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Toxic Potential, Health and Environmental Risks of Pollutants Detected in the Waters of Oued Larbaa, Taza, Northern Morocco

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ABSTRACT

The Moroccan Inaouen River suffers from significant pollution caused by various human activities. This study aimed to evaluate the concentrations of potentially toxic elements (PTEs) in surface and groundwater from the tributaries of the Inaouen River near Taza, Morocco. The eventual pollution from the public dump of Taza City was investigated using eight sites and fifteen parameters: Temperature, Electrical Conductivity, pH, and twelve PTEs were used to assess the Heavy Metal Pollution Index (HPI), Hazard Quotient (HQ), Hazard Index (HI), and cancer index (CI). Results showed that Al, As, Cd, and Pb concentrations exceeded WHO limits across all sites. Mn, Fe, Ba, and Ni exceeded limits at O2, O3, O4, and O6, closest to the public dump and in the direction of water flow. In contrast, Co, Cr, Cu, and Zn remained within permissible limits. In addition, HPI exceeded permissible limit across all sites. HQ and HI associated with using contaminated water indicated that the HI for Zn, Cu, Ba, Ni, As, Pb, Cr, Mn, Co, and Cd were greater than 1, signifying a potential risk for users of this water. Finally, the CI values of the studied elements allowed them to be ranked in ascending order of toxicity, from least to most toxic: Pb>As>Cr>Cd>Ni. The present results showed that water pollution by PTEs is more significant in surface waters that receive the leachate from the public dump and is not negligible in groundwater, which can have serious repercussions on human health and living organisms, necessitating urgent remediation efforts.

Keywords: Cancer Index, Hazard Index, Hazard Quotient, Heavy Metal Pollution Index

Introduction

In Morocco, the use of surface water for irrigation and human consumption has evolved in response to population growth, increasing agricultural demands, and climatic challenges. Historically, the country has developed significant hydraulic infrastructure, including 104 large dams with a total capacity of 16,091 million m³, regulating approximately nine billion m³ of water to meet irrigation and drinking water needs. However, water availability per capita has declined, dropping from 3,500 m³ per person in 1960 to 645 m³ in 2015, far below the "water poverty" threshold of 1,000 m³. This situation becomes more intense due to the growing water demand, estimated to increase by 3% annually, and the effects of climate change. At the same time, the pollution of surface water resources poses a significant challenge. Industrial discharges, agricultural runoff rich in pesticides and fertilizers, and untreated urban wastewater contribute to water quality degradation.

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This pollution negatively affects water availability for irrigation, creates health risks for human consumption, and harms aquatic ecosystems, emphasizing the need for stricter management and increased efforts for pollution control.4 In this context, the Taza region in Morrocco, part of the Inaouen River's watershed regions, suffers from human activities putting substantial pressure on its water bodies, resulting in physicochemical degradation.3 Potentially toxic elements (PTEs) are critical contaminants in aquatic ecosystems due to their persistence in the environment and their propensity to bioaccumulate within the tissues of fish and other aquatic organisms.^{5,6} Some PTEs, including Zn, Cu, Ni, Co, and Mn, are essential for living organisms' growth and development. They contribute to various biochemical processes at low concentration and play crucial physiological roles.^{7,8} However, their toxicity depends on factors such as the nature of element, concentration, bioavailability, mobility, and the characteristics of the surrounding medium.9 Conversely, other substances, such as Hg and Pb, lack any known physiological function in aquatic species and are considered solely harmful. 10 Even at low concentrations, PTEs like Cu, Pb, As, Cd, and Hg can inhibit photosynthesis and phytoplankton development, resulting in delayed embryonic development, deformities, and stunted growth in fish, mollusks, and crustaceans, and may also impact humans. 11 Several studies have investigated the pollution of the Inaouen River basin, particularly near Taza City, Morocco. Ben-Abbou et al. (2014)¹² reported high levels of physicochemical and bacteriological contamination in the Oued Larbaâ watershed due to untreated urban discharges. More recently, Rezouki et al. (2023, 2024)3,13 examined the effects of heavy metals on macroinvertebrate biodiversity, revealing significant pollution in the upper Inaouen River. However, these studies

did not identify the specific sources of contamination or assess the associated health risks. To address these gaps, this study aims to evaluate the concentrations of potentially toxic elements (PTEs) in surface and groundwater samples from the tributaries of the Inaouen River near Taza. It further examines the relationship between PTE distribution and proximity to the public dump and evaluates the noncarcinogenic and carcinogenic health risks associated with water exposure.

