Total mercury pathways from artisanal and small-scale gold mining in Sukabumi using system dynamics model

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Abstract. Artisanal and small-scale gold mining (ASGM) has been operated in Sukabumi District, West Java, Indonesia, for more than two decades. ASGM uses mercury in a ball mill gold ore processing, and the waste is released into the environment during and after this process. Previous studies have found that mercury-contaminated water, air, sediments, soil, and aquatic biota. This study aimed to predict and analyze total mercury pathways from ASGM in the air, water, sediment, fish, and humans using a system dynamics model. The results showed that the total mercury concentration in water was low and still meets the standard, while the total mercury concentration in sediment had already exceeded the standard. Biomagnification occurred to plankton feeder fish and top predator fish, but still below the level of tolerance mercury. Mercury levels in top predator fish and humans take a long time to exceed the standard (77 and 67 months after entering the body, respectively). The percentage error of 17.67% compared to the experimental data showed that the prediction of the developed system dynamics model is acceptable. Therefore, the model can be used to predict the total mercury pathways in the environment, especially in the ASGM area.

1. Introduction
Mercury (Hg) contamination from artisanal and small-scale gold mining (ASGM) has been one of the environmental concerns in Sukabumi District, West Java, Indonesia, for several years. ASGM that illegally operated in these areas uses Hg in a ball mill gold ore processing or gold extraction [1], and the waste was released into the environment during and after this process that potentially spreads to all environmental media, like air, water, and soil. Previous studies have found that Hg from ASGM contaminated water, air, sediment, soil, and aquatic biota [2-7]. Furthermore, Hg was also found in the hair sample of people who lived in the ASGM area [8-12].

Mercury exists in three forms: elemental mercury, inorganic mercury compounds, and organic mercury compounds. The sum of all mercury compounds is defined as total mercury (THg). All forms of mercury are pretty toxic; it has short and long-term effects in humans, such as the central nervous system, abnormalities of development, and harm the brain, heart, kidneys, lungs, and immune system of people of all ages [13]. Moreover, Hg can be accumulated in fish and biomagnified through the aquatic food chain by rapid diffusion and tight binding to protein. It can denature proteins, inactivate enzymes, and cause severe disruption in the physiological processes of any tissue [14].

Modeling the pathways of contaminants can be a valuable tool for assessing the fate and its impact in the environment and organism, for which System Dynamics Model can play an important role
because, in most cases, this cannot be measured directly [15]. Several Hg residue models in the environment have already been described [16-18]. Each of these Hg models has its strengths and weaknesses and focuses on a specific area of Hg dynamics. To our knowledge, the study regarding the mercury contamination model in Indonesia, notably in Sukabumi, was scant.

This study aimed to predict and analyze THg pathways from ASGM in the environment and aquatic biota using a system dynamics model. The model was built to examine the relationships between each variable in river systems, follows Hg from the water column, air, and sediment, through microbial conversion and subsequent concentration, through the food chain from plankton to top predator fish and humans. Findings from this study will be valuable for the local government to evaluate and support the government decision to phase out Hg as a part of the National Action Plan of Indonesia under the ratification of the Minamata Convention [19].

2. Methodology
2.1. Data collection

The primary data of THg concentration in water and sediment (Table 1) were obtained from laboratory experiments using the analytical method for total mercury determination in water and sediment adapted from Standard Methods APHA 3112 B and EPA/SW-864 Methods 7471 A, respectively [20-21]. From four sampling sites of different rivers, the primary data used in this model were THg concentration from Ciletuh River in dry (August 2020) and wet (March 2021) seasons.

| Sampling site     | THg concentration (ppm) |          |
|-------------------|--------------------------|----------|
|                   | August 2020              | March 2021|
| Water             | < 0.0005                 | < 0.0005 |
| Sediment          | 0.8759                   | 1.5683   |

The secondary data for model variables (table 2) were obtained from previous studies, published data, and literature with a similar condition. The variable's value was mainly in a percentage unit estimated from mass balance calculation from secondary data.

