# Geochemical Assessment of Trace Metals in Peri-Urban Drainage and Bioaccumulation in Selected Food Crops in the Kumasi Metropolis, Ghana

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# Abstract

This paper evaluates some geochemical properties of trace metals in peri-urban drainage and bioaccumulation in cassava, plantain, lettuce and sugarcane in the Kumasi metropolis in Ghana, West Africa. The aim is to establish water quality and food safety. Water, sediment and the food crops were sampled along the profiles of Wiwi and Subin rivers for analysis. T-test statistic shows that pH, HCO<sub>3</sub>, Cl, Cu, As, Pb and Ni are significant in water and sediment. Mean concentrations of Cu, As, Pb and Ni in water and sediment are (0.01 mg/kg), (3.08 mg/kg), (4.9 mg/kg), (0.034 mg/kg), (3.08 mg/kg), (0.034 mg/kg), (3.08 mg/kg), (6.034 mg/kg), (0.021 mg/kg), (6.05 mg/kg), (0.024 mg/kg), (3.08 mg/kg), (3.08 mg/kg), (0.034 mg/kg), (3.08 mg/kg), (3.08 mg/kg), (3.08 mg/kg), (0.034 mg/kg), (3.08 mg/kg), (3.08 mg/kg), (0.034 mg/kg), (3.08 mg/kg), (3.08 mg/kg), (0.034 mg/kg), (3.08 mg/kg),  $(3.08 \text$ 

Keywords: Bioaccumulate, Translocation, Subin, Wiwi, Excluders, Sediment, Water, Attenuation

# 1. Introduction

Pollutants in soils are becoming higher by the day due to increasing anthropogenesis (Taghipour, Mosaferi, Armanfar, & Gaemmagami, 2013). Weathering of rocks often mobilizes elements which, when exposed to agents of erosion are transported and re-distributed in the environment (Khirbash & Semhi, 2015). Trace elements distribution in soils depends on the nature of parent material, weathering processes, human activity and climatic conditions (Rezapour, Golmohammad, & Ramezanpour, 2014; Huot, Simonnot, & Morel, 2015). Metals such as As, Pd and Cd can be highly toxic and exhibit complex behaviours and can enter the food chain; exposure of the elevated levels of trace metals in the environment can pose threat to health and life (Xie, Peng, Wang, & Chen, 2017; Hu, Jia, Hu, Xu, Xia, & Li, 2017).

According to Lago-Vila, Arenas-Lago, Andrade and Vega (2014), the availability of metal contents in soil depends on the availability of water, metals present and soil properties. The characteristics of the metals are controlled by the drainage chemistry of the ecosystems, which serves as sinks for the pollutants and constitute ecological risks (Wuana & Okieimen, 2011). The bioavailable fractions of the contaminants present in the ecosystem or geo-matrix provide indicators for risk-based regulatory guidelines for the improvement of food safety (Lago-Vila et al., 2014). Contaminant refers to elements in the available fraction of soils that relates to the concentration of elements in soil solutions and the capacity of transfer from the solid phase (Lago-Vila et al., 2014).

Rapid urbanization in the Kumasi metropolis in Ghana has led to the increased generation of waste and trace metals distribution in geo-hydrologic media (Ahmed & Dinye, 2012; Amoateng, Cobbinah, & Owusu-Adade, 2013). As

noted by Serfes, Spayd and Herman (2005) and O'Shea, Stransky, Leitheiser, Brock, Marvinney and Zheng (2015), trace metals distribution may also be attributed to regional geologic processes, as well as the influx of seasonal metal-laden fine dust from the Sahel region (He, Breuning-Madsen, & Awadzi, 2007). Vehicular movement on feeder roads in the metropolis and rainfall run-offs may contribute trace metals distribution.

An assessment of Pb, Cu, Zn, Ni, and Cd in soils and common food crops such as cassava and plantain was conducted within a small-scale gold-mining environment in the Wassa-Amenfi-West District of Ghana (Zango, Anim-Gyampo, & Ampadu, 2013). Results show the metal concentrations in the soil samples were within the permissible limits of EU standards even though Pollution Load Index indicated significant metal loading. Pb, Cd, Zn and Cu contents in food crops were higher than in soils and exceeded FAO/WHO recommended values for plantain and cassava and pose long-term health conditions from dietary intake (Zango et al., 2013).

