Bull Environ Contam Toxicol (2016) 96:102–106
DOI 10.1007/s00128-015-1695-1

# Groundwater Molybdenum from Emerging Industries in Taiwan

Kuo-Sheng Tsai[1] · Yu-Min Chang[1] · Jimmy C. M. Kao[2] · Kae-Long Lin[3]

Received: 16 March 2015 / Accepted: 11 November 2015 / Published online: 26 November 2015


**Abstract** This study determined the influence of emerging industries development on molybdenum (Mo) groundwater contamination. A total of 537 groundwater samples were collected for Mo determination, including 295 samples from potentially contaminated areas of 3 industrial parks in Taiwan and 242 samples from non-potentially contaminated areas during 2008–2014. Most of the high Mo samples are located downstream from a thin film transistor-liquid crystal display (TFT-LCD) panel factory. Mean groundwater Mo concentrations from potentially contaminated areas (0.0058 mg/L) were significantly higher ($p < 0.05$) than those from non-potentially contaminated areas (0.0022 mg/L). The highest Mo wastewater concentrations in the effluent from the optoelectronics industry and following wastewater batch treatment were 0.788 and 0.0326 mg/L, respectively. This indicates that wastewater containing Mo is a possible source of both groundwater and surface water contamination. Nine samples of groundwater exceed the World Health Organization's suggested drinking water guideline of 0.07 mg/L. A non-carcinogenic risk assessment for Mo in adults and children using the Mo concentration of 0.07 mg/L yielded risks of 0.546 and 0.215, respectively. These results indicate the importance of the development of a national drinking water quality standard for Mo in Taiwan to ensure safe groundwater for use. According to the human health risk calculation, the groundwater Mo standard is suggested as 0.07 mg/L. Reduction the discharge of Mo-contaminated wastewater from factories in the industrial parks is also the important task in the future.

**Keywords** Groundwater · Molybdenum · Groundwater standards

✉ Yu-Min Chang
ymchang@ntut.edu.tw

[1] Institute of Environmental Engineering and Management, National Taipei University of Technology, No. 1, Sec. 3, Chung-Hsiao E. Rd, Taipei 106, Taiwan, ROC

[2] Graduate Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC

[3] Department of Environmental Engineering, National Ilan University, Ilan, Taiwan, ROC

The rise in emerging industries in Taiwan in the past few decades has caused several soil and groundwater contamination events. Groundwater is a critical water resource for agricultural and domestic demand in Taiwan. Preventing groundwater pollution from emerging industries, especially the wafer fabrication, semiconductor, optoelectronic materials and components manufacturing industries is an important issue for residents and government. Molybdenum (Mo) is a trace element that has caused recent health risk concerns. Previous investigations into the distribution of Mo in the groundwater in Taiwan are limited. The lack of a groundwater Mo standard in Taiwan has also caused concern in residents living near wafer fabrication, semiconductor, and optoelectronic materials manufacturing industries. The environmental protection administration (EPA) of Taiwan has therefore considered revising the existing groundwater standards for local developed industries.

The development of semiconductor and optoelectronics industries in Taiwan has led the world, especially the thin film transistor liquid crystal display (TFT-LCD) industry. The Taiwan flat panel display industry contributed 32.6 % of the global output value (175,339 million US dollars) in 2014. In 2010, Taiwan held 41.7 % of the global TFT-LCD market, leapfrogging Japan (9.7 %) and placing it second in the world behind S. Korea (42.2 %) (Hung et al. 2012). Molybdenum is widely used in the semiconductor and optoelectronics industries. Thin-film sputtering of TFT-LCD substrate uses Mo in the manufacturing process. Sputtering is used to create a thin film of Mo onto the substrate. Aluminum etching solution is subsequently used to remove the part that is not photoresist coated and protected, and the mask pattern is then transferred to the film. Therefore, the high concentration aluminum etching solution contains waste Mo, which is the main source of Mo in wastewater. Molybdenum is regarded as an essential trace element for human health, with an estimated daily absorption for adults of 0.075–0.25 mg (National Academy of Sciences 1989). The Mo content in rocks is in the range of around 1–5 mg/kg (Das et al. 2007). Molybdenum is commonly concentrated in sulphide rich ore zones and in sulphidic sedimentary rocks, such as black shale (Wilde et al. 2004; Das et al. 2007). Mineral sources also include the Mo oxides wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$) and the more common Fe, Mn and Al oxides (Wichard et al. 2009; Essilfie-Dughan et al. 2011).