| Variable                                         | Value          | Method/Reference |
|--------------------------------------------------|----------------|-----------------|
| The use of Hg in ASGM                            | 390 kg/month   | [8]             |
| Fraction for Hg residue in river                 | 41%            | Estimated from [22] |
| Hg emission                                      | 32%            | [23]            |
| Inorganic Hg in air                              | 40%            | [24]            |
| Deposition (wet and dry)                         | 50%            | Estimated from [25] |
| Hg volatilization                                | 10%            | [26]            |
| MeHg in water (microbial conversion)*            | 8.1 – 11.0%    | [27]            |
| MeHg in sediment (microbial conversion)*         | 0.22 – 2.17%   | [27]            |
| Fraction for MeHg in plankton                    | 26.67%         | Estimated from [28] |
| Fraction for MeHg in plankton feeder fish        | 35%            | [26]            |
| Excretion level of MeHg in plankton feeder fish  | 6.1%           | Estimated from [29] |
| Fraction for MeHg in top predator fish           | 15.58%         | Estimated from [30] |
| Excretion level of MeHg in top predator fish     | 5.6%           | Estimated from [29] |
| Human body weight                                | 55 kg          | Assumption      |
| Level of fish consumption                        | 3.19           | [31]            | kg/capita/month |
3

2.2. Model development and analysis

The steps for developing a model are described as follow: 1) determine the variable; 2) draw a causal loop diagram (CLD) to understand the interaction between each variable; 3) create a stock-flow diagram (SFD); 4) input or estimate the value of each variable and initial condition; 5) write the equation that determines the flows; 6) simulate the model; 7) result analysis; and 8) model validation.

A model for describing THg pathways was developed in the system dynamics software using Vensim PLE (Ventana System, Inc.) based on several assumptions and equations below. Seven assumptions were considered to formulate the model:

(i) There was no delay in THg pathways in the air, water, sediment, and aquatic food chain.
(ii) The pathway of THg in soil was being ignored since it was not the scope of this study.
(iii) The Time unit that was used in the model simulation was a month.
(iv) Plankton in model simulation is defined as both phytoplankton and zooplankton.
(v) The plankton feeder fish used in this model was *Barbodes bimotatus*, while the top predator fish was *Oreochromis mossambicus*. Those fish were found in the river around the ASGM area and consumed by people who lived in the ASGM area with the local name *Wader* and *Mujair*, respectively [33]. We assumed that the average human body weight was 55 kg, and fish consumption for plankton feeder fish was 40%, while for top predator fish was 60% of the total fish consumption.
(vi) The equation used in the model simulation used all values in table 2, as shown in figure 1.
(vii) The initial condition for THg concentration in Ciletuh River (water and sediment) was estimated from Widodo [22], and for MeHg concentration in fish and humans was estimated from Suryono et al. [25].

### Table 1

| Variable                                      | Value   | Assumption |
|-----------------------------------------------|---------|------------|
| Plankton feeder fish consumption              | 1.276   |            |
| kg/capita/month                               |         |            |
| Top predator fish consumption                 | 1.914   |            |
| kg/capita/month                               |         |            |
| Fraction for MeHg excretion via urine         | 10%     | [32]       |
| Fraction for MeHg excretion via feces         | 90%     | [32]       |

*The percentage of methyl mercury (MeHg) in THg concentrations

2.1. Equation of model simulation

\[
\text{Plankton feeder fish consumption} = 1.276 	ext{ kg/capita/month}
\]

\[
\text{Top predator fish consumption} = 1.914 	ext{ kg/capita/month}
\]

\[
\text{Fraction for MeHg excretion via urine} = 10\% 
\]

\[
\text{Fraction for MeHg excretion via feces} = 90\%
\]

Figure 1. Equations of model simulation.
2.3. Model validation
The model was validated with a result obtained from primary data (table 1). Mean Absolute Percentage Error (MAPE) test was used to validate THg concentration obtained from model simulation compared to experimental results. MAPE is calculated using the absolute error in each period divided by the observed values evident for that period [34]. Then, averaging those fixed percentages, as shown in equation (1).

\[
MAPE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{X_d - X_m}{X_d} \right| \times 100\% \tag{1}
\]

Where \( n \) is period, \( X_d \) is the actual value, and \( X_m \) is simulated/predicted value. The model was good if the MAPE percentage error was less than 10%, and it was acceptable if less than 20%.

