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Pollution and Potential Ecological Risk Assessment of Heavy Metals Around the Active Bukit Mendi Palm Oil Mill Area, Bera Pahang, Malaysia

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ABSTRACT

The study on the impact of palm oil mill processing activities on the environment of Bukit Mendi Palm Oil Mill was conducted by determining the distribution of six heavy metal concentrations Cadmium (Cd), Copper (Cu), Manganese (Mn), Lead (Pb), Iron (Fe) and Zinc (Zn) and the selected pollution indices. This study provided some information on the accumulation of heavy metals in the selected area and served to identify the potential sources contributing to these heavy metals. Soil samples were collected from eight sampling sites around the palm oil mill and analysed for the selected metals using ICP-OES. Three types of pollution indices were used to observe the pollution level of the area, namely Enrichment Factor (EF), potential ecological risk index (PERI), and Contamination Factor (CF) of heavy metal content. The average total concentration of the selected metals was found to increase in the order of Fe, Mn, Zn, Cd, Pb, and Cu. The metal Fe showed the highest metal content, followed by Mn at 1573.00 mg/kg and 154.00 mg/kg, respectively. The values of EF showed that the metal was unevenly distributed throughout the sampling areas, where heavy metal content ranged from minimal to extremely high enrichment. The potential ecological risk ranging from low to severe was observed in this study. The CF values revealed that the area was heavily contaminated with Cd and only slightly contaminated with Pb. The pollution indices determined in this study suggested that the study area was moderately contaminated with metals, and the metal Cd was found to be the only metal potentially posing an ecological risk to the area.

Keywords: *ICP-OES, palm oil mill, heavy metals, soil pollution, pollution indices*

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INTRODUCTION

Pollution is defined as contaminating the atmosphere that harms the ecosystem. Some contaminants are present in nature, but excessive levels can negatively impact the environment [1]. Environmental pollutants are grouped into air pollution, water pollution, and soil pollution. Soil pollution has now become a major environmental issue [2]. The effects of soil contamination on human health, particularly heavy metals, have been thoroughly investigated in metropolitan areas, mining areas, adjacent industrial areas, and agricultural fields [3].

Heavy metal concentrations that exceed the usual concentrations in the earth's crust are deemed contaminated and pose a significant pollution danger [4]. Some elements, such as sodium (Na), aluminium (Al), and iron (Fe), were found in high concentrations in the soil because they are prevalent in soils. According to the US Environmental Protection Agency (EPA), the heavy metals most typically detected in polluted soil include As (arsenic), Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Pb (lead), Zn (zinc), Co (cobalt), and Ni (nickel). Due to their high contamination levels, these nine heavy metals are frequently given extra attention in soil pollution investigations [5].

Malaysia's palm oil business has boomed in recent years, making it one of the world's major producers and exporters of palm oil [6]. A wet procedure was used to obtain crude palm oil, acquired by pressing and cleaning the palm fruit. This procedure produces solid, liquid, and gaseous waste [7]. The danger of environmental and health hazards increases due to combustion processes (incineration). The principal pollutants released into the environment by burning are dioxin, lead, other heavy metals, and toxic fumes. Particulate matter typically comprises a variety of hazardous metals with negative effects on people when concentrations reach a specific level [8].

Burning empty fruit bunches (EFB) potentially releases fine particles such as tar and soot into the environment. Over the years, these pollutants accumulate in the surrounding soil and can affect the environment, especially soil properties and fertility [9]. The palm oil mill industry is considered one of the possible polluters of the environment, especially Malaysia. This study was conducted to investigate the impact of palm oil mill processing activities on the accumulation of heavy metals in the soils surrounding the Bukit Mendi Palm Oil Mill in Bera District, Pahang, Malaysia. Residential houses and farms surround the mill site. The selected palm oil mill was built almost 20 years ago and has been in operation since. The mill is considered as one of the major palm oil mills in Pahang that processes certified fresh fruit bunches. Since the mill is located near a residential area, its processing activities may likely impact the environment and the people in the vicinity.