Materials and Methods

The study area and sampling sites

The study's sampling locations were chosen along the lower reaches of the Inaouen River (Figure 1). Six (O1-O6) sampling stations were carefully selected at specific points along the main Inaouen river tributaries positioned before and after the city of Taza's public dump. Two groundwater samples, designated as P1 to P2 were also taken. O5 and P2 served as a reference point far from the municipal solid waste dump and the urbanized area.

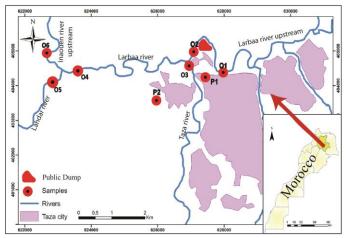


Figure 1: Location of the sampling sites in the studied area

Sampling and pre-processing of samples

Water samples were collected using the grab sampling technique. These samples were taken from key locations, including proximity to the public dump, proximity to residents, and distance from them. Temperature, electrical conductivity (EC), and pH were measured onsite following the standards described in Rodier.14

Physico-chemical analyses

Atomic Absorption Spectrophotometry (model AA-6200Shimadzu, Japan) was used to detect traces of the following Potentially Toxic Elements (PTEs): Al, Fe, Mn, Zn, Pb, Ba, Ni, Cd, Co, Cr, Cu, and As following the standards described by Montarges. 15

Determination of water quality using the heavy metal pollution index

Many authors used the HPI to evaluate the effect of the different heavy metals on the water quality 5,16-18 using the following formula in Equation 1 described by Mohan. 19:

$$HPI = \frac{\sum_{i=1}^{n} QiWi}{\sum_{i=1}^{n} Wi}$$
 (1)

Where;

Qi and Wi are the sub-index and unit weight of the ith parameter, respectively. Therefore, the sub-index (Qi) was calculated by the formula in Equation 2:

$$Qi = \sum_{i=1}^{n} \frac{\frac{M-Ii}{(Si-Ii)}}{(Si-Ii)} \times 100$$
 (2)

Where; "Wi" is the value inversely proportional to the recommended standard "Si" of the corresponding parameter which was calculated following the formula in Equation 3.¹⁹

$$Wi = \frac{1}{Si} \qquad (3)$$

Where; "Mi", "Ii " and "Si " are the monitored heavy metals, the ideal and the standard values of the ith parameter, respectively. According to Mohan *et al.* (1996)¹⁹, an HPI value of 100 is considered

the critical threshold for the pollution index.

Health risk assessment

The risks associated with PTE contamination in water was assessed through two primary exposure pathways, ingestion and dermal absorption, among adults and children residing in the affected area. Both non-carcinogenic and carcinogenic health risk indices were employed, following the methodology outlined by Yahaya et al. (2022)²⁰ and Ougrad et al. (2024).6

Non-carcinogenic risk index

a. Hazard quotient (HQ)

The "HQ" was calculated using the formula shown in Equations 4 to

$$HQ = ADD/RfD \dots (4)$$

Where; RfD is the daily dose likely to have no harmful effects on the consumer's life, and "ADD" is the average daily dose of the PTE absorbed through the skin or ingested, calculated using Equations 7 and 8. "ADD" and "RfD" are expressed in μg/kg/day.

