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Investigation of inorganic nutrients available in Mula and Mutha River from Origin to Pune City, India

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Abstract

The study was aimed to identify the availability of inorganic nutrients in Mula and Mutha River. These were checked at selected locations from their origin to Pune city. The nutrients play an important role in the growth of plants and maintenance of overall aquatic diversity. Even as it becomes very necessary to understand the extent of nutrient pollution levels in rivers as waste discharges are on the rise day by day. The study was based on the hypothesis that lower concentrations of inorganic nutrients are available in waters of Mula and Mutha at the origin places as watershed areas while nutrients are in high concentrations in the city plains. Changes in nutrients could also give ideas about sources of pollution levels alongside the rivers. Overall, the purpose was to collect useful baseline data related to variations in nutrients for designing a river restoration plan.

Keywords: Nutrients, Mula-Mutha, Anions, Cations, Seasonal Variation

Introduction

Hydrological and biogeochemical pathways have been focused by researchers, especially while studying the flowing water bodies as it passes through vegetation, infiltrates the soil, and also becomes part of the groundwater. Many workers have carried out studies on stream chemistry with varying flow conditions¹⁻³. Climate, topography, soil structure, water holding capacity of rocks and overall geologic nature of the basin play an important role in the export of nutrients by rivers. The hydrological cycle governs about the seasonal variations and additions of the freshwaters into the river ecosystems⁴. In general, all rivers have the same stage of structural appearance and every river can be divided into 1) Source zone or productions zone 2) Transfer zone and 3) Deposition zone⁵. The production zone is a steep slope with rapidly flowing waters while the transport zone settles out larger sediments while remaining sediments move ahead with the flow and the last deposition zone accumulates all reaming sediments and materials⁶.

Chemical weathering of rocks, soil leaching, temperature, rainfall, and anthropogenic activities affect the overall chemical composition of the river⁷. Nitrates, nitrites, phosphates, sulfates, and chlorides are the major anions in river water. Nitrogen and phosphorus are the building blocks for enzymes, amino acids, proteins, and other organic compounds hence the most important nutrients8. Nitrogen-fixing bacteria like cyanobacteria fix out the dissolved nitrogen into oxidized forms namely nitrates and ammonium⁸.

Weathering is a major process by which phosphorus comes again into the environment. It is a limiting nutrient in freshwater ecosystems for biota as is always with a low concentration⁹. Phosphorus plays a key role in governing productivity in river waters while low primary production also causes low secondary production of invertebrates and fish¹⁰. Chemical or microbial reactions can cause sulfur to come in water or sediments while sulfur from hydrogen sulfide gas can diffuse into the sediments¹¹. Weathering of rocks and ion exchange in soils cause chloride to come into the river water. Sodium chloride, potassium chloride and potassium, magnesium chloride hexahydrate are common chloride associated minerals¹².

Cations present in river water are sodium, calcium, magnesium, potassium, and ammonium. Various salts and weathering of limestone rocks are the common sources of sodium in river waters. Potassium occurs at lower concentrations than sodium in surface waters but actively participated in the biological process. Carbonate rocks (limestones, dolomites) are the major sources of calcium in river water while gypsum is another source of calcium that is present in sedimentary rocks. Magnesium in river water is mainly due to weathering and dissolution of dolomites, marls, and other rocks (Nikanorov and Brazhnikova). The organically bound nitrogen is transformed into ammonium. It is soluble in water, but in natural conditions, it is not very stable and ammonium is oxidized into nitrates¹³.

Volcanic eruptions act as a natural source which releases trace elements in the atmosphere and hydrosphere¹⁴. Various trace elements act as catalysts in the processes of life, hence are essential for growth and health ecosystems¹⁵.

The trace elements are generally divided into two groups, nonessential and essential elements. Essential elements, mainly Fe, Cu, Mn, and Zn are very much necessary for the metabolism of organisms and all organisms use in the active sites of important enzymes and other proteins¹⁶.