This study was conducted to evaluate the dispersion pattern of the selected heavy metals, determine the corresponding pollution index, and quantitatively assess the pollution risk in the

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study area. It is hoped that this study's results will help establish the baseline data on the level of heavy metal deposition in the vicinity. The results of this study can also be used to identify the possible sources that contributed to these heavy metals.

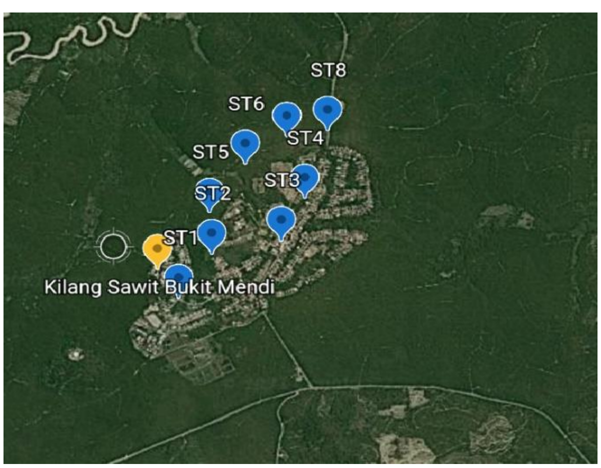
EXPERIMENTAL

Study Area

The surroundings of the Bukit Mendi Palm Oil Mill in Bera District, Pahang, Malaysia (Latitude 03 12'20.89 "N, Longitude 102 18'12.39" E) were selected as the sampling location in this study. There are no large industries in the area, primarily agricultural activities, residential homes, and small local businesses.

Sample Collection

Surface soil samples (0-15 cm depth) were collected in triplicate from eight (8) sub-stations spread over the study area. Figure 1 depicts the locations of the sampling stations. A stainless-steel auger was used to collect composite samples from the sites. Each site's composite sample was made up of five subsamples. Each site's subsamples were totally mixed.



Sampling Station	Position	
ST1	3 º 11’ 59’’N	102º 18’ 18’’E
ST2	3 º 12’ 10’’N	102º 18’ 24’’E
ST3	3 º 12’ 14’’N	102º 18’ 31’’E
ST4	3 º 12’ 16’’N	102º 18’ 26’’E
ST5	3 º 12’ 22’’N	102º 18’ 22’’E
ST6	3 º 12’ 32’’N	102º 18’ 23’’E
ST7	3 º 12’ 39’’N	102º 18’ 32’’E
ST8	3 º 12’ 39’’N	102º 18’ 41’’E

Figure 1: Map of the study area and location of each sampling station

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Samples Pre-treatment

All irrelevant materials attached to the surface of the soil samples were thoroughly removed. The samples were dried overnight in an oven at a constant temperature of 60 ^{0}C before being ground with a porcelain mortar and pestle. Before analysis, the grounded soil samples were passed through a 1 mm stainless steel sieve and stored in plastic containers.

Sample Treatment and Analysis

Soil samples were treated according to the procedure recommended by the USEPA [10]. All reagents used for metal content analysis were of analytical grade. For metal analysis, HNO_3 (65 %) and H_2O_2 (34.5 %) (Sigma-Aldrich, Germany) were used to prepare the solutions required for the digestion of the samples. 2 g of soil, 8 mL of HNO_3 (v/v), and 2 mL of H_2O_2 (v/v) were added. The hot plate digestion technique brought the soil sample into liquid form. The mixture was heated for about 5 minutes until brown vapours were formed. The solution was then filtered and diluted with distilled water to a final volume of 50 ml. For metal analysis, a certified standard stock solution (Multielement Standard Solution 6 for ICP, TraceCERT, Sigma-Aldrich, Taufkirchen, Germany) was used to calibrate the instrument before running the samples. All samples were analysed for the concentration of Cd, Cu, Mn, Pb, Fe, and Zn.

The blank samples were prepared using the same procedure but without sediment. A total of three replicates were prepared for each sample. The concentrations of the selected metals were measured using the Perkin Elmer Optima 5300DV ICP-OES. All glassware was soaked in 10 % HNO3 for 24 hours and rinsed with double distilled water for quality assurance and quality control.