An HO < 1 indicates an acceptable level of risk, while a value greater than 1 indicates an unacceptable non-carcinogenic level of risk.21 The hazard quotient meanings and values of the above parameters are represented in Tables 1 and 2, as given by Ougad et al. (2024).6

$$HQ_{ing} = \frac{ADD_{ing}}{RfD_o}$$
 (5)

$$HQ_{der} = \frac{ADD_{der}}{RfD_{der}}$$
 (6)

$$ADD_{ing} = \frac{CWxIRxEFxED}{BWxAT}$$
 (7)

$$ADD_{der} = \frac{CWxSAxKpxETxEFxEDxCF}{BWxAT}$$
 (8)

b. Hazard index (HI)

The "HI" calculated using Equations 9, 10, and 11 was used to assess the health risks of PTEs in water. An HI > 1 indicates an unacceptable non-carcinogenic health risk.21

$$\begin{aligned} &\text{HI}_{\text{ing}} = \Sigma \text{ HQ}_{\text{ing}} & \qquad \qquad (9) \\ &\text{HI}_{\text{der}} = \Sigma \text{ HQ}_{\text{der}} & \qquad (10) \\ &\text{HI} = \text{HI}_{\text{ing}} + \text{HI}_{\text{der}} & \qquad (11) \end{aligned}$$

Carcinogenic risk (CR) and the cancer index (CI)

The "CR" is used to assess the carcinogenic health hazards associated with exposure to PTEs using the formula in Equation 12. It represents the probability of an individual developing cancer over their lifetime due to prolonged exposure to carcinogenic substances.

$$CR = ADD \times CSF \dots (12)$$

element and each route of exposure. "CSF" is the cancer slope factor; its values are shown in Table 3, and "ADD" is the average daily dose of PTEs.

This study calculated the "CR" for five elements: Cd, Cr, Pb, As, and Ni, known to be carcinogenic, and for the two exposure routes, following the formulas represented by Equations 13 and 14. The "CI" was calculated following the formulas represented by Equation 15. A "CR" and "CI" value greater than 10-4 indicates a high risk of human

$$CR_{ing} = ADD_{ing} \times CSF_{O}$$
 (13)
 $CR_{der} = ADD_{der} \times CSF_{ABS}$ (14)
 $CI = \Sigma CR$ (15)

Statistical analysis

In order to simplify the results, a descriptive statistic was conducted using Microsoft Office Excel.

Table 1: Hazard quotient measurement parameters ⁶

Parameters	Unit	Description	Value		
	Unit	Description	Adult	Children	
		-ADDing is the Average Daily Dose of PTE			
ADD	ug/kg iour	taken by ingestion	Cita aposifia		
ADD	μg/kg-jour	-ADDder is the Average Daily Dose of PTE	Site specific		
		taken by skin contact			
RfD	μg/kg-jour	Reference dose, specific to PTE	Site specific		
Cw	$\mu g/L$	PTE average concentration in water	Site specific		
IR	L/day	Ingestion Rate	2	0.64	
EF	days/year	Exposure Frequency	350	350	
ED	Year	Exposure Duration	30	6	
BW	Kg	Body Weight	70	15	
	dovo	Averaging Time			
AT	days	For non-carcinogens	ED x 350	ED x 350	
		For carcinogens	365 x 70	365 x 70	
SA	cm^2	Exposed skin area	18	6.6	
ET	h/day	Exposure time during bathing and shower	0.58	1	
Kp	cm/hr	Skin Permeability Coefficient in water	Chemical specific		
CF	L/cm ³	Conversion factor	10^{-3}	10^{-3}	

Table 2: Kp and RfD values for the elements studied

Parameters	Kp (cm/h)	RfD ₀ (μ	RfD ₀ (μg/kg/day)		g/kg/day)
		Value	Reference	Value	Reference
Cd	10^{-3}	0.5	29	0.025	29
Co	4×10^{-4}	0.3	29	0.06	29
Cu	10^{-3}	40	29	8	29
Zn	6×10^{-4}	300	29	60	29
Ni	2×10^{-4}	20	29	0.8	29
Mn	10^{-3}	24	29	0.96	29
As	10^{-3}	0.3	29	0.123	29
Cr	2×10^{-3}	3	29	0.075	29
Pb	10^{-3}	1.4	29	0.42	29
Ba	10^{-3}	200	29	14	29
Al	10^{-3}	1000	30	10	30
Fe	10^{-3}	700	30,31	140	30

a. RfD dermal calculated - n.d: not detected

Table 3: CSF values by ingestion and dermal exposure ⁶

Parameters	CSF _o		CSF _{ABS}	CSF _{ABS}		
	Value (mg/kg-jour)-1	Reference	Value (mg/kg-jour) ⁻¹	Reference		
Cd	6.30	32	76.3	a		
Ni	1.70	33	4.25	33		
As	1.50	32	1.50	34		
Cr	0.5	32	20	33		
Pb	0.0085	32	0.085	a		

a: calculated using the following formula: $CSF_{ABS}\!=\!CSF_{o}\,/\,ABS_{gi}$

 $ABS_{gi} \hbox{: gastrointestinal absorption factor} \ ^{35} \hbox{: } ABS_{gi}(Cd) = 0.08; \ ABS_{gi}(Pb) = 0.1$