Study Area: The current population of Pune city is approximately 5.9 million. The river Mula originates near Mulshi, 50 km west of Pune city, and meets Pavana at Dapodi. It joins the Mutha at Sangam and together they flow as the Mula-Mutha to Bhima along with Indrayani and Ghod rivers. Pimpri-Chinchwad, Chakan, Talegaon and Ranzangaon industrial areas have significantly to nearby Pune and adjoining areas. Hundreds of large, medium and small scale industries have located nearby Pune. Mulshi dam is built on river Mula, whereas river Mutha is with Temghar, Panshet, and Kadakwasla dam. Mula and Mutha rivers are the major sources of drinking water and irrigation for the people of Pune and nearby areas.

Source and depositional zones are associated with Mula and Mutha river till Pune city. Mula originates at Mulshi and moves eastward towards Akole, PaudGaon, Bhare, and enters Pune city at Balewadi, then passes from Banera-Aundh towards Khadki. It finally meets the Mutha river at Samgamwadi. Source zone for Mula occurs in between Mulshi to Bhare (latitudes 18°31'50.37" and 18°31'44.32") whereas transfer zone for Mula occurs between Balewadi and Khadki (latitudes 18°35'12.02" and 18°34'24.20"). Mutha originates in Vegre village in Mulshi tehsil and moves eastward towards Pune passing through Temghar, Muthagaon, Bahuli, Khudje, and Shivne villages. Mutha enters in Pune city at Warje and moves ahead to Erandwane, Deccan and Kumbharwada and is joined by river Mula at Sangamwadi.

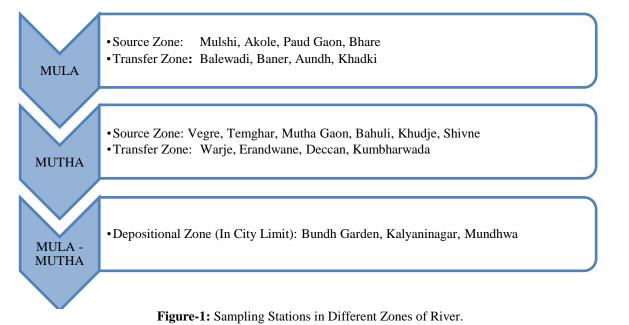
Source zone for river Mutha occurs between Vegre and Shivne in the latitudes of 18°27'49.32" and 18°27'42.65" whereas transfer zone occurs between Warje and Kumbharwada (latitudes 18°28'27.72" and 18°31'54.71"). Mula and Mutha rivers after their confluence at Sangamwadi move forward as Mula-Mutha river towards Bund Garden which occurs in the transfer zone of the river.

Materials and methods

Sampling was carried out for January, February, and March 2017. Grab sampling method was used to collect samples in plastic water bottles. All the samples were analyzed for anions (nitrates, nitrites, sulfates, and phosphates), cations (sodium, potassium, ammonium, magnesium, and calcium) ions of hydrogen and microelements (manganese, iron, zinc, and copper). Microelements are the heavy metals that were analyzed with the help of AAS.

HPIC: Anions and cations were analyzed on HPIC instrument available at the Department of Geology, Savitribai Phule Pune University. The Dionex Integration HPIC System is an integrated high-pressure ion chromatography that provides components and electronics for testing of ion analysis. The basic system includes an eluent area, system status LEDs, an insulated compartment for housing columns and valves, a compartment for housing pump components. It also has a compartment for housing a detector and related devices.

AAS: Heavy metals, namely Zn, Cu, Fe, and Mn were analyzed by using Atomic Absorption Spectrometry (AAS). A more accurate and qualitative analysis of samples is possible with AAS. Metals were analyzed by using the AAS instrument facility available at the Department of Geology, Savitribai Phule Pune University.



Results and discussion

The values of anions, cations and selected trace elements are shown in tabular form. These were collected for the months of January, February and March 2017. The values were collected

for source zone, transfer zone and depositional zones of the rivers. The variations in the selected parameters were reported and possible reasons behind it are quoted.

Table-1: Anions,	Cations and	Heavy I	Metals a	t Source	Zone	of M	ula-Mutha	River.

