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Title: Evaluation of the Heavy Metals Levels in PM10 Particles in air of an urban site of Leon City, in the cold dry climatic season 2018

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Introduction

Currently, air quality degradation represents a serious threat to human health and ecosystems (Molina L. & Molina N., 2004). According to the World Health Organization (WHO), air pollution cause 2 millions of premature deaths a year in the whole world (WHO, 2006).

Particulate matter is a mixture of liquid and solid particles, organic and inorganic substances, which are suspended in the air. The composition of the particulate material is very varied and we can find, sulfates, nitrates, ammonia, sodium chloride, coal, mineral dust, metallic ash and water, as well as certain metals such as As, Cd, Fe, Zn, Cr, Cu, Al, V, Ni and P (Wichman & Peters, 2000). The risks caused by heavy metals in the atmosphere are manifested when their absorption and accumulation in animal tissues exceeds certain limits; however there are metals that are toxic even at low concentrations, such as: Pb, Cd, As and Hg (OSHA). Atmospheric particles are also classified according to their size and, in the field of air quality, we speak of PM10, whose theoretical aerodynamic diameter would be less than or equal to 10 µm.

The general objective of this study was to evaluate the atmospheric levels of trace heavy metals in PM10 particles, their origin and their relationship with criteria pollutants, as well as their impact on health at a site in the city of Leon, Guanajuato during the cold dry climatic season 2018.

Methodology

Study area & Sampling.

León, Guanajuato, México.	
Altitude	1, 798 AMSL
Site location	21.13°N, - 101.68°W
Population	1, 578, 626 inhabitants

The Institute of Ecology of Guanajuato State has an atmospheric monitoring network, measuring the criteria air pollutants and reporting emissions inventories since 2006.

The sampling technique used is a modification of the PM10 reference method described in the United States Code of Federal Regulations (40 CFR part 50, appendix J).

PM10 Sampling using the Minivol sampling device. *Source: Own elaboration from photographs taken at the study site.*

Before sampling, the filters were conditioned at constant temperature and humidity values.

→

After the samples were collected, they were conditioned again at constant temperature and humidity.

→

Each filter was weighed in triplicate with a Sartorious LA 130 SF Analytical Microbalance (with 1 mg resolution) and the results were recorded.

The calculation of the gravimetric concentration is given by the following equation:

$$CPM_{10} = \frac{W_f - W_i}{Vol.} \times 10^6$$

Where:
CPM10 = Gravimetric concentration
Wf = final weight
Wi = starting weight
Vol = standard sample volume

Methodology

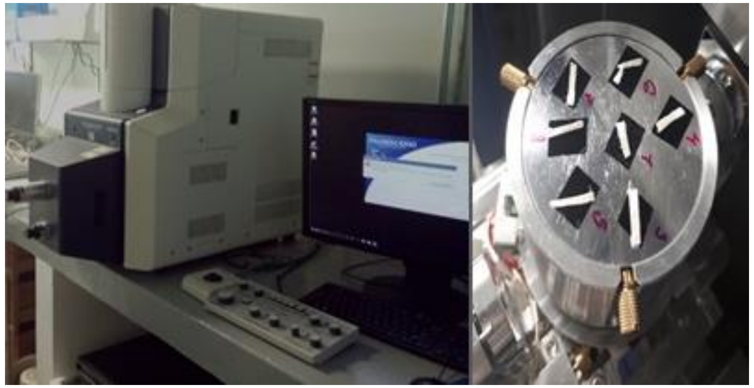
Determination of heavy metals on PM10 (AAS).

Atomic Absorption Spectrophotometer, Thermo Scientific Brand, model iCE 3000 Series AAS used in this work. *Source: Own elaboration from pictures taken in the Laboratory.*

Acid digestion of metals (Machado et al., 2007). For the analysis of the samples, an atomic absorption spectrophotometer was used. Measurements were carried out according to the standard conditions recommended by the spectrophotometer manual, that is, specific wavelengths for each metal. In all measurements, a deuterium lamp was used as a background corrector (Mahecha et al., 2015).

Scanning Electronic Microscopy- Energy Dispersive Spectroscopy Analysis (SEM/EDS) of selected particles.

The analysis was made according to the guide for the monitoring of particles published in 1998 by the EPA. The morphology of the particles and their elemental composition with respect to metal content was evaluated using a Hitachi FLEXSEM-SU1000 (Scanning Electron Microscope) scanning electron microscope equipped with an Energy Dispersive (EDS) X-ray detection system TM 40000 Quantax 75/80 of Bunker that works at 20kV. The low vacuum scanning electron microscope was calibrated with a copper (Cu) grating, a filament current of 300 mA, and a working distance of 5 cm. A 1 mm x 0.5 mm rectangle was cut for analysis and the filters were analyzed as received after sampling, that is, no pre-treatment was necessary for this analysis.