Results and Discussion

Descriptive statistics of studied variables

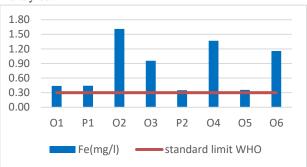
Table 4 compares physicochemical water quality attributes with the WHO Standard Limit (WHO_SL). ²² Based on the result shown in Table 4, the average water temperature and pH were within an acceptable range. However, the average EC exceeded the WHO limit, indicating elevated dissolved salts and ions, likely from natural or anthropogenic sources. Several PTEs exceeded the WHO limits, including aluminum (0.69 mg/L), iron (0.84 mg/L), manganese (1.35 mg/L), lead (0.23 mg/L), nickel (0.17 mg/L), cadmium (0.09 mg/L), cobalt (0.17 mg/L), chromium (0.07 mg/L), and arsenic (0.03 mg/L), indicating significant contamination and health risks. In contrast, zinc (0.60 mg/L) and copper

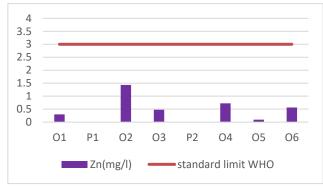
1.5 1 0.5 02 06 Al(mg/l) standard limit WHO 3 2.5 2 1.5 1 0.5 0 Ρ1 02 03 P2 04 05 ■ Mn(mg/l) standard limit WHO 1 0.8 0.6 0.4 0.2 0 03 P2 01 P1 02 04 05 06 Pb(mg/l) standard limit WHO 0.3 0.2 0.1 02 P2 04 05 06 standard limit WHO ■ Ni(mg/l)

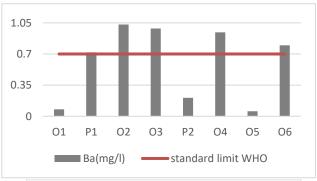
(0.16 mg/L) remain within safe limits, while barium (0.60 mg/L) approaches the threshold, suggesting doubtful contamination.

Spatial distributions of PTEs

Figure 2 illustrates the spatial distribution of PTEs across sampling sites O1, O2, O3, O4, O5, O6, P1, and P2. Fe and Al concentrations exceeded the WHO limit at all the sites. On the other hand, these sites recorded concentrations lower than the WHO limits for Zn and Cu. Surface waters at most sites (O2, O3, and O4) located downstream of the public dump recorded concentrations exceeding the limits for most PTEs analyzed: Al, Fe, Mn, Pb, Ba, Ni, Cd, Cr, and As, suggesting contamination from the public dump. However, groundwater (P1 and P2) recorded concentrations did not exceed the limits for most PTEs analyzed.







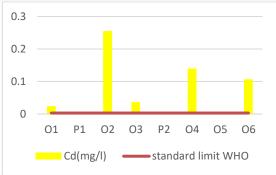




Figure 2: Spatial distributions of PTEs in samples in the study area

Table 4: Descriptive Statistics for Physicochemical and Biological Parameters

Parameter	Unit	Average	SD	min	max	WHO_SL			
T	°C	23.50	2.59	20.3	28.74	Acceptable			
pН	-	7.71	0.40	7	8.27	6.5 < pH < 8.5			
EC	$\mu S/cm$	1736.30	1172.70	874.88	4478.88	2700			
Al	mg/l	0.69	0.24	0.312	0.981	0.2			
Fe	mg/l	0.84	0.50	0.352	1.612	0.3			
Mn	mg/l	1.35	1.18	0.05	2.8	0.5			
Zn	mg/l	0.60	0.46	0.098	1.432	3			
Pb	mg/l	0.23	0.34	0.001	0.895	0.01			
Ba	mg/l	0.60	0.42	0.056	1.032	0.7			
Ni	mg/l	0.17	0.13	0.01	0.323	0.02			
Cd	mg/l	0.09	0.09	0.0028	0.255	0.003			
Co	mg/l	0.17	0.29	0.002	0.754	0.05			
Cr	mg/l	0.07	0.06	0.011	0.184	0.05			
Cu	mg/l	0.16	0.07	0.067	0.265	2			
As	mg/l	0.03	0.01	0.008	0.045	0.01			
	SD: standard deviation								