						Source	Zone							
January	Anions							Cation	IS	Trace Elements				
Mula River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH_4	K	Mg	Ca	Zn	Cu	Fe	Mn
Mulshi	11.32	9.44	27.09	1.16	nd	2.89	0.30	0.44	2.17	5.01	0.13	0.18	0.39	0.04
Akole	10.72	6.92	11.62	nd	nd	2.01	0.27	0.52	1.96	4.91	0.12	nd	0.38	nd
PaudGaon	7.56	0.94	11.87	0.81	nd	2.54	0.39	0.49	2.01	5.52	0.02	0.9	0.042	nd
Bhare	12.22	3.62	13.82	1.95	nd	5.92	0.04	0.24	9.64	24.12	0.09	nd	0.56	nd
Mutha River	Cl	NO_2	SO_4	NO ₃	PO_4	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
Vegre	11.04	1.61	4.97	3.74	nd	4.92	0.8	0.41	3.47	10.22	0.09	Nd	0.45	0.004
Temghar	9.42	9.11	3.83	0.23	nd	3.72	0.11	0.28	1.34	8.72	0.08	nd	0.6	nd
Mutha Gaon	10.54	0.94	4.31	nd	nd	3.66	0.24	0.25	7.78	7.31	0.09	nd	0.4	nd
Bahuli	8.44	2.41	3.64	0.28	nd	3.59	0.39	0.35	2.71	12.65	0.12	nd	0.32	0.072
Khudje	8.34	0.76	3.14	0.62	nd	2.99	0.29	0.24	1.98	4.79	0.18	nd	0.14	nd
Shivne	9.44	0.52	3.71	0.75	nd	4.99	0.04	0.27	1.78	4.94	0.13	nd	0.09	0.025
February			Anions	1	r		1	Cation		1			Elements	
Mula River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
Mulshi	12.07	10.63	29.6	1.18	nd	3.64	0.32	0.59	2.29	5.60	0.15	0.20	0.49	0.05
Akole	11.3	8.62	12.8	nd	nd	3.65	0.39	0.67	2.41	5.71	0.13	nd	0.44	nd
PaudGaon	8.61	1.14	13.41	0.83	nd	3.67	0.49	0.60	2.57	6.61	0.03	0.10	0.58	nd
Bhare	23.44	4.11	14.19	2.14	nd	8.26	0.09	0.39	12.35	35.21	0.16	nd	0.35	nd
Mutha River	Cl	NO_2	SO_4	NO ₃	PO_4	Na	NH_4	K	Mg	Ca	Zn	nd	Fe	Mn
Vegre	11.25	1.86	5.04	4.49	nd	5.60	0.12	0.42	4.39	11.14	0.19	nd	0.34	0.006
Temghar	10.31	1.04	4.83	0.89	nd	4.62	0.14	0.39	1.83	9.26	0.10	nd	0.59	nd
Mutha Gaon	11.31	1.08	5.95	nd	nd	4.39	0.32	0.36	8.11	8.91	0.11	nd	0.48	nd
Bahuli	9.61	2.89	3.83	0.36	nd	4.79	0.43	0.49	3.58	13.96	0.14	nd	0.43	nd
Khudje	8.77	0.55	3.71	1.09	nd	3.33	0.31	0.36	2.00	6.11	0.23	nd	0.159	0.051
Shivne	10.12	1.18	4.01	0.91	nd	6.06	0.07	0.35	10.23	6.53	0.14	nd	0.153	0.025
March			Anions					Cation	is	Trace Elements				
Mula River	Cl	NO_2	SO_4	NO ₃	PO_4	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
Mulshi	13.9	11.43	33.6	1.20	nd	3.73	0.39	0.62	2.38	5.69	0.17	0.21	0.51	0.05
Akole	12.6	10.42	13.01	nd	nd	3.92	0.42	0.83	3.21	6.21	0.14	nd	0.47	nd
PaudGaon	9.61	1.16	8.30	0.85	nd	4.30	0.56	0.72	3.42	7.30	0.04	0.11	0.68	nd
Bhare	9.84	11.43	14.44	2.99	nd	4.48	0.11	0.59	3.16	8.74	0.18	nd	0.92	nd
Mutha River	Cl	NO_2	SO_4	NO ₃	PO_4	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
Vegre	13.17	1.89	5.30	5.91	nd	5.38	0.10	0.49	6.04	12.62	0.19	nd	0.48	0.007
Temghar	11.02	1.50	5.04	1.05	nd	4.92	0.16	0.49	2.09	9.60	0.13	nd	0.70	nd
Mutha Gaon	12.01	2.00	6.37	nd	nd	5.69	1.36	0.57	10.3	9.74	0.14	nd	0.52	nd
Bahuli	10.55	3.14	4.12	0.42	nd	4.87	0.09	0.59	4.38	14.30	0.16	nd	0.49	0.073
Khudje	8.42	1.24	3.38	0.05	nd	3.08	0.34	0.26	2.09	5.74	0.23	nd	0.21	nd
Shivne	11.91	70.71	2.89	1.18	nd	7.83	0.11	0.38	3.91	7.29	0.15	nd	0.17	0.026