3. Results and discussion
3.1. Causal loop diagram and stock-flow diagram

Figure 2 shows a CLD of THg pathways from ASGM in Sukabumi. All the signs in the CLD were positive, and the inside loops (R1-R4) indicated that the increase of one variable would increase another variable. The CLD was divided into five sectors: human, atmosphere, water, sediment, and biomagnification to classify each variable and more precise insight.

Hg can be released to the atmosphere in vapor form natural volatilization and anthropogenic sources like emissions from ASGM. The emission of Hg into the atmosphere came from the burning stage of gold amalgam in its elemental form (Hg\(_0\)) [4]. Deposition of atmospheric Hg is the pathway for Hg entering the water body [35-36].

ASGM also discharged waste containing Hg into the river as a result of the gold extraction process. In aqueous environments, inorganic mercury, as a part of total Hg, is converted into organic mercury compound, primarily methyl mercury (MeHg), by various microorganisms [37]. This biotransformation process can occur in the water column or the sediment. MeHg is a stable organic mercury compound with the most toxic form of Hg in the environment [2]. MeHg contamination in water and sediment is the primary source of bioaccumulation and biomagnification of MeHg through a food chain. Figure 2 shows that the biomagnification occurred from plankton – plankton feeder fish – top predator fish – and humans exposed to MeHg through fish consumption.
Based on CLD, the model of THg pathways from ASGM was built with Vensim PLE software, a system dynamics modeling tool that uses stocks and flows to simulate the changes of the component or variable in a system. The system being modeled is a river, and the variable that moves or changes in the system is THg and MeHg. The formulation of the model is shown in SFD (figure 3).

**Figure 3.** Stock flow diagram of THg pathways from ASGM.

### 3.2. Model prediction of total mercury concentration

Figure 4 shows the increase of THg concentration in water and sediment for 24 months of model simulation as we can see that the THg concentration in water will exceed the standard from month 21, which is more than 0.002 ppm of mercury concentration referred to government regulation for class II of water quality standard [38]. While THg concentration in the sediment will exceed the standard since month 1 referred to Canadian Environmental Quality Guidelines for Mercury and US EPA (more than 0.17 ppm and 0.2 ppm, respectively.)

**Figure 4.** Model prediction of THg in water (a) and THg in sediment (b).

THg concentration in water was lower than THg concentration in sediment because mercury is naturally present in waters at a low level, and it has a high tendency to bound to sediments. A large
proportion of Hg in the water phase is attached to suspended particles [39]. Therefore, mercury discharged in the aquatic system is generally lost to sediment by precipitation. In surface sediments, up to 62% of the Hg present is bound to sulfur-containing organic and inorganic particles [40]. Only a tiny portion of mercury in sediments is released into the pore water.

3.3. Model prediction of biomagnification

The Hg compound simulated in the biomagnification process was MeHg because more than 90% of Hg in aquatic biota was present as MeHg [2]. MeHg transfer in the water system occurred mainly through feeding relationships in the aquatic food chain, even from a low concentration [41]. The first level includes plankton (phytoplankton and zooplankton), which obtains Hg from adsorption through water column and sediment, followed by plankton feeder fish, top predator fish, and finally exposure to exposure humans. Figure 5 show the model prediction of MeHg presence in plankton feeder fish (*Barbodes binotatus*), top predator fish (*Oreochromis mossambicus*), and human.

![Figure 5](image)

**Figure 5.** Model prediction of MeHg in plankton feeder fish (a), top predator fish (b), and human (c).

MeHg concentration in top predator fish was more than in plankton feeder fish; it also will exceed the level of MeHg for top predator fish, which is 1 mg MeHg/kg [42] since month 77. At the same time, MeHg concentration in plankton feeder fish is still below the limit of 0.5 mg MeHg/kg [42]. Several studies have shown that MeHg concentrations in fish generally tend to increase with age, and therefore size, owing to MeHg accumulation with increasing exposure time [43-45].

MeHg is entering the human body through fish consumption. The concentration of MeHg in humans, as shown in figure 5, will exceed the limit of 1.6 mg MeHg/kg [42] from month 67. MeHg in humans will be accumulated, and the whole-body half-life of MeHg was estimated to be 70–80 days [46]. The daily excretion of MeHg mainly via the urine and feces as MeHg and Hg^2+ [46].