The Kumasi metropolis has a history of annual flooding, which results in the replenishment of overbank sediments with plant nutrients and trace metals. Pollution studies in the metropolis by Keraita, Drechsel and Amoah (2003) focussed on the impacts of biological parameters in drainage. Also, Boateng, Opoku, Acquaah and Akoto (2015) show that well-water from the Ejisu-Juaben area has trace elements pollution concerns. Amonoo-Neizer and Amekor (1993) evaluated Total As in soils, water and biological samples in the Kumasi area and published a range from 0.07 to 7.20 mg/kg. All these pieces of research, however, did not highlight mechanisms of the behaviours of the parameters.

A process model to explain the mobility of trace metals in drainage using a relevant conservative tracer is described in Berger, Bethke, and Krumhansl (2000) and Svensson, Lovett and Likens (2012). The model uses the influence of external water, mixing with background water to express the geochemical behaviour of elements (Berger et al., 2000). Chloride (Cl) is commonly used as a conservative tracer because of its low mobility (Svensson et al., 2012). The mobility of Cl is mainly dependent on physical conditions, rather than chemical processes, unless it is present in very high concentrations (Snyder, 2011).

In situations where Cl is too low, an available copiously mobilised anion such as  $SO_4$  may be used as the conservative tracer (Berger et al., 2000) to avoid turning out erroneous interpretations due to low Cl contents (Svensson et al., 2012). Berger et al. (2000) plotted metal contents against the  $SO_4$  and deduced mixing lines by linking the two extremes of the paired data points. Plot values above a mixing line indicate addition of metal ion species to solution through mineral dissolution/desorption while the converse implies the removal from the drainage. Foli, Gawu and Nude (2015) used  $SO_4$  as a conservative tracer in the Obuasi mine environment in Ghana and noted that Fe and As were desorbed into the drainage.

Food crops such as cassava and plantain, together with fruits and vegetables, traditionally serve as food or dietary energy input for humans in sub-Saharan Africa (Chen, Huang, Lai, & Chen, 2015). In the research area, cassava, plantain, sugar cane and cabbage are highly patronised by communities within the catchment of the rivers, where they are grown on both commercial and subsistence basis in areas influenced by overbank sediment or irrigated by water from the drainage systems.

This study evaluated (1) geochemical characteristics of some trace metals in peri-urban drainage; (2) bioaccumulation status of the trace metals in the selected food crops that grow in the drainage environment. The aim was to ensure water quality and food safety in related environments.

# 2. Methods

# 2.1 The Study Area

The study area is located at the extreme north end of the Paleoproterozoic Kumasi basin between the grid limits of 6.5997°N-6.7068°N and 1.5148°W-1.76237°W and covers a land surface area of about 144km<sup>2</sup>. Vegetation is of the semi-equatorial type with annual average temperature and rainfall of about 28°C and 1,340mm, respectively. Drainage pattern is relatively dense and dendritic (Keraita et al., 2015), with flow patterns having a general direction of North-South at the rate of some 0.243m<sup>3</sup>s<sup>-1</sup> (Ahmed & Dinye, 2012).

The underlying geology consists of the Paleoproterozoic Birimian metasedimentary rocks, within about an 80km wide anticlinal basin and intruded by granite-granodiorite suites (Chudasama, Porwal, Kreuzer, & Butera, 2015). The basin is dissected by a 10-20km wide NE-SW trending shear systems permeated by hydrothermal fluid flow and gold mineralisation (Chudasama et al., 2015), with associated sulphide minerals dominated by arsenopyrite and pyrite (Oberthur, Vetter, Mumm, Weiser, Amanor, Gyapong, Kumi, & Blenkinsop, 1994). The sulphide minerals decompose to release trace metals such as copper (Cu), arsenic (As), lead (Pb), nickel (Ni) and zinc (Zn) into soils (Foli & Gawu, 2017, 2018). Auriferous sediments overly the bedrocks and constitute sources of extensive small-scale mining activities (Buadee, Gawu, & Foli, 2018).

## 2.2 Water and Sediment Sampling

Water and overbank sediment samples were taken from 18 sampling sites (SP), 9 each along the profiles of the Wiwi and Subin rivers as presented in Figure 1.