Electronic Microscope used for the elemental and morphological analysis of PM10 particles and view of the filters mounted on the equipment. *Source: Own elaboration from pictures taken in the Laboratory.*

Methodology

Health risk assesment.

The exposure to heavy metals in PM10 was expressed in terms of the daily dose per lifetime (LADD), which helps determine the amount in which a pollutant has negative effects on health when it is absorbed by the human body in a given period of time, and is calculated with the following equations (Di Vaio et al., 2018).

$$LADD = E \times C \qquad (1)$$

$$E = \frac{IR}{BW} \times \frac{ET \times EF \times ED}{AT \times 365} \qquad (2)$$

Where for equation (1), C is the concentration of the metal of interest in PM10, which is assumed to be the same at the point of exposure, while E in equation (1) is obtained from equation (2), where IR ($m^3\ h^{-1}$) is the rate of air inhalation, ET (24 h day^{-1}) is the exposure time, EF (350 day $year^{-1}$) is the exposure frequency, ED (years) is the duration of the exposure, BW (Kg) is the body weight and finally AT (days) is the average time, using ATc for carcinogenic risk and ATn for non-carcinogenic risk (U.S. EPA, 2009).

CR represents the increased likelihood of disease caused by tumors above average due to the impact of compounds that produce carcinogenic effects. Values below 10^{-6} are considered negligible. For carcinogenic substances the CR is determined with the following equation:

$$CR = LADD \times CSF \qquad (3)$$

Where, CR = probability of cancer occurrence during a life time of 70 years, LADD is expressed in mg $Kg^{-1}day^{-1}$. Carcinogenic risk is defined as the increased likelihood of a person experiencing cancer during a lifetime as a result of exposure to a specific carcinogenic potential (U.S. EPA 2009). The SF is calculated with the following equation:

$$SF = IUR \times \frac{BW}{(IR \times ET)} \times 1000 \qquad (4)$$

Where, IUR=Reference value reported in data base by EPA. Inhalation risk units (IUR) and reference concentrations (RfC), only have values for Cd, Co and Mn and are reported by EPA.

Methodology

Health risk assesment.

The non carcinogenic risk, the THQ (risk coefficient) is calculated as follows:

$$THQ = \frac{ADI}{RfDi} \quad (5)$$

Considering that for THQ there is an exposure level (RfDi) below which it is unlikely for any type of population to experience adverse health effects. When the exposure level (ADI) exceeds the stated value of 1, there may be concern about possible non-carcinogenic health risks; THQ values greater than 1 could suggest further concern. The RfDi represents the inhaled dose at which there are considered no negative effects (EPA, 2009) and is defined as:

$$RfDi = RfC \times \frac{20m^3}{day} \times \frac{1}{70kg} \quad (for\ adults) \quad (6)$$

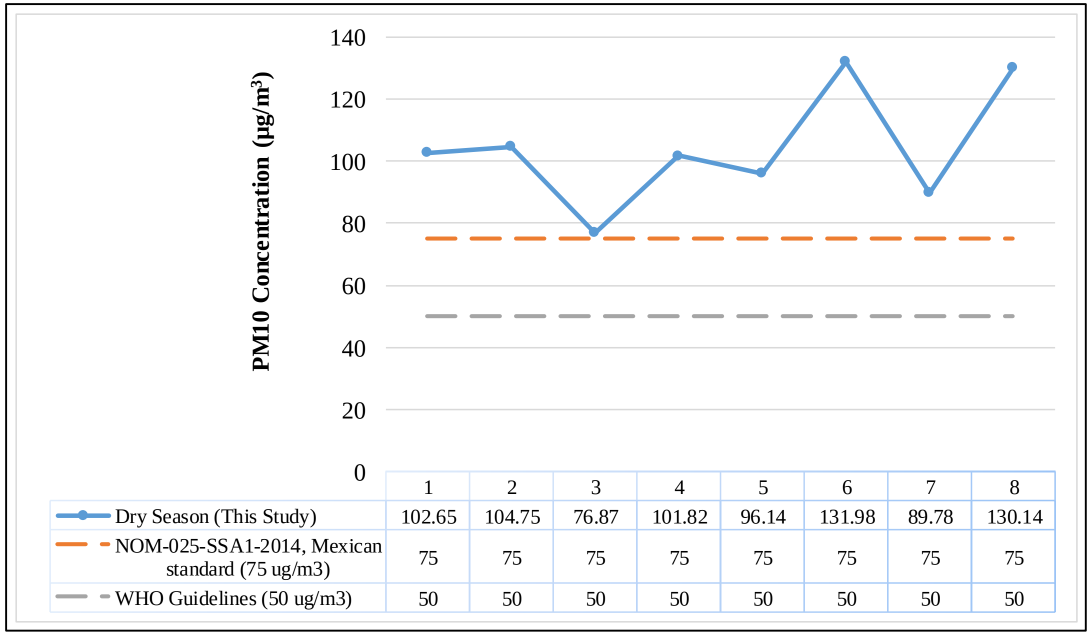
$$RfDi = RfC \times \frac{7.6m^3}{day} \times \frac{1}{15kg} \quad (for\ children) \quad (7)$$