Water quality using the heavy metal pollution index (HPI)

Based on the average concentrations of the studied parameters, the HPI values represented in Figure 3 ranged from 104.91 (at O5) to 5068.79 at O2 (the nearest site to the public dump). Indeed, the mean value of the HPI for surface waters is 2376.85, which places them above the pollution limit thresholds defined for this index. Similarly, the mean value recorded for well water was 172.51, indicating significant contamination.

These observations highlight a generalized pollution by heavy metals across all the stations sampled. According to the HPI index represented in the Figure 3, the stations were ranked in ascending order of pollution

as follows: O5 has the lowest HPI index (104.91), followed by P2 (137.19), P1 (207.83), O1 (505.90), O3 (1313.84), O6 (3165.48), O4 (4102.16) and O2 which had the highest index (5068.79). The high HPI value at station O2 can be explained by its proximity to the public dump and the reception of leachate. This value is much higher than the values in other aquatic environments receiving industrial discharges, domestic wastewater, and public dump leachate. ²³ The present results showed that water pollution by heavy metals is more significant in surface water than that of groundwater, which can have serious repercussions on human health and living organisms.

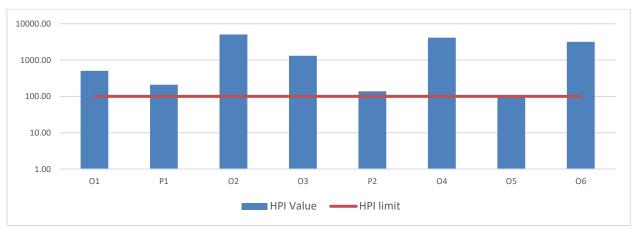


Figure 3: HPI Variation for all sites

Health risk indices

Non-carcinogenic health risk indices

As shown in Table 5, in adults, HQing values ranged from 0.02 for (Al) to 11.64 for (Co), and HQder values ranged from 0.0009 to 411,95 for Al and Co, respectively. In children, HQing values ranged from 0.03 (Al) to 17.39 (Co), and HQder values ranged from 0.002 (Al) to 1215.33 (Co). The elements Mn, As, Cd, Pb, and Co had an HQing greater than 1, and the elements Zn, Cu, Ba, Ni, As, Pb, Cr, Mn, Co, and Cd had an HQder greater than 1 in both children and adults. These results indicate that the above-mentioned elements pose a significant risk to human

health. The HI intervals were 0.02-415.9 in adults and 0.03-1221.23 in children. The HI values of the trace elements studied follow an ascending order: Al, Fe, Zn, Cu, Ba, Ni, As, Pb, Cr, Mn, Co, and Cd. The HI index values of the elements Zn, Cu, Ba, Ni, As, Pb, Cr, Mn, Co, and Cd are greater than 1 and thus present a danger for users of the waters of the Inaouen basin. Children are more exposed to the risks of trace elements through both the digestive and dermal routes since the HQ and HI values are higher in children. The HQder values of the studied elements were higher than those of HQing except for Al in adults and children.