Figure 1. A Sketch map showing study area, water and sediment sample locations

About 500ml-sized clean plastic bottles were used for the water sampling, while about 500g of sediment samples were taken with a clean plastic trowel. Water samples were filtered with cellulose nitrate membrane filters of pore size 0.45µm using vacuum filtration. The filtrates were analysed for pH, bicarbonate (HCO<sub>3</sub>), chloride (Cl), sulphate (SO<sub>4</sub>) and nitrate (NO<sub>3</sub>). Filtrates were acidified using concentrated HNO<sub>3</sub> at pH 2 for trace metals determination.

Split portions of the sediment samples were oven-dried 90°C overnight and digested in aqua regia composed of a mixture of 11.5N HCl and 15.5N HNO<sub>3</sub> at 90-100°C for 1 hour and allowed to stand for 30 minutes. Decanted sample solutions were, filtered and used for the analyses of elements such as copper (Cu), arsenic (As), lead (Pb), nickel (Ni) and zinc (Zn). 100ml of distilled water was added to 200g of the other split samples and prepared for the determination of pH and the anions. Details can be found in Eppinger, Briggs, Rosenkrans and Ballestrazze (1999) and also in a summarised form in Foli and Nude (2012).

#### 2.3 Water and Sediment Sampling

Root and shoot samples of cassava, lettuce, plantain and sugar cane were sampled from three different sites. The samples were washed with distilled water and oven-dried at 60°C to attain a constant weight. The samples were crushed and 2 grams of each sample was digested over a period of 30-60 minutes in a Kjeldahl tube using perchloric, nitric acid and hydrochloric acid in the ratio of 1:2:3 at a temperature of 450°C (Nagornyy, 2013). The mixtures were decanted into volumetric flasks and topped-up to the 100ml mark for trace metals analyses.

## 2.4 Analytical Procedures

The Corning pH/C 107 meter was used to measure pH values, while anions were analysed using ion chromatography (IC) at a detection limit of 0.01mg/l (APHA, 1999). Dilute HCl was prepared to desk reagent standards and then standardised against 40ml 0.05N Na<sub>2</sub>CO<sub>3</sub> using pH meter as an indicator, and used for the titration to determine alkalinity (APHA, 1999). The metals were determined using the ICP-OES at a detection limit of 0.0002mg/l (e.g. Hou & Jones, 2000).

Field-split duplicates were used to estimate analytical precision. Standard solutions containing 10.0mg/l for specific analytes were spiked by adding equal volumes of known concentrations determined at selected sites. The spiking results fall within the acceptable limits of  $\pm 10\%$  when compared with the expected (e.g. Foli & Nude, 2012).

#### 2.5 Metal Ratios and Geochemical Process Modelling

The metal ratio (MR) of the trace metals in the environment can be expressed as:

 $MR = \frac{Concentration of the element in sample}{Background concentration of element} Equation (1)$ 

The MR is interpreted as Low if MR <1; moderate for the range 1-3; considerable for 3-6; and very high for MR  $\ge 6$  (e.g. Olatunji, Abimbola, & Afolabi, 2009). The primary maximum contamination levels (1° MCL) in water and continental crust values for the parameters in sediment are taken from Wilson and Salomon (2002) and Windom (1988), respectively. Binary plots of the trace metals and Cl concentrations in water were generated and the extreme paired data points linked to define a mixing line for determining of the metal availability (Berger et al., 2000; Svensson et al., 2012).

### 2.6 Translocation and Bioaccumulation Factors

Plant-soil relationships were assessed for trace metal accumulation in the plants as translocation factor (TF):

$$TF = \frac{Concentration of the element in shoot}{concentration of the element in root} Equation (2)$$

TF>1 indicates that the plants translocate metals effectively from the root to the shoot (Baker & Brooks, 1989). The higher the TF value, the higher the mobility or availability of the element. Bioaccumulation factor (BF) is defined as

$$BF = \frac{Concentration of the element in plant}{concentration of the element in sediment}$$
Equation (3)

BF >1 indicates that the plant accumulates, while <1 implies that the plant is an excluder (Mganga, Manoko, & Rulangaranga, 2011). Similar as TF, the higher the BF value, the higher the availability of the element in the plant that can be taken up the food chain.

