of 0.14 to 0.21 mg/kg/day. Villagers were examined for gout-like symptoms and levels of copper, uric acid, molybdenum and xanthine oxidase in blood, with similar data collected for a population with normal molybdenum intake of 1 to 2 mg/day. Higher rates of gout-like symptoms were reported in villagers (31%), as well as higher rates of elevated uric acid in blood. Blood uric acid level was found to be directly correlated with increasing residency time in the region. EPA used these results to establish a human LOAEL of 0.14 mg/kg/day based on observed increases in blood uric acid levels.[8]

Carcinogenicity/Mutagenicity

No data on the carcinogenicity or mutagenicity of molybdenum could be located.

Reproductive and Developmental Toxicity

The effects of supplemental dietary molybdenum on estrus activity, fetal development and fertility were studied in female rats.[9] Groups of weanling rats were given water with 0, 5, 10, 50 and 100 mg/L sodium molybdate (0, 0.9, 1.6, 8.3 and 16.7 mg Mo/kg/day) until day 21 of gestation. Groups at concentrations of 10 mg/L and above exhibited significantly prolonged estrus cycles, decreased gestational weight gain and evidence of increased rates of fetal resorption and spinal cord myelination. No effects on fertility were observed at any dose level.

Interactive Effects

Results from a number of studies suggest that the absorption and excretion of molybdenum may be affected by copper intake. The toxic effects of molybdenum may be lessened with concurrent copper exposure, and it has been suggested that the formation of a copper-tetrathiomolybdate complex in the gastrointestinal tract may play a role in the toxic effects associated with excessive molybdenum exposure.[10] A interaction between the metabolism of molybdenum and a number of sulfur compounds has been theorized, but has been demonstrated with less consistency than the interaction between molybdenum and copper.

Environmental Fate

Atmospheric

Once released into the environment, molybdenum may settle by wet or dry deposition. Little is known about the chemical transformations that molybdenum compounds may undergo in the atmosphere.

Terrestrial

Molybdenum in soil can be readily taken up in plants, depending on species and soil characteristics. Higher concentrations are generally found in leafy vegetables and legumes with lower content in edible roots.

Analytical Methods

Analysis for molybdenum is most commonly carried out by inductively-coupled plasma (ICP) spectrophotometry (method 3120B) and flame or graphite furnace atomic absorption (AA) spectrophotometry (method 3113B). Detection limits for ICP and graphite furnace AA methods are 1 µg/L.[11]

U.S. EPA Regulatory Position

EPA MCLG & MCL:	None
EPA Reference Dose:	0.005 mg/kg/day
EPA Reference Concentration:	None
EPA Lifetime Health Advisory:	40 µg/L
EPA Carcinogenicity Classification:	D, not classifiable as to human carcinogenicity.

Recommendations and Conclusions for Molybdenum

In 1993, EPA issued a reference dose of 0.005 mg/kg/day for molybdenum. This was based on a LOAEL of 0.14 mg/kg/day from the epidemiological study showing gout-like effects in an Armenian geoprovince. EPA applied an uncertainty factor of 30 (10 for use of a LOAEL and 3 for protection of sensitive human subpopulations). From this value, EPA established a corresponding lifetime health advisory based on an adult body weight of 70 kg, a 20% relative source contribution and a water intake of 2 L/day:

$$\frac{(0.005 \text{ mg/kg/day})\ (70 \text{ kg})\ (0.2)}{(2 \text{ L/day})} = 0.04 \text{ mg/L } (40 \text{ µg/L})$$

In accordance with Chapter 160 of Wis. Stats., the Department of Health and Family Services recommends adoption of a groundwater enforcement standard based on EPA's lifetime health advisory:

Recommended enforcement standard:	40 µg/L
Recommended preventive action limit factor:	20%
Recommended preventive action limit:	8 µg/L

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MOLYBDENUM

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Four adult males were given diets containing sorghum with varying molybdenum content for ten days to examine the effect of dietary molybdenum on uric acid and copper excretion. Urinary excretion of copper increased with increasing dietary molybdenum, with a daily intake of 22 µg/kg/day resulting in excretion of copper at twice the normal level. No effect of dietary molybdenum on uric acid excretion was observed.[6]