All data was processed for contamination, enrichment, and potential ecological risk index to assess the area's environmental quality. Quality control of the analytical procedure was performed by analysing the standard reference material SRM-CC141. The SRM was analysed (in triplicate) similarly to the actual samples. The results showed that all elements could be analysed with 80 to 121 % recovery, which was considered acceptable [11].

The limit of detection (LOD) was considered the lowest amount of analyte that can be quantified with a known degree of confidence in the analytical procedure. In contrast, the limit of quantification (LOQ) refers to the concentration of quantitative results with reasonable confidence. These were determined using a statistical approach based on the measurement of replicate blank samples [12]. The LOD was calculated as 3.3 (SD/m), and the LOQ as 10 (SD/m), where SD is the standard deviation of the blank sample and m is the slope of the calibration curve. The respective wavelengths, linear correlation coefficients (R^2), LOD and LOQ of Cd, Cu, Mn, Pb, Zn, and Fe, are shown in Table 1.

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Table 1: The respective SD, linear correlation coefficients (R^2), the limit of detection (LOD) and limit of quantitation (LOQ) of Cd, Cu, Mn. Pb, Zn and Fe

Element	Wavelength (nm)	R^2	LOD (mg/kg)	LOQ (mg/kg)
Cd	228.802	0.9999	0.1067	0.3233
Cu	324.754	0.9999	0.1012	0,3066
Mn	403.076	0.9997	0.2062	0.6079
Pb	405.781	0.9999	0.1139	0.3451
Zn	213.857	0.9996	0.2351	0.7124
Fe	259.940	0.9998	0.5627	1.7052

Metal Pollution Indices

Heavy metals are natural constituents of soils, and their concentration varies depending on parental materials. Human activities such as fertilisers, pesticides, industries, waste disposal, and air pollution have increased the concentration of heavy metals in soils. The life capacity of soils is reduced because of these activities, particularly if the natural background is already high due to natural parental material richness in heavy metals. Distinguishing between natural background values and anthropogenic contributions is critical, as is understanding that background values vary from area to area and with the scale of the site studied.

Several indices have been developed to assess the degree of soil contamination and its potential impact on human health, such as contamination factor, enrichment factor, contamination degree, and a lot more. These indices aid in understanding the status of soil contamination and exposure risks for humans and are also used to determine the presence and severity of anthropogenic pollutant deposition on the surface soil.

Enrichment Factor (EF)

The enrichment factor (EF) measures how much metals are enriched or reduced compared to a given source and can distinguish between metals from human intrusions and those from natural sources. It works by comparing the properties of a measured metal to those of a reference metal. Al, Ca, Fe, Mg, and Mn are commonly used as reference elements. Fe was chosen as the reference element in this study because it occurs naturally in most soils and sediments and is not associated with other heavy metals [13]. EFs were calculated using the following Equation 1:

$$EF = [\frac{Ci}{Cref}]\text{ sample} \div [\frac{Bn}{Bref}]\text{ background} \quad (1)$$

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Where Ci is the heavy metal concentration, Cref is the concentration of the reference heavy metal. Bn and Bref are the background concentration of the heavy metal and the background concentration of the reference heavy metal, respectively [14].

Potential Ecological Risk Index Method (PERI)

The potential ecological risk index method (PERI) proposed by Swedish scientist Hakanson in 1980 has been widely used to assess the harmfulness of heavy metals. This score of PERI has been used to describe the human sensitivity to heavy metals and the high environmental risk from total contamination [10]. The method is described as in Equation 2 [15]:

$$RI=\Sigma E_f^i=\Sigma T_r^i\,(C_s^i\,/C_n^i\,) \qquad (2)$$

Where RI is the sum of all the potential risk factors for all heavy metals, E_f^i is the potential risk for single heavy metal. E_f^i was calculated as in Equation 3:

$$C_f^i \times T_f^i$$

T_f^i is the toxic-response factor for single heavy metal conta,mination and C_f^i is the pollution index for a given heavy metal, which can be defined as in Equation 4:

$$C_f^i = C_s^i\,/C_n^i \quad , \qquad (4)$$

Where C_s^i is the present concentration of heavy metal and C_n^i is the reference value for heavy metal. The relationship between E_f^i, RI and pollution levels are shown in Table 2.