#### 3. Results and Discussions

#### 3.1 Parameter Distributions in Water and Sediment Samples

Parameter values were assessed for p-values at 95% confidence level (CL) using the Anderson-Darling test criteria in the Minitab release 14 software are listed in Tables 1 and 2.

S. No.	pН	HCO <sub>3</sub>	Cl	$SO_4$	NO <sub>3</sub>	Cu	As	Pb	Ni	Zn
1	6.6	32	1.11	6.0	1.3	0.005	2.428	0.024	0.012	0.004
2	6.8	31	1.14	6.0	1.0	0.005	2.904	0.024	0.011	0.003
3	6.9	19	0.42	6.0	1.1	0.008	2.952	0.025	0.016	0.005
4	7.0	20	0.45	7.0	1.2	0.005	2.857	0.032	0.011	0.004
5	7.1	33	0.46	7.0	1.4	0.006	2.743	0.024	0.011	0.003
6	7.1	29	0.81	6.0	1.2	0.006	2.381	0.028	0.023	0.003
7	7.1	38	0.89	9.0	1.3	0.005	2.351	0.029	0.016	0.005
8	7.2	36	0.84	9.0	1.1	0.012	2.842	0.033	0.009	0.004
9	7.3	33	0.88	8.0	1.9	0.015	2.402	0.033	0.008	0.003
10	6.9	44	1.13	6.4	1.4	0.009	3.423	0.041	0.021	0.005
11	6.8	52	1.13	6.0	1.1	0.007	4.343	0.041	0.028	0.004
12	6.9	29	0.73	6.0	1.1	0.009	2.753	0.038	0.022	0.003
13	6.1	31	0.74	6.0	1.7	0.020	4.011	0.044	0.046	0.005
14	6.8	32	1.47	9.0	1.5	0.010	3.548	0.042	0.031	0.004
15	6.7	41	1.47	9.0	1.3	0.017	3.743	0.04	0.044	0.004
16	6.7	39	1.22	9.5	1.1	0.012	3.088	0.036	0.016	0.004
17	6.9	46	1.26	9.0	1.8	0.012	3.412	0.041	0.031	0.005
18	6.7	28	0.98	9.0	1.8	0.018	3.204	0.032	0.021	0.004
Mean	6.9	34	0.95	7.4	1.4	0.010	3.077	0.034	0.021	0.004
p-values	0.187	0.502	0.574	< 0.005	0.024	0.077	0.406	0.145	0.059	< 0.005

Table 1. Parameter con	centrations in	i water sam	pies
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Inorganic parameters are in mg/kg, while pH is quantified in values

S. No.	pН	HCO <sub>3</sub>	Cl	$SO_4$	NO <sub>3</sub>	Cu	As	Pb	Ni	Zn
1	5.9	44.0	1.2	11	4.6	2.1	4.7	4.5	7.8	1.9
2	5.9	39.0	1.1	11	5.2	1.5	5.1	5.8	7.6	2.0
3	5.6	65.0	2.3	12	3.3	2.2	4.2	4.2	5.4	2.0
4	5.8	71.0	2.1	15	3.9	4.7	5.0	4.3	5.5	1.8
5	5.5	55.0	2.2	14	5.2	2.9	4.2	50	7.9	1.9
6	6.0	37.0	1.8	18	2.8	2.1	4.3	5.7	7.7	1.3
7	5.5	41.0	2.4	20	2.7	2.7	4.8	4.5	6.3	1.7
8	5.7	62.0	2.1	13	2.9	3.6	4.8	5.8	4.8	1.4
9	5.8	66.0	3.1	15	3.1	2.5	4.7	3.9	6.8	1.4
10	7.2	55.0	3.6	18	5.3	4.5	5.1	6.2	5.0	1.4
11	6.6	78.0	3.8	14	5.5	2.5	4.4	6.9	4.3	1.5
12	6.5	63.0	3.5	10	5.2	3.1	5.4	7.2	5.2	1.5
13	6.3	61.0	3.4	12	4.4	3.0	5.6	7.1	5.5	1.4
14	6.6	44.0	3.2	19	3.6	5.3	5.2	7.8	5.2	1.9
15	6.4	57.0	2.5	20	2.9	3.8	6.2	8.0	6.6	1.7
16	6.6	42.0	3.2	15	3.1	5.5	5.5	9.4	6.4	1.7
17	6.5	48.0	2.7	12	2.8	3.5	4.3	6.3	5.1	1.5
18	6.3	53.0	3.7	12	2.7	2.8	4.5	9.0	6.6	1.8
Mean	6.2	55	2.7	15	3.8	3.2	4.9	8.7	6.1	1.7
p-values	0.250	0.603	0.352	0.081	0.005	0.225	0.531	0.572	0.134	0.076