Where ADI, is the estimated dose that the recipient receives from exposure to polluted air (Di Vaio et al,, 2018), and is calculated with the same variables for cancer risk.

$$ADI = E \times C \quad (8)$$

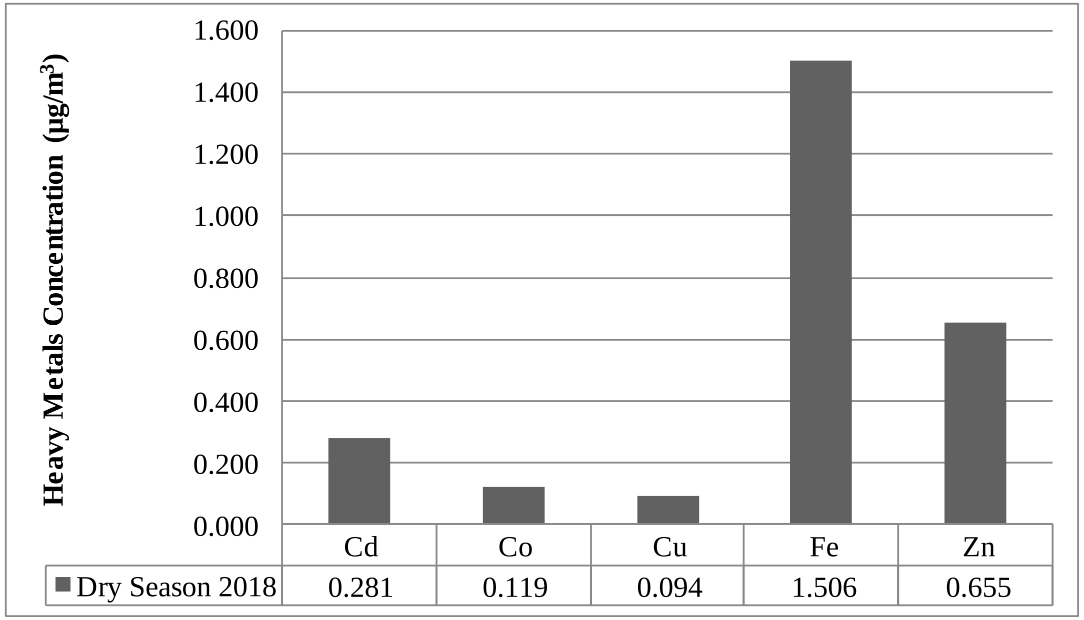
Results

PM10 concentration are shown in the graph below, the daily average values observed in this study were within the range of 76.8 to 130.1 (µgm-3), with an average of 104.2 (µg m -3), exceeding NOM-025-SSAI-2014 where maximum permissible exposure limit in 24 h is 75 (µg m-3), and 2005 WHO guide that indicates risk for the exposed population when the limit of 50 (µg m-3) is exceeded.



This fraction of particulate material is related to primary particles that are mechanically generated in the atmosphere, such as the re-suspension of dust and particles that can come from unpaved highways and roads.

Five metals were detected, Fe and Zn were the metals with the highest concentrations during the study period, probably because Fe is one of the most abundant elements in the earth's crust (Acevedo et al., 2004). Followed in abundance were Cd and Co, Cadmium is observed to exceed the limit established by the WHO (0.015 µg m-3). The anthropogenic contribution of Cd is due to the iron and steel foundry industry (Oldiges & Glaser, 1986) and since this region is an important production area for the foundry industry, the high concentrations found at the site are not surprising.



Results

Morphology and elemental content of particles.