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Table 2: Relationship between E_f^i, RI and pollution levels

Potential Ecological Risk Index (E_f^i)	Ecological Risk Level Single Factor Pollution	Potential Toxicity Index (RI)	Level of Potential Ecological Risk
< 40	Low	<150	Low grade
40-80	Moderate	150-300	Moderate
80-160	Higher	300-600	Severe
160-320	High	≥ 600	Serious
≥ 320	Serious		

Contamination Factor (CF)

Contamination levels of all selected metals were assessed using contamination factor (CF) and degree of contamination (Cdeg). The CF is calculated using the following Equation 5 as suggested by Hakanson [13]:

$$C_F = C_M / C_B \qquad (5)$$

Where C_F is the contamination factor, C_M is the mean concentration of each heavy metal in soil, and C_B is the background concentration of the metal.

The CF is the single-element index whereas Cdeg is a multielement index which is computed by adding contamination factors of all metals studied as:

$$C\text{deg} = \sum CF_i \qquad (\mathbf{6})$$

The results were interpreted as [29] CF < 1 = low contamination, 1 ≤ CF < 3 = moderate contamination, 3 ≤ CF < 6 = considerable contamination, 6 ≤ CF = very high contamination, Cdeg < 8 = low degree of contamination, 8 ≤ Cdeg < 16 = moderate degree of contamination, 16 ≤ Cdeg < 32 = considerable degree of contamination, and 32 ≤ Cdeg = very high degree of contamination.

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RESULTS AND DISCUSSION

Distribution of Metal Concentrations

Table 3 shows the concentration of heavy metals (Cd, Cu, Mn, Pb, Fe and Zn) contained in the soil samples collected from the nearby Bukit Mendi Palm Oil Mill and the controlled samples collected around UiTM Jengka, Pahang. The average total heavy metal concentration contained in the studied samples were in the increasing order of Fe > Mn > Zn > Cd > Pb > Cu. The data also shows that the concentration of the studied metals was substantially dependent on the position and distances from the factory site. The metals were found unevenly distributed throughout the sampling stations.

Table 3: Distribution of heavy metals concentration (mg/kg) in soil samples

Sampling Station	**Heavy metal concentration (mg/kg dry weight)**					
	Cd	Cu	**Mn**	**Pb**	**Zn**	**Fe**
ST1	23.25±0.11	25.00±0.19	86.00±2.31	15.75±1.51	36.75±0.33	1573±15
ST2	36.25±0.09	9.75±0.09	40.25±1.55	35.00±2.19	35.25±0.67	998±52
ST3	25.75±0.12	13.25±0.11	59.00±2.02	16.75±1.11	20.75±0.22	1332±21
ST4	26.50±0.08	32.00±0.18	68.75±3.02	28.50±1.54	125.50±1.99	1433±39
ST5	12.50±0.14	16.00±0.09	78.25±3.06	11.50±0.98	30.00±1.21	860±22
ST6	1.00±0.04	36.25±0.21	154.00±12.0	5.75±0.11	18.75±0.99	1357±42
ST7	75.25±0.21	5.00±0.03	27.00±1.02	20.00±1.09	13.50±0.13	628±33
ST8	51.25±0.19	8.25±0.08	40.50±1.33	19.00±1.00	17.50±0.15	1081±65
Average	31.46±23.12	18.18±11.56	69.21±39.82	19.03±9.21	37.25±36.67	1157.75±320.48
Control	4.00±0.07	3.00±0.02	14.00±0.78	6.50±0.45	5.25±0.09	1391±3.71

The concentration of Zn was found higher (125.50 mg/kg) at sampling station 4, which is located 200 metres from the mill, while Cd was found in the highest concentration at sampling station 7, which is close to the factory site. In general, most of the studied metals were measured in higher concentrations compared to the metals of the controlled sample. This indirectly indicates that the soil samples may have been contaminated with the metal deposition originated from the mill processing activities located nearby.