Table-2: Anions, Cations and Heavy Metals at Transfer Zone of Mula-Mutha River.

							er Zon									
January	Anions						Cations	Trace Elements								
Mula River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	N	H_4	K	Mg	Ca	Zn	Cu	Fe	Mn	
Balewadi	204.1	0.24	33.41	Nd	10.56	71.96	14	.90	4.69	21.01	77.98	0.11	nd	0.14	nd	
Baner	192.01	0.26	61.43	Nd	17.86	67.01	22	.79	7.44	20.79	72.46	0.19	nd	0.43	0.013	
Aundh	146.9	0.96	62.74	Nd	9.95	44.91	10	.11	17.19	8.32	57.55	0.20	0.02	0.39	0.02	
Khadki	127.7	1 02	60.42	Nd	11.93	34.10	10	.89	7.84	9.99	44.64	0.13	0.04	0.50	0.12	
Mutha River	Cl	NO ₂	${ m SO}_4$	NO ₃	PO_4	Na	N	H_4	К	Mg	Ca	Zn	Cu	Fe	Mn	
Warje	68.46	1.28	9.02	Nd	10.08	22.38	0.	.06	4.44	9.02	35.42	0.24	0.20	0.28	0.045	
Erandwane	70.39	1.98	14.47	Nd	9.92	24.93	8.	96	5.06	7.01	26.41	0.20	nd	0.80	nd	
Deccan	68.11	2.02	14.92	Nd	9.04	24.55	10	.79	2.89	7.14	25.76	0.19	nd	0.80	0.005	
Kubharwada	67.94	1.06	22.69	Nd	5.82	22.92	11	.26	3.22	7.11	28.17	0.08	0.09	0.68	nd	
February			Anions	-					Cations			Trace Elemer			its	
Mula River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH ₄		Κ	Mg	Ca	Zn	Cu	Fe	Mn	
Balewadi	211.01	0.39	35.60	Nd	11.62	73.76	15.13		5.43	22.30	78.33	0.18	nd	0.29	nd	
Baner	194.04	0.46	62.33	Nd	18.46	68.89	23.18		8.39	22.83	73.63	0.20	nd	0.50	0.013	
Aundh	148.3	1.21	63.89	Nd	10.77	47.33	10.39		18.49	9.44	58.93	0.21	0.03	0.29	0.03	
Khadki	128.8	1.31	61.12	Nd	12.84	40.86	12.33		8.22	10.39	45.33	0.13	0.05	0.48	0.14	
Mutha River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH ₄		K	Mg	Ca	Zn	Cu	Fe	Mn	
Warje	69.10	0.92	9.92	Nd	10.81	24.30	0.08		5.38	8.90	36.09	0.26	0.22	0.31	0.045	
Erandwane	71.69	2.42	15.58	Nd	10.86	26.53	9.54		5.13	8.32	30.46	0.21	Nd	0.82	nd	
Deccan	69.32	2.32	15.22	Nd	9.75	26.37	12.13		4.98	8.43	27.77	0.22	Nd	0.85	0.006	
Kubharwada	68.43	1.81	23.89	Nd	6.10	24.8	12.32		4.22	9.12	27.31	0.15	0.10	0.71	nd	
March			Anions			Cations						Trace Elements				
Mula River	Cl	NO_2	SO_4	NO ₃	PO_4	Na	NH ₄		Κ	Mg	Ca	Zn	Cu	Fe	Mn	
Balewadi	223.25	10.42	39.61	Nd	12.12	76.93	15.42		6.44	24.2	79.18	0.24	Nd	0.36	nd	
Baner	208.25	0.92	63.81	Nd	19.78	70.96	24.20		9.15	23.60	74.27	0.20	Nd	0.56	0.014	
Aundh	151.05	1.47	64.48	Nd	11.07	52.42	10.57		19.76	10.80	59.55	0.23	0.04	0.21	0.05	
Khadki	131.87	2.13	61.34	Nd	13.46	45.13	13.02		8.41	12.67	45.62	0.13	0.06	0.54	0.16	
Mutha River	Cl	NO ₂	\mathbf{SO}_4	NO ₃	PO_4	Na	NH ₄		K	Mg	Ca	Zn	Cu	Fe	Mn	
Warje	70.21	2.89	10.01	Nd	11.47	25.32	0.10		5.83	12.87	38.11	0.28	0.24	0.34	0.047	
Erandwane	72.60	2.99	16.82	Nd	11.45	27.33	9.87		5.37	9.01	28.75	0.23	Nd	0.85	nd	
Deccan	71.69	2.42	15.58	Nd	10.17	26.24	13.98		6.39	9.02	29.75	0.24	Nd	0.87	0.006	
Kubharwada	72.36	2.51	24.58	Nd	6.97	26.61	13.85		5.17	9.80	32.03	0.19	0.12	0.73	nd	