Table 2. Parameter concentrations in sediment samples

Inorganic parameters are in mg/kg, while pH is quantified in values

In Tables 1 and 2, pH values and concentrations in both media for CO<sub>3</sub>, Cl, Cu, As, Pb and Ni are significant at p-values >0.05 while NO<sub>3</sub>, SO<sub>4</sub> and Zn are insignificant at p-values <0.05. The mean values of the significant parameters in both water and sediment, respectively, are pH (6.9; 6.2), HCO<sub>3</sub> (34.0mg/l; 55.0mg/kg), Cl (0.95mg/l; 2.7mg/kg), Cu (0.01mg/l; 3.2mg/kg), As (3.08mg/l; 4.9mg/kg), Pb (0.034mg/l; 8.7mg/kg) and Ni (0.021mg/l; 6.1mg/kg).

The concentrations of As, Pb and Ni in water are above the 1° MCL values of 0.05mg/l, 0.015mg/l and 0.020mg/l, respectively, while Cu is below the 1° MCL value of 1.3mg/l. In sediment, Cu, Pb and Ni concentrations are below continental crust background values of 55mg/kg, 12.5mg/kg and 75mg/kg, respectively. The As concentration in this study is thus above the continental crustal background value of 1.8mg/kg and can mobilise in the environment.

The near-neutral mean pH of 6.9 in water probably for accounted for the low concentrations of Cu, Pb and Ni in water, but responsible for the mobilisation of As in the water (e.g. Appelo & Postma, 2005; Foli & Nude, 2012). The dominance of As in the environment may be due to redistribution of elements from mineralised zones associated with deep-seated shear zones flanking the Paleo-Proterozoic Kumasi basin (Chudasama et al., 2015).

Trace metals distribution can be attributed to regional geologic processes such as hydrothermal fluid flow through shear zones (Serfes et al., 2005; O'shea et al., 2015). From these sources, the elements may have migrated by geo-hydrologic processes within the sub-surface into environmental receptors such as streams, rivers, overbank sediments and soils. The low Cl levels in the environment may be explained by the fact that Cl concentrations are very low in in-situ materials. Svensson et al. (2012) noted that Cl has low mobility that is mainly dependent on physical conditions, rather than chemical processes; as such, most rocks release very little of the element into drainage (Snyder, 2011).

## 3.2 Trace Metals Enrichment in Water and Sediment

From equation (1), the metal ratios in both water and sediment are presented in Figure 2.



Figure 2. Metal ratios in water (left) and sediment (right)

In Figure 2 (left), the metal ratio (MR) of 61.60 for As indicates very high contamination in the water, while the MR for Pb and Ni as 2.3 and 1.05 indicates moderate contaminations. MR <1 for Cu imply that the water is lowly contaminated with the metal. In Figure 3(b), As has MR of 2.7, which represents moderate contamination in the sediment, while MR<1 for Pb, Cu and Ni indicates that the sediment is lowly contaminated with the metals. The order of contamination of the metals in both media is generalised as As>Pb>Ni>Cu. Clearly, As, Pb and Ni are of health concern in water for direct consumption since the MR>1. The availability of the element in the aqueous state was estimated from the geochemical process models using Cl as a conservative tracer.

## 3.3 Geochemical Process Model of Trace Metals in Water

From the geochemical model plots for the metals, data points above the mixing line indicate the addition of ions to the drainage, either from mineral dissolution/desorption. Conversely, data points below the mixing line indicate removal of ions from the drainage through mineral precipitation/adsorption. Equal distribution of data points about the mixing line signifies equilibrium between the two scenarios stated above. The model plots are presented in Figure 3.



Figure 3. Process model plots for the significant trace metals using Cl as the conservative tracer

From Figure 3, the data point distribution about the mixing line and the stability interpretations of As, Pd, Ni and Cu are established and presented in Table 3.