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The Mn concentrations were higher in almost all sampling stations because Mn is one of the major heavy elements in soils and sediments [16]. Pb and Cu were slightly lower than the other metals in average concentration. The decomposition of organic matter may contribute to the accumulation of this metal in the soil [17]. This factor was also attributed to the Cd concentration. According to Zhang *et al.* [18], Cd would associate together with Cu, Pb, and Zn in the soil samples.

Enrichment Factor (EF)

All the EF values of the selected metals of the soil around the mill are summarised in Table 4. The result shows that the measured EF values were varied throughout the mill. The average EF values indicate that the soils of the studied area were significantly enriched with the metals Cd, Cu, Mn, and Zn, while the metal Pb was moderately enriched. In general, the order of enrichment of the selected heavy metals in the soil samples is as follows: Cd > Zn > Cu > Mn > Pb. The highest EF value of Cd (EF > 40) categorised the soil as extremely enriched with this metal at ST7. In contrast, the other sampling stations were significantly increased with the metal Cd except for ST6.

Table 4: Enrichment Factor (EF) for selected heavy metals in soil samples

Element / Station	Enrichment Factor								
	ST1	**ST2**	**ST3**	**ST4**	**ST5**	**ST6**	**ST7**	**ST8**	**Average**
Cd	5	13	7	6	5	0	42	16	11.8
Cu	7	5	5	10	9	12	4	4	7.0
Mn	5	4	4	5	9	11	4	4	5.8
Pb	2	8	3	4	3	1	7	4	4.0
Zn	6	9	4	23	9	4	6	4	8.1

EF value; < 2: Deficiency to minimal enrichment, 2-5: Moderate enrichment, 5-20: Significant enrichment, 20-40: Very High Enrichment and >40: Extremely High Enrichment

Significantly enriched Cu at all sampling stations can be observed, except for sampling stations ST7 and ST8 (the far distances from the mill), where the soils were classified as a deficiency to minimal enriched with Cu. The soils at sampling stations ST1, ST4, and ST5 were significantly enriched with Mn, while the other stations were sows moderately enriched with this metal. With the average of the EF recorded as 4, the soil of all sampling stations was moderately enriched with Pb except for stations ST2 and ST7, which were recorded significantly enriched. Highly enriched with Zn was recorded for the soil at the sampling station ST4, enriched

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significantly for stations ST1, ST9, ST5 and ST6. In contrast, the soil at sampling stations ST3, ST6 and ST8 was deficient to minimal enrichment.

Potential Ecological Risk Index Method (PERI)

The potential ecological risk index is one of the useful methods to evaluate the risk caused by heavy metals. It is a comprehensive index that can show the influence of heavy metals on the ecological environment. Table 5 shows the potential ecological risk and toxicity response indices for the selected heavy metals in the studied palm oil mill environment.

Table 5: Potential Ecological Risk Indices and Potential Toxicity Response Indices of the selected heavy metals

Sampling Station	**Potential ecological risk indices for single heavy metals (C_f^i)**					**Potential Toxicity Response Indices for heavy metals (RI)**
	Cd	**Cu**	**Mn**	**Pb**	**Zn**	
1	174	42	6	12	7	241
2	272	16	3	27	7	325
3	193	22	4	13	4	236
4	199	53	5	22	24	303
5	94	27	5	9	6	141
6	8	60	11	4	4	87
7	564	8	2	15	3	592
8	384	14	3	13	3	417

The results (Table 5) show that the content of the three elements (Mn, Pb, and Zn) poses a low ecological risk, as the values were below 40 for all sampling points. On the other hand, Cd was measured at sampling stations 7 and 8, where the values were 564 and 346, respectively, indicating a serious ecological risk. Preliminary studies have shown that the distribution of Cd is closely related to the intensive use of phosphate fertilisers since phosphate fertilisers contain significant amounts of metals, especially particulate Cd, as impurities. Cu content was not high, but stations 1, 4, and 6 showed moderate risk at 42, 53, and 60, respectively. In general, it was found that the single risk indices of heavy metals were ranked in the order of Zn < Mn < Pb < Cu < Cd.