Elemental Content	Identification Code of selected particles				
Al	**991**	**999**	**1005**	**1013**	**1034**
Ba	0.35	0.51	0.39	0.21	0.35
C	12.33		0.39		
Ca	4.59	4.5	7.78	4.47	2.37
Cl	0.49	12.85	0.62		0.23
Cr		0.16		2.08	
Cu					
Fe					
Mg	0.23	0.36	25.29		
Mn	0.31	0.24	0.27		0.40
Na			0.32		
O	0.96	0.34	0.71	0.45	16.36
P	45.88	53.74	42.92	27.09	51.38
Pb		5.5			
S				54.07	
Si	2.48		0.53		9.28
Zn	32.39	21.31	20.78	10.76	18.52
Summation (%)	**100**	**100**	**100**	**100**	**100**

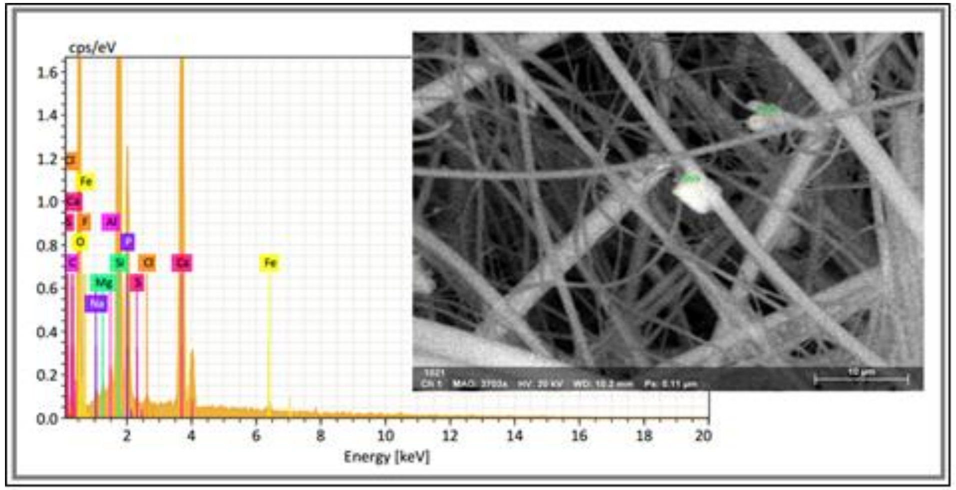
Only the 5 most representative particles are shown for the analysis of their elemental content and 2 micrographs of the three most representative types of particles.

- As it can be observed in the table, particle marked as 991 is rich in C, Ca, P and Zn.
- Particle identified as 999 showed a high content of Cl, P, Zn, Pb and Ca, whereas, particle labelled as 1005 showed high mass percentages of Ca, Mg, P and Zn.
- Particles marked as 1013 and 1034 showed high content of Ca, Cr, P, S and Zn; and Ca, O, P, Si and Zn, respectively.

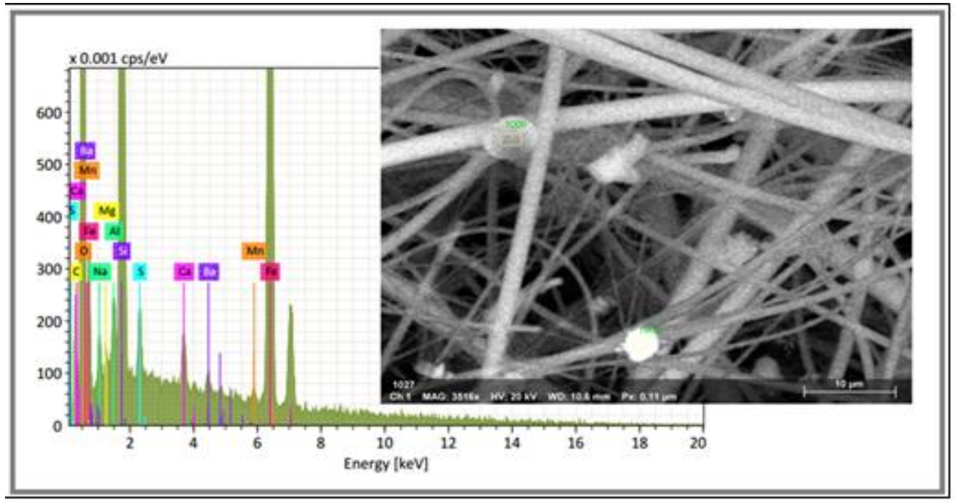
The presence of zinc, phosphorus, calcium and magnesium in the analyzed particles shows the influence of agricultural activities in the area on PM10 particles, since these metals could come from the application of fertilizers on crops. The Bajío area is characterized not only by being an important industrial zone but also by the rise of agriculture at the national level.

Results

Morphology and elemental content of particles.



The particle marked 999 denotes a typical formation of Calcium Carbonates (Calcite). Various studies attribute this mineral to the brick, ceramic and cement industries. The presence of these particles is closely related to processes that involve the firing of bricks and ceramics, where Silica is also present to obtain the products, although little is known about the transformations undergone by the silicate and carbonate phases at the interfaces of reaction (Cultrone et al., 2001).



The spherical shape of particle 1005 is a typical indicator of iron oxides (ferrites). The formation