Metal	Data points above mixing line	Data points below mixing line	Process	
Pb	50%	50%	Equilibrium	
Cu	50%	50%	Equilibrium	
As	31.25%	68.75%	Adsorption	
Ni	37.5%	62.5%	Adsorption	

Table 3. Interpretation of trace metals behaviours in drainage

From Table 3, Pb and Cu are at equilibrium in both media, while As and Ni are adsorbing from water into the sediment. The implications are that Cu and Pb are likely to have a high residence time in the aqueous state and therefore have the potential for plants uptake, when there is an increase in concentration, whereas As and Ni would attenuate with time under closed conditions.

3.4 Bioaccumulation of Trace Metals in Food Crops

Mean concentrations of the trace metals in soils, roots, shoots and plant (root and shoot) are compared with references for safe consumption (Kabata-Pendias, 2011) as shown in Table 4.

Metal	Soils	- C	Cassava	Lettuce	Plantain	Sugar cane	
	mg/kg dry wt.	Sample	mg/kg dry wt.				
Cu		Root	0.70	0.65	0.78	0.57	
		Shoot	0.74	0.68	0.84	0.52	
	3.2	Plant	0.72	0.67	0.81	0.55	
		Reference	3-6	6-8	1.1-2	73.30	
	4.9	Root	0.016	0.015	0.020	0.010	
As		Shoot	0.021	0.016	0.018	0.020	
		Plant	0.189	0.016	0.019	0.015	
		Reference	10-20	20-50	NA	0.5-62	
	6.2	Root	0.006	0.003	0.025	0.030	
DI.		Shoot	0.005	0.007	0.020	0.011	
Рб		Plant	0.006	0.005	0.023	0.021	
		Reference	0.5-3	0.7-3.6	0.30	111-186	
	6.1	Root	0.065	0.065	0.087	0.080	
NI:		Shoot	0.045	0.075	0.049	0.078	
N1		Plant	0.055	0.070	0.068	0.079	
		Reference	0.29-1.0	0.6-3.3	67.90	10-24	

Table 4. Bioaccumulation data for selected food crops

From Table 4, the mean concentrations of all the four trace metals in the crops are below the reference concentrations published in Kabata-Pendias (2011). The results show that the toxicity levels for dietary intake of the crops are low and therefore pose no risk for consumers. From the shoot, root and soil concentrations, translocation and bioaccumulation factors were estimated using equations 2 and 3 to establish the mobility and availability of the metals in the food crops as represented in Figure 4.



Figure 4. Chart for Translocation and Bioaccumulation Factors of the elements in the food crops

From Figure 4, cassava, lettuce and plantain have TR>1 for Cu; cassava, lettuce and sugarcane have TF>1 for As, while plantain and lettuce have TF>1 for both Pb and Ni. This indicates that the listed plants can translocate the respective metals effectively from the root to shoot. All the food crops have BF<1 for all the trace metals and are therefore excluders in the current state. That notwithstanding, food crops having TR>1 are likely to bioaccumulate the respective trace metals when left too long in the field. Overall, Cu shows the highest tendency of bioaccumulation in the food crops with a significant average BF value of 0.20.

#### 4. Conclusions and Recommendation

The order of contamination of the trace metals in both media is As>Pb>Ni>Cu. Under the current environmental conditions, As, Pb and Ni concentrations are above 1° MCL values for drinking water. From geochemical process models, As and Ni would attenuate in water over time in closed systems, while Cu and Pd are in equilibrium may affect water quality at higher concentrations. The toxicity levels for dietary intake of the food crops are very low and pose no risk for consumers in the current state. All the food crops have bioaccumulation factor (BF) <1 for the trace metals and can, therefore, be considered as excluders under the current conditions. Food crops having translocation factor (TR) >1 for whichever trace metal(s), may bioaccumulate the respective trace metal(s) in the food crop(s) over a prolonged period of growth. It is recommended that the use of the untreated water for direct consumption be avoided to prevent direct intake of high concentrations of As, Pb and Ni. Food crops, grown within the overbank sediments, floodplains or where the water from the rivers is used for irrigation purposes should not be left to overgrow in the field before harvesting.

# **Conflict of interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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