Although fish are regarded as the primary source of MeHg exposure to the human body, in some places, they are the only source of protein available for human consumption. Especially in the ASGM area, which are mainly people living in poverty. For this reason, fish cannot quickly be banned from the diets of people in the ASGM area.
3.4. Model validation

Model validation was conducted using the MAPE test that has been expressed in equation (1). MAPE test can help evaluate the accuracy of a prediction and indicates how much error in predicting compared with the actual value [15].

The THg concentration in water and sediment has been determined previously by laboratory experiments (table 1). THg concentration in water from model prediction cannot be validated because the THg concentration from experimental data was below the limit detection (<0.0005 mg L⁻¹). The model prediction of THg concentration in water for August (month 8) and March (month 15) was 0.0003 ppm and 0.0008 ppm, respectively (figure 4a).

Refer to THg concentration in sediment from the model prediction (figure 4b), the concentration of THg in sediment for August (month 8) and March (month 15) were 0.5790 ppm and 1.0015 ppm, respectively. At the same time, the experimental THg concentration in sediment (Table 1) was 0.8759 ppm for August and 1.5683 ppm for March. The percentage error of experimental value and model prediction using the MAPE test is 17.67%, acceptable (<20%). Therefore, it indicates that the model can predict the THg pathways in the environment, notably in the ASGM area.

4. Conclusion

The total mercury pathways from artisanal and small-scale gold mining (ASGM) in Sukabumi have been predicted and analyzed using a system dynamics model. The model simulated the fate of total mercury and methylmercury from the water column into aquatic biota and humans in several steps. With a 17.67% percentage error compared to the experimental data, it can be concluded that the prediction of the developed model was acceptable, and the model can be used to predict the total mercury pathways from ASGM. Regulatory decision-makers can use findings from this study to evaluate and support the government's decision to phase out mercury.