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The RI values obtained for the area ranged from 87 to 592, with sampling station 6 having the lowest RI value of 87. This indicates that sampling station 6 has a low potential ecological risk. In contrast, sampling station 7, located in the northern portion of the mill, and sampling station 4, located in the eastern part of the mill, had RI values of 592 and 303, respectively. The high values of Cd directly influenced the high RI values. The RI values at sampling stations 7 and 8 are considered detached. The RI values detected at all sampling stations could be influenced by smoke dispersion from the nearby mill stack. The overall RI values detected do not indicate a serious potential ecological risk in the selected study area.

Contamination Factor (CF)

As shown in Table 6, the contamination factors of heavy metals at each sampling site varied. The contamination factor of Cd, Cu, Mn, Pb, and Zn for all samples ranged from 0.25 to 18.81, 1.67 to 12.08, 1.93 to 11.00, 0.88 to 5.38, and 2.57 to 23.90, respectively, indicating a low to medium contamination factor. On average, Pb had the lowest, and Cd had the highest CF values with 2.89 and 7.87, respectively. Sampling station 4 showed a very high degree of contamination with a C_{deg} reading of 50.49. This is possible because this sampling station is located farthest from the mill. The factors of wind direction and wind speed probably led to the higher deposition of heavy metals on the site. On the other hand, sampling station 5, located 50 metres away from the mill, had the lowest pollution level of 21.35.

Table 6: Contamination Factor and degree of contamination for selected heavy metals in soil samples

Sampling Station	Contamination Factor (CF)					Degree of Contamination
	Cd	Cu	Mn	Pb	Zn	
1	5.81	8.33	6.14	2.42	7.00	29.70
2	9.06	3.25	2.88	5.38	6.71	27.28
3	6.44	4.42	4.21	2.58	3.95	21.60
4	6.63	10.67	4.91	4.38	23.90	50.49
5	3.13	5.33	5.41	1.77	5.71	21.35
6	0.25	12.08	11.00	0.88	3.57	27.78
7	18.81	1.67	1.93	3.08	2.57	28.06
8	12.81	2.75	2.89	2.69	3.33	24.47
Average	7.87	6.19	4.92	2.89	7.09	28.84

CF Value; ≤ 1: No contamination, 1-2: Suspected, 2-3.5: Slight, 3.5-8: Moderate, 8-27: Severe and 27: Extreme Cdeg < 8 = low degree of contamination, 8 ≤ Cdeg < 16 = moderate degree of contamination, 16 ≤ Cdeg < 32 = considerable degree of contamination, and 32 ≤ Cdeg = very high degree of contamination

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CONCLUSION

The present study showed a divergent disparity of selected metals in the surface soil around the chosen study area of the palm oil mill in Bera, Pahang, Malaysia. The results also showed that the metals were unevenly distributed throughout the study area. Based on the average concentration of the metals, Fe was the dominant metal found in the soil sample, followed by Mn, Zn, Cd, Pb, and Cu. The pollution indices measured in the study showed that the area is polluted to some extent with the studied metals. The enrichment factor obtained demonstrated that the soils of the area were significantly enriched with Cd, Cu, Mn, and Zn, while Pb was observed to be moderately enriched. In general, the soil's degree of contamination (Cdeg) is considered a high degree. Sampling station ST4, which was located at a middle distance from the mill, showed a very high degree of contamination with C_{deg} value of 50.49. The results of the PERI index indicated that the individual ecological risks for all metals in the soil samples were low.

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AUTHOR'S CONTRIBUTION

Mohd Zahari Abdullah conducted the research, wrote, and revised the article. Nur Najihah, as a student, collected and analysed the sample and organised the data.

CONFLICT OF INTEREST STATEMENT

As the principal author of the manuscript, I, Mohd Zahari Abdullah, declare that this research was undertaken without self-interest, commercial or financial conflicts, and I have no conflicts of interest with sponsors.

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