Depositional Zone														
January		Anions				Trace Elements								
Mula-Mutha River	Cl	NO ₂	SO_4	NO ₃	PO ₄	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
BundhGarden	159.41	0.32	7.65	nd		23.2	13.94	14.11	8.44	36.21	0.09	nd	0.47	0.066
Kalyaninagar	92.91	0.42	11.22	nd	8.91	24.16	2.10	4.24	9.72	25.35	0.96	nd	0.42	0.046
Mundhwa	93.29	1.02	27.77	nd	8.25	26.81	13.79	6.71	8.42	33.82	0.01	0.04	0.58	0.003
February	Anions						Trace Elements							
Mula-Mutha River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH_4	К	Mg	Ca	Zn	Cu	Fe	Mn
BundhGarden	163.10	1.23	8.34	nd		26.7	14.48	14.98	9.31	37.42	0.11	nd	0.51	0.067
Kalyaninagar	94.80	0.89	12.8	nd	9.14	28.36	2.59	5.31	10.02	26.71	0.12	nd	0.53	0.046
Mundhwa	96.3	1.28	28.3	nd	8.89	29.49	13.83	7.02	9.75	35.81	0.02	0.04	0.62	0.004
March			Anions				Trace Elements							
Mula-Mutha River	Cl	NO ₂	SO_4	NO ₃	PO_4	Na	NH ₄	K	Mg	Ca	Zn	Cu	Fe	Mn
BundhGarden	164.2	1.32	9.72	nd		37.04	16.5	6.92	10.56	38.08	0.12	nd	0.51	0.069
Kalyaninagar	100.29	0.91	14.47	nd	9.85	34.89	3.17	6.95	10.80	27.34	0.13	nd	0.57	0.048
Mundhwa	99.77	1.31	30.79	nd	9.55	35.36	13.95	7.11	10.60	36.50	0.02	0.05	0.66	0.004

Phosphates remain always abundant in sediment and organic particulates. Phosphates are moderately soluble. They are not very mobile in soils and water bodies. The solubility of phosphates is low in river water as they have a strong affinity to suspended particles present in water and also become part of biological systems¹⁷. The phosphates were not detected in the source zone of both the rivers. On the other hand, there are urban and agricultural sources of phosphates that cause them to come into the water. Phosphates are the common constituents of agricultural fertilizers, manure, and organic wastes of sewage and industrial effluents¹⁸. In the current investigation, both agricultural and urban discharges are on the high level that could have caused the availability of the phosphorous in the river especially at the transfer zone as well as a depositional zone.