Chronic

In a comparative oral feeding study, white rats were fed 10-500 mg of molybdenum sulfide, molybdenum trioxide, calcium molybdate or ammonium molybdate for periods up to 232 days. Animals fed molybdenum sulfide displayed no adverse effects at any dose, while animals fed the other three compounds exhibited rough coat, loss of appetite, and unusually listless and quiet behavior.[4]

The relationship between dietary intake of molybdenum, serum uric acid levels and gout-like symptoms was examined in an Armenian village with high soil concentrations of molybdenum.[7] Villagers from Ankava were estimated to have daily molybdenum intakes ranging from 10 to 15 mg/day, corresponding to doses of 0.14 to 0.21 mg/kg/day. Villagers were examined for gout-like symptoms and levels of copper, uric acid, molybdenum and xanthine oxidase in blood, with similar data collected for a population with normal molybdenum intake of 1 to 2 mg/day. Higher rates of gout-like symptoms were reported in villagers (31%), as well as higher rates of elevated uric acid in blood. Blood uric acid level was found to be directly correlated with increasing residency time in the region. EPA used these results to establish a human LOAEL of 0.14 mg/kg/day based on observed increases in blood uric acid levels.[8]

Carcinogenicity/Mutagenicity

No data on the carcinogenicity or mutagenicity of molybdenum could be located.

Reproductive and Developmental Toxicity

The effects of supplemental dietary molybdenum on estrus activity, fetal development and fertility were studied in female rats.[9] Groups of weanling rats were given water with 0, 5, 10, 50 and 100 mg/L sodium molybdate (0, 0.9, 1.6, 8.3 and 16.7 mg Mo/kg/day) until day 21 of gestation. Groups at concentrations of 10 mg/L and above exhibited significantly prolonged estrus cycles, decreased gestational weight gain and evidence of increased rates of fetal resorption and spinal cord myelination. No effects on fertility were observed at any dose level.

Interactive Effects

Results from a number of studies suggest that the absorption and excretion of molybdenum may be affected by copper intake. The toxic effects of molybdenum may be lessened with concurrent copper exposure, and it has been suggested that the formation of a copper-tetrathiomolybdate complex in the gastrointestinal tract may play a role in the toxic effects associated with excessive molybdenum exposure.[10] A interaction between the metabolism of molybdenum and a number of sulfur compounds has been theorized, but has been demonstrated with less consistency than the interaction between molybdenum and copper.

Environmental Fate

Atmospheric

Once released into the environment, molybdenum may settle by wet or dry deposition. Little is known about the chemical transformations that molybdenum compounds may undergo in the atmosphere.

Terrestrial

Molybdenum in soil can be readily taken up in plants, depending on species and soil characteristics. Higher concentrations are generally found in leafy vegetables and legumes with lower content in edible roots.

Analytical Methods

Analysis for molybdenum is most commonly carried out by inductively-coupled plasma (ICP) spectrophotometry (method 3120B) and flame or graphite furnace atomic absorption (AA) spectrophotometry (method 3113B). Detection limits for ICP and graphite furnace AA methods are 1 µg/L.[11]

U.S. EPA Regulatory Position

EPA MCLG & MCL:	None
EPA Reference Dose:	0.005 mg/kg/day
EPA Reference Concentration:	None
EPA Lifetime Health Advisory:	40 µg/L
EPA Carcinogenicity Classification:	D, not classifiable as to human carcinogenicity.

Recommendations and Conclusions for Molybdenum

In 1993, EPA issued a reference dose of 0.005 mg/kg/day for molybdenum. This was based on a LOAEL of 0.14 mg/kg/day from the epidemiological study showing gout-like effects in an Armenian geoprovince. EPA applied an uncertainty factor of 30 (10 for use of a LOAEL and 3 for protection of sensitive human subpopulations). From this value, EPA established a corresponding lifetime health advisory based on an adult body weight of 70 kg, a 20% relative source contribution and a water intake of 2 L/day:

$$\frac{(0.005 \text{ mg/kg/day})\ (70 \text{ kg})\ (0.2)}{(2 \text{ L/day})} = 0.04 \text{ mg/L } (40 \text{ µg/L})$$

In accordance with Chapter 160 of Wis. Stats., the Department of Health and Family Services recommends adoption of a groundwater enforcement standard based on EPA's lifetime health advisory:

Recommended enforcement standard:	40 µg/L
Recommended preventive action limit factor:	20%
Recommended preventive action limit:	8 µg/L

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