Table 5: Non-carcinogenic health risk indices

PTEs	ADDing μg/kg/jour		ADDder µg/kg/jour		HQ ingestion		HQ dermal		HI	
PIES	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Al	18.85	28.15	0.10	0.29	0.02	0.03	0.0009	0.002	0.02	0.03
Fe	22.89	34.18	119.47	352.46	0.03	0.05	0.17	0.50	0.20	0.55
Mn	32.36	48.32	168.90	498.28	1.35	2.01	175.94	519.05	177.28	521.06
Zn	12.33	18.42	64.37	189.92	0.04	0.06	1.07	3.17	1.11	3.23
Pb	6.40	9.55	33.39	98.52	4.57	6.82	79.51	234.57	84.08	241.39
Ba	16.51	24.65	86.17	254.22	0.08	0.12	6.15	18.16	6.24	18.28
Ni	3.60	5.38	18.81	55.48	0.18	0.27	23.51	69.35	23.69	69.62
Cd	1.97	2.95	10.30	30.38	3.95	5.89	411.95	1215.33	415.90	1221.23
Co	3.49	5.22	18.23	53.79	11.64	17.39	303.90	896.58	315.55	913.96
Cr	1.55	2.32	8.09	23.88	0.52	0.77	107.93	318.41	108.44	319.18
Cu	3.26	4.86	17.00	50.16	0.08	0.12	2.13	6.27	2.21	6.39
As	0.62	0.93	3.26	9.61	2.08	3.11	26.50	78.17	28.58	81.27
Sum					24.54	36.65	1138.76	3359.55	1163.30	3396.20
									ΣHI	4559.50

Carcinogenic health risk indices

As shown in the Table 6, the total carcinogenic risk index (CI) of the elements As, Ni, Cd, Cr, and Pb ranged from 0.0007 to 0.2029 and 0.0012 to 0.345 in children and adults, respectively. These values are higher than 1×10^{-4} indicating that the use of surface and groundwater in the region studied represents a toxic risk for its inhabitants. The CI values of the elements studied allow them to be classified in ascending order, from the least toxic to the most toxic: Pb > As > Cr > Cd > Ni. The CRing and CRder values recorded in adults were higher than those observed in children. In adults, the CRing values were between 0.00002 and 0.0053, and CRder values were between 0.0012 and 0.3425. In children, the CRing and CRder values were between 0.00001 and 0.00154, and between 0.00072 and 0.202, respectively. Cd presented the highest carcinogenic risk when absorbed through the digestive tract,

while Ni presented the highest carcinogenic risk when absorbed through the skin, both for children and adults. Prolonged exposure to these two elements can endanger the living species. Studies have shown the accumulation of certain elements in the tissues of fish living in aquatic environments contaminated by heavy metals. ^{24,25} At low concentrations, cadmium accumulates in tissues and can cause urinary, pulmonary, renal, and bone dysfunction. ²⁶ Cadmium toxicity also affects plants by inhibiting their growth and causing cellular damage by producing reactive oxygen species. ²⁷ Exposure to nickel can lead to pulmonary, renal, nasal, skin, gastrointestinal, cardiovascular diseases, and cancers. ²⁸ Thus, the health risk assessment reveals a trace element hazard for residents who use surface and groundwater for their daily activities

Children Adults Adults Children **PTEs** ADDder ADDing ADDder **ADDing CRing CRder** CI **CRing CRder** Cd 0.00085 0.00441 0.00025 0.00260 0.00533 0.33655 0.34188 0.00154 0.19858 0.20012 Ni 0.00154 0.008060.00046 0.00476 0.00262 0.34254 0.34517 0.00078 0.20211 0.20290 0.00027 0.00140 0.00008 0.00082 0.00040 0.00210 0.00250 0.00012 0.00124 0.00136 As 0.00066 0.00347 0.00020 0.00205 0.00033 0.06938 0.06971 0.00010 0.04094 0.04104 Cr Pb 0.00274 0.01431 0.000820.00844 0.00002 0.00122 0.00124 0.00001 0.000720.00072 0.00871 0.75179 0.76049 0.00255 0.44358 0.44613 Total

Table 6: Carcinogenic health risk indices

Conclusion

This study reveals severe contamination of the Inaouen River near Taza, Morocco, by potentially toxic elements (PTEs), including Al, As, Cd, and Pb. Many elements exceeded WHO limits, with the concentrations of Mn, Fe, Ba, and Ni notably high downstream of a public dump. The Heavy Metal Pollution Index (HPI) confirmed critical pollution levels, peaking at 5068.79. Health risk assessments indicated significant non-carcinogenic risks, particularly for children. Carcinogenic risks from Cd, Ni, As, Cr, and Pb were also identified, with Ni being the most toxic. The results necessitate urgent remediation efforts and enhanced waste management strategies.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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