Nitrites are the intermediates in the nitrogen cycle, are unstable. They are transformed into nitrates or ammonia. Nitrites are also usually used in preservatives. Their presence in water could be associated with municipal, industrial, and mining wastes and with water coming out from artificially fertilized fields¹⁹. Nitrites were observed in the transfer zone and depositional zone of Mula and Mutha as these zones occur in city limits.

In the present study, nitrates were observed in source zone but not in transfer zone and depositional zone because even though nitrates concentration often increases with the flow for the rivers and there is frequently low nitrate concentrations at slow to intermediate flow²⁰, as this study was done in months of January to March which is essentially dominated by spring season these nitrates levels were observed.

Sulfate is the steadiest form of sulfur. Weathering and leaching from sediments are the main sources of sulfate. Natural sulfur emissions have been overtaken by anthropogenic emissions, mainly from the burning of fossil fuels²¹. Sulfate levels in Mula and Mutha river were less in source zone as compared to the transfer zone. Anthropogenic activities mainly sewage, burning of fossil fuels, use of fertilizers, fungicides, and insecticides could be the reasons for the significant presence of sulfate in both zones.

Chloride occurs naturally as a major anion in water bodies. Movement of chloride is not retarded by the interaction of water with soils, sediments and rocks. The concentration of chloride can be used as an indicator of other types of contamination²².

In the present study, chloride levels were comparatively higher in transfer and depositional zone than the source zone. Sewage, agricultural and industrial effluents could be the possible sources of chlorides in the transfer zone and depositional zone.

Magnesium and calcium are highly available alkali metals in the environment²³. Magnesium in water results from the dissolution of aluminosilicates, limestone, magnesium, limestone, magnesite, gypsum, and other minerals. The basic sources of calcium are carbonate rocks (limestones, dolomites). Calcium is more dominated in natural waters than magnesium content. The higher concentrations of calcium were observed in all zones of Mula and Mutha.

Potassium is similar to sodium in terms of its content in Earth's crust and solubility. It has a weak ability to form compounds and can be absorbed by living plants and micro-organisms²⁴ thus Potassium levels were observed to be lesser in selected zones of Mula-Mutha as there was a large infestation of hydrophytes in both the zones of Mula Mutha potassium levels were less.

Zinc is widely recognized as one of the most important trace elements in plant and animal growth and nutrition. It is widely found in fertilizers, animal feed and vitamin supplements²⁵, this is the main reason for zinc to be detected in all zones of river Mula-Mutha as there were agricultural fields near both rivers.

In most aquatic systems, iron is present in higher concentrations than manganese and it interacts more strongly with phosphorus and sulfur compounds²⁶. Our studies also confirmed the higher concentration of iron all the zones rivers. The chief source of manganese in soils comes from crustal foundations. The addition of manganese in soils can result from atmospheric deposition, wastewaters, death, and decay of plants and animal bodies²⁷.

Conclusion

Both the rivers at transitional and depositional zones are on lower altitudes, the velocity of water is lower and the river bed is much wider. As the speed of the rivers is reduced, the concentrations of the inorganic nutrients had increased compared to the stations in the source zone. In addition, the accumulation of nutrients has been observed in the transfer zone and in the depositional zone. Dams are the obstacles for natural flow of water by that way also cause changes in nutrient composition. This is evident from the concentration levels of nutrients observed at Temghar and Akole. The rivers Mula and Mutha, at these sampling stations were on a very low slope rather it was on the plains and had a very slow velocity of flow. At one point these two rivers meet and flow together as a Mula-Mutha. As the flow of water is slower on the plain, the concentrations of inorganic nutrients were observed to be highest compared to the source zone. The sudden increase in chlorides in the depositional zone could be due to anthropogenic

activities like agriculture, sewage treatment plant, dumping of untreated waste in the Mula-Mutha river. Apart from the longitudinal structure, human activities on the rivers at different zones have affected the concentrations of the nutrients. The presence of certain excessive nutrients in the depositional zone has affected the aesthetic as well as the drinking water quality of the Mula and Mutha.

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