The toxicity of Mo is a function of the physical and chemical state of the element, the exposure pathway and dietary Cu and S concentrations (WHO 2011a). Mo is essential for human health; however, excessive exposures to Mo may affect male reproductive health (Meeker et al. 2008, 2010). According to the health effects from chronic exposure to Mo, the health-based guideline value for Mo in drinking water was modified to 0.07 mg/L (WHO 2011b). In Taiwan, the Mo chemical compounds are used primarily as optoelectronic materials in the production of TFT-LCD panels. However, the groundwater distribution Mo is poorly known. The lack of in situ investigations and political regulation of emerging contaminants has further threatened groundwater safety. Hence, the purposes of this work were to determine the Mo groundwater distribution in the study area, and evaluate the concentrations of Mo relative to published drinking water quality standards of the World Health Organization in health risk calculations.

## Materials and Methods

The main semiconductor and optoelectronics industries are located in 3 industrial parks in Taiwan (Fig. 1), regarded as the potentially contaminated areas for groundwater Mo contamination. Groundwater samples (n = 537) were collected for Mo analysis, including 295 samples from potentially contaminated areas (i.e., wells within industrial parks) and 242 samples from non-potentially contaminated areas (i.e., wells not within industrial parks) during 2008–2014. At least three wellbore volumes of groundwater were pumped before sampling. Dissolved oxygen (DO), temperature, pH, electrical conductivity (EC), and electrical potential (Eh) were measured in a flow-through cell every 5 min during well purging. Cell sensors were calibrated with reagent grade standard solutions (purchased from Merck, Taipei, Taiwan) for pH (4.00, 7.00 and 10.0), EC (1413 µS/cm), and Eh (280 mV) before measuring any of these parameters in the field (ASTM 1992). Water samples were collected only after pH and EC stabilized and the pH fluctuations and relative EC were <0.1 and 5 %, respectively. Groundwater Mo was measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES; Model ICAP 9000, Jarrell-Ash, Franklin, MA, USA). A total of 15 samples including the blank, spike, duplicate and check samples [ultra-high purity grade (99.99 %) Mo standard solutions and nitric acid from Merck] were measured sequentially (USEPA 2001). The lower detection limit was 0.001 mg/L. Variances in duplicate measurements were less than 10 %. Recoveries of Mo-spiked samples were between 90 and 110 %. The descriptive statistics for the analytical results and *t* test for Mo concentrations between potentially and non-potentially contaminated areas were calculated using SPSS software (SPSS Inc. 1998).

Mo groundwater health risk assessment, the new criteria formulation for health risk assessment takes into account the local health risk calculation methods and parameters and the collection and compilation of basic information on the physicochemical properties and toxicology (Taiwan EPA 2008a). Due to the lack of a cancer slope factor for Mo, the non-carcinogenic risk via different exposure pathway is hence assessed using Eq. (1).

$$HI = \sum HQ_{oral} + \sum HQ_{inh} + \sum HQ_{dermal} \quad (1)$$

*HI* means the non-carcinogenic risk of Mo by different exposure pathways. $HQ_{oral}$, $HQ_{inh}$, $HQ_{dermal}$ means the hazard quotient of Mo by accidental ingestion of groundwater, breathing of vaporized pollutants from groundwater in the air, and absorption through the skin, respectively. The most conservative residential exposure scenario for both adults and children exposed were considered (Fig. 2). The hazard quotient of different exposure pathway is estimated using Eq. (2)

$$HQ = \frac{Intake}{R_f D} \quad (2)$$

where the *Intake* means the dose from different exposure pathways, including accidental ingestion of groundwater, breathing of vaporized pollutants from groundwater in the air, and absorption through the skin. The *Intake* calculations followed Andelman (1990), USEPA (1989), (2004); $R_fD$ is the reference dose of ingestion (0.005 mg/kg per

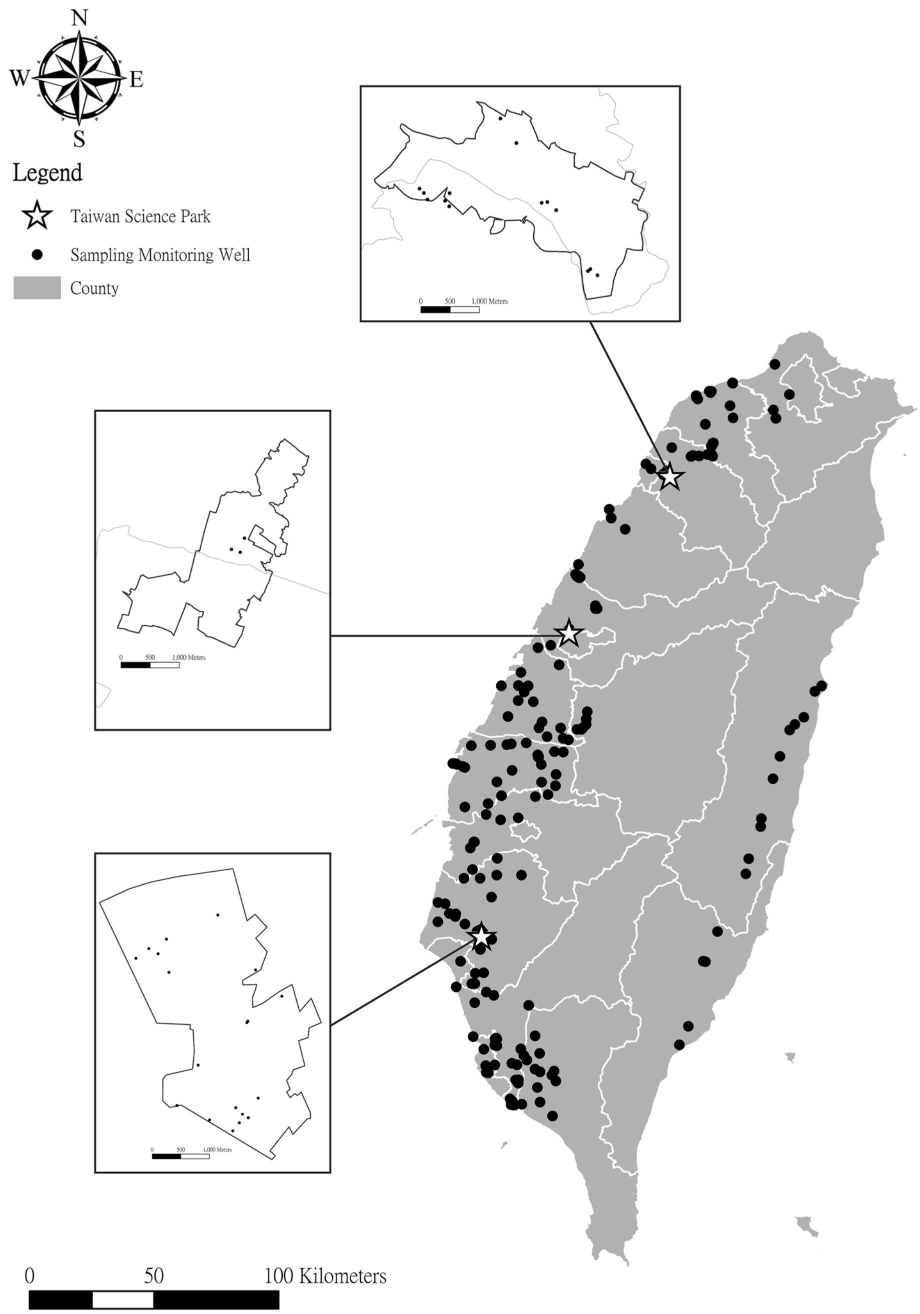


**Fig. 1** Distribution of sampling monitoring wells in 3 industrial parks (groundwater Mo potentially contaminated areas) and non-potentially contaminated areas

day). The drinking water quality standard (0.07 mg/L) of the World Health Organization (WHO 2011b) was adopted for the starting value to assess the acceptable non-carcinogenic risk, 1.

## Results and Discussion

Groundwater Mo concentrations ranged from ND-0.138 mg/L with an average of 0.0058 mg/L in potentially contaminated areas, and ND-0.456 mg/L with an average of 0.0022 mg/L in non-potentially contaminated areas, respectively. Molybdenum concentrations in most groundwater samples were lower than the detection limit (0.001 mg/L), including 168 and 238 samples in potentially and non-potentially contaminated areas, respectively. Low Mo concentrations also resulted in large statistical variability. However, the groundwater Mo concentrations from potentially contaminated areas were significantly higher ($p < 0.05$) than those from non-potential areas, indicating the importance of establishing a national groundwater standard, especially in the areas of the industrial parks. Smedley

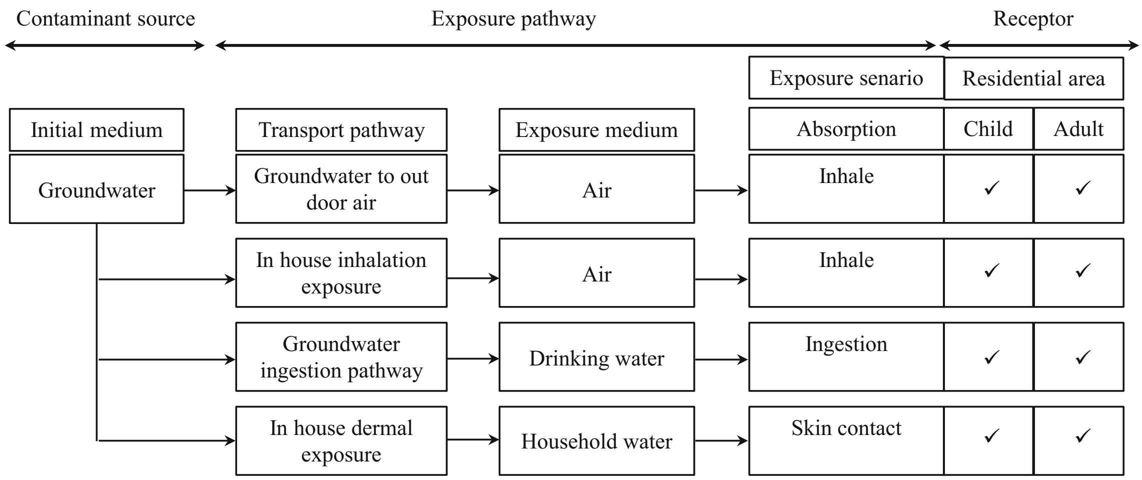


**Fig. 2** Exposure pathway for health risk assessment

**Table 1** Non-carcinogenic risk assessment of groundwater molybdenum

| Starting value (mg/L) | Non-carcinogenic risk and contribution | Exposure pathway | | | | | Risk |
|---|---|---|---|---|---|---|---|
| | | Drinking | Absorption via vaporization | | | Skin contact | |
| | | | Bathe | Cleaning | Outdoor | | |
| 0.07 | Adult | $5.45 \times 10^{-1}$ | – | – | – | $1.57 \times 10^{-3}$ | $5.46 \times 10^{-1}$ |
| | Contribution (%) | 99.67 | – | – | – | 0.33 | 100 |
| | Child | $2.14 \times 10^{-1}$ | – | – | – | $9.39 \times 10^{-4}$ | $2.15 \times 10^{-1}$ |
| | Contribution (%) | 99.67 | – | – | – | 0.33 | 100 |

et al. (2014) indicated that Mo in British groundwater was in the range of ND to 0.0892 mg/L (1735 samples) with an average of 0.0087 µg/L and concentrated largely in major aquifers. According to the difference of Mo concentrations between potentially and non-potentially contaminated areas in Taiwan, the anthropogenic sources of Mo are critically more threatening than the environmental background content.

According to previous studies by EPA of Taiwan (Taiwan EPA 2008b, 2010), wastewater Mo concentration from the semiconductor, TFT-LCD, and LED manufacturing plants in the industrial park ranged from ND-0.012, 0.084–1.91 and ND-0.062 mg/L, respectively. Molybdenum content from TFT-LCD manufacturing plants comprised up to 99.5 % of the total amount in the southern industrial park (Southern Taiwan Science Park Branch 2011). The highest Mo wastewater concentrations in the effluent from the optoelectronics industry and science park were 0.788 and 0.489 mg/L, respectively. Following wastewater batch treatment, Mo concentrations in the effluent were measured as 0.00094–0.0326 and 0.0279–0.523 mg/L, respectively (Taiwan EPA 2010). The Mo concentrations in fertilizer effluent water, artificial fiber, chemical materials and electric cell manufacturing plants were ND-0.0186, ND-0.0311, ND-0.0368, and ND-0.0730 mg/L, respectively (Taiwan EPA 2012).

Following the plant effluent discharge into the receiving water body, the Mo concentration was 0.186–0.2 mg/L, which is higher than the water quality background level (0.0008 mg/L) (Chunghwa Picture Tubes Ltd. 2009; Longtan Aspire Intelligent Industrial Park Administration 2009). Concentrations at four well sites on the riverbank were in the range of 0.0042–0.0616 mg/L, and in the range of 1.20–4.71 mg/kg in nearby irrigated soil, higher than the soil background level. In addition, the concentration in sediment was in the range of 0.264–0.474 mg/kg (Taiwan EPA 2011). As Mo-containing material is used in the manufacturing process (mostly indium tin oxide (ITO) transparent electrodes and molybdenum sisquioxide), Mo may enter wastewater and influence the environmental water body. Due to low soil sorption coefficients ($K_d = 20$ L/kg) for Mo, Mo may readily infiltrate downward through the soil and rock strata to contaminate the groundwater.

For the 3 industrial parks surveyed in this study, Mo may enter the subsurface environment due to damaged underground pipelines or wastewater disposal (Taiwan 2012). The main exposure pathway for human risk is groundwater. The risk associated with soil and/or sediment can be neglected. Based on toxicity data from the International Agency for Research on Cancer database (IARC 2013) and the Integrated Risk Information System (USEPA 2013), Mo has no carcinogenic effect on living organisms (Geng et al. 2014), and 0.005 mg/kg/day of toxicity value was adopted for risk assessment. Therefore, only non-carcinogenic risk was assessed using 0.07 mg/L as the starting value. Table 1 shows the risk assessment for molybdenum. In the exposure pathways for adults and children, non-carcinogenic risk is <1. The standard for groundwater Mo is hence recommended as 0.07 mg/L. Based on this suggested standard, concentrations of 9 samples in this study exceeded 0.07 mg/L. The health risks of adults and children which are calculated by the highest groundwater Mo concentration from potentially contaminated areas (0.138 mg/L) is 1.08 and 2.12, respectively. These high groundwater Mo concentrations were all located downstream of a main TFT-LCD panel factory in Taiwan. Reduction the discharge of Mo-contaminated wastewater from factories in the industrial parks is also the important task in the future.

**Acknowledgments** The authors are grateful to the Environmental Protection Administration of Taiwan R.O.C (EPA-100-GA103-02-A234 and EPA-102-G13-03-A121) for the financial support of this work.

## References

Andelman JB (1990) Total exposure to volatile organic compounds in potable water, Ch. 20. In: Ram NM, Christman RF, Cantor KP (eds) Significance and treatment of volatile organic compounds in water supplies. Lewis Publishers, Inc, Boca Raton

ASTM (1992) Standard guide for sampling groundwater monitoring wells, D4448-85a. http://www.astm.org/Standards/D4448.htm

Chunghwa Picture Tubes Ltd. (2009) Response strategies and differential analysis of environmental impact of industry, Taiwan

Das AK, Chakraborty R, Cervera ML, de la Guardia M (2007) A review on molybdenum determination in solid geological samples. Talanta 71:987–1000

Essilfie-Dughan J, Pickering IJ, Hendry MJ, George GN, Kotzer T (2011) Molybdenum speciation in uranium mine tailings using X-ray absorption spectroscopy. Environ Sci Technol 45:455–460

Geng C, Gao Y, Li D, Jian X, Hu Q (2014) Contamination investigation and risk assessment of molybdenum on an industrial site in China. J Geochem Explor 144:273–281

Hung SW, Tsai JM, Cheng MJ, Chen PC (2012) Analysis of the development strategy of late-entrants in Taiwan and Korea's TFT-LCD industry. Technol Soc 34:9–22

International Agency for Research on Cancer (IARC) (2013) IARC monographs on the evaluation of carcinogenic risks to humans. World Health Organization (WHO), Geneva

Longtan Aspire Intelligent Industrial Park Administration (2009) Response strategies and differential analysis of environmental impact of intelligent industrial park, Taiwan

Meeker JD, Rossano MG, Protas B, Diamond MP, Puscheck E, Daly D, Paneth N, Wirth JJ (2008) Cadmium, lead, and other metals in relation to semen quality: human evidence for molybdenum as a male reproductive toxicant. Environ Health Perspect 116:1473–1479

Meeker JD, Rossano MG, Protas B, Padmanahban V, Diamond MP, Puscheck E, Daly D, Paneth N, Wirth JJ (2010) Environmental exposure to metals and male reproductive hormones: circulating testosterone is inversely associated with blood molybdenum. Fertil Steril 93:130–140

National Academy of Sciences (1989) Recommended dietary allowances, 10th edn. National Academy Press, Washington

Smedley PL, Cooper DM, Ander EL, Milne CJ, Lapworth DJ (2014) Occurrence of molybdenum in British surface water and groundwater: distributions, controls and implications for water supply. Appl Geochem 40:144–154

Southern Taiwan Science Park Branch (2011) Statute advocacy of environmental engineering center. Taipei, Taiwan

SPSS Inc. (1998) SPSS BASE 8.0—application guide. SPSS Inc., Chicago

Taiwan EPA (2008a) Investigation, verification and technical support of soil and groundwater pollution, Taipei, Taiwan

Taiwan EPA (2008b) Investigation of industrial wastewater pollution characteristics and promotion of pollution self-reduction, Taipei, Taiwan

Taiwan EPA (2010) Investigation of industrial wastewater pollution and establishment of controlling scheme, Taipei, Taiwan

Taiwan EPA (2011) Investigation, verification and technical support of soil and groundwater pollution, Taipei, Taiwan

Taiwan EPA (2012) Investigation of industrial wastewater pollution and establishment of controlling scheme, Taipei, Taiwan

USEPA (1989) Risk assessment guidance vol. I human health evaluation manual (Part A), EPA/540/1-89/002. Office of Emergency and Remedial Response, Washington

USEPA (2001) Trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry. method 200.7, revision 5.0, EPA-821-R-01-010. Office of Science and Technology, Washington

USEPA (2004) Risk assessment guidance for superfund volume I: human health evaluation manual (part E, supplemental guidance for dermal risk assessment) interim, EPA/540/R/99/005. Office of Emergency and Remedial Response, Washington

USEPA (2013) Integrated risk information system. Office of Emergency and Remedial Response, Washington

WHO (2011a) Guidelines for drinking water quality, fourth edition. World Health Organization. http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf

WHO (2011b) Molybdenum in drinking water. Background document for development of WHO guidelines for drinking-water quality. World Health Organization.(WHO/SDE/WSH/03.04/11/Rev/1), Geneva

Wichard T, Mishra B, Myneni SCB, Bellenger JP, Kraepiel AML (2009) Storage and bioavailability of molybdenum in soils increased by organic matter complexation. Nat Geosci 2:625–629

Wilde P, Lyons TW, Quinby-Hunt MS (2004) Organic carbon proxies in black shale: molybdenum. Chem Geol 206:167–176