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References

[1] Esdaile LJ and Chalker JM 2018 Chem - A. Eur. J. 24(27) 6905–6916
[2] Marrugo-Negrete J, Verbel JO, Ceballos EL and Benitez LN 2008 Environ. Geochem. Health 30(1) 21–30
[3] Carroll RWH and Warwick JJ 2016 J. Am. Water. Resour. Assoc. 52(5) 1207–1222
[4] Tomiyasu T, Kono Y, Kodamatani H, Hidayati N and Rahajoe JS 2013 Environ. Res. 125
[5] Gworek B, Dmuchowski W, Baczewska AH, Brągoszewska P, Bemowska-Kałabun O and Wrzosek-Jakubowska J 2017 Water, Air, Soil Pollut. 228(4) 123
[6] Gafur N, Sakakibara M, Sano S and Sera K 2018 Water 10(11) 1507
[7] Green CS, Lewis PJ, Wozniak JR, Drevnick PE and Thies ML 2019 Sci. Total. Environ. 647 400–410
[8] Harianja AH, Saragih GS, Fauzi R, Hidayat MY, Syofyan Y, Tapriziah ER, et al 2020 J. Heal. Pollut. 10(28) 1–11
[9] Basri, Sakakibara M and Sera K 2017 Toxics 5(1) 7
[10] Arifin Y, Sakakibara M and Sera K 2015 Geosciences 5(2) 160–176
[11] Ekawanti A and Krisnayanti BD 2015 J. Heal. Pollut. 5(9) 25–32
[12] Bose-O’Reilly S, Schierl R, Nowak D, Siebert U, William JF, Owi FT, et al 2016 Environ. Res. 149 274–281
[13] EPA 2016 Mercury Compounds United States p 7
[14] Vasanthi N, Muthukumaravel K and Sathick OJS 2019 Res. J. Life. Sci. Bioinformatics, Pharm. Chem. Sci. 5(364) 364–76
[15] Sunaryani A and Rosmalina RT 2021 *IOP Conf. Ser. Earth. Environ. Sci.* 623(1)
[16] Zhu S, Zhang Z and Liu X 2017 *Water* 2017 9(9) 643
[17] Harris R, Pollman C, Hutchinson D, Landing W, Axelrad D, Morey SL, Dukhovskoy D and Vijayaraghavan K 2012 *Environ. Res.* 119 53–63
[18] Ethier ALM, Atkinson JF, DePinto JV and Lean DRS 2012 *Environ. Pollut.* 161 335–42
[19] Presiden Republik Indonesia 2019 *Peraturan Presiden Republik Indonesia Nomor 21 Tahun 2019 tentang Rencana Aksi Nasional Pengurangan dan Penghapusan Merkuri* Indonesia p 32
[20] American Public Health Association 1992 *Standard Methods for Water and Wastewater* 18th ed. (Washington DC: American Public Health Association) p 3–19
[21] Environmental Protection Agency *Mercury, elemental* CASRN 7439-97-6 United States
[22] Widodo W 2008 *Indones. J. Geosci.* 3(3) 139–49
[23] Wilson S, Kindbom K, Yaramenka, K, Steenhuisen F and Telmer K 2012 *Part A: global emissions of mercury to the atmosphere* p 254
[24] Environmental Protection Agency 2000 *To regulate mercury and other air toxics emissions from coal- and oil-fired powerplants*
[25] Suryono DD and Pujilestari E 2019 *J. Segara.* 13(3) 179–193
[26] UNEP 2013 *Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport* UNEP Division of Technology, Industry and Economics, Chemicals Branch International Environment House p 44
[27] Baralkiewicz D, Gramowska H, and Goldyn R 2006 *Chem. Ecol.* 22(1) 59–64
[28] Azizah M and Paramitha GA 2021 *Edubiotik. J. Pendidikan. Biol. dan Terap.* 6(01) 83–90
[29] Bacakszilar NG and Onsel N 2013 *31st International Conference of the System Dynamics Society*
[30] Marsyalita F, Raharja BS and Cahyoko Y 2012 *J Ilm Perikan dan Kelaut.* 4(2) 113–8
[31] Ministry of Marine and Fishery 2019 *Angka Konsumsi Ikan di Jawa Barat* https://statistik.kkp.go.id/home.php?m=aki&i=209#panel-footer accessed June 21, 2021
[32] National Research Council 2000 *Toxicological Effects of Methylmercury* Washington DC National Academies Press p 364
[33] Wulandari I, Shanida SS, Husodo T, Megantara EN and Tresna D 2019 *BIODIVERSITAS* 20(10) 2781–2789
[34] Khair U, Fahmi H, Al Hakim S and Rahim R 2017 *J. of Physics: Confer. Ser.* 930
[35] Buehler SS and Hites RA 2002 *Environ. Sci. Technol.* 36(17) 354A-359A
[36] Rolffhus KR, Sakamoto HE, Cleckner LB, Stoor RW, Babiazar CL, Back RC, Manolopoulos H and Hurley JP 2003 *Environ. Sci. Technol.* 37(5) 865–87237
[37] Jeremiason JD, Engstrom DR, Swain EB, Nater EA, Johnson BM, Almendinger JE, Monson BA and Kolka RK 2006 *Environ. Sci. Technol.* 40(12) 3800–3806
[38] Presiden Republik Indonesia 2001 *Peraturan Pemerintah Nomor 82 tahun 2001 tentang Pengelolaan Kualitas Air Dan Pengendalian Pencemaran Air* Indonesia p 32
[39] Ullrich SM, Tanton TW and Abdrashtiova SA 2001 *Environ. Sci. Technol.* 31(3) 241–93
[40] Smol JP 2008 *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective* (United States: Blackwell Publishing) p 383
[41] Feng X, Meng B, Yan H, Fu X, Yao H and Shang L 2018 *Springer Singapore* p 339–389
[42] UNEP 2019 *Global Mercury Assessment 2018* UN Environment Programme Economy Division Switzerland p 62
[43] Kannan K, Smith RG, Lee RF, Windom HL, Heitmuller PT, Macauley JM, et al 1998 *Arch. Environ. Contam. Toxicol.* 34(2) 109–18
[44] Mirlean N, Andrus VE and Baisch P 2003 *Mar. Pollut. Bull.* 46(3) 331–334
[45] Sampaio da Silva D, Lucotte M, Paquet S and Davidson R 2009 *Environ. Res.* 109(4) 432–446
[46] Boerleider RZ, Roeleveld N and Scheepers PTJ 2017 *AIMS. Environ. Sci.* 4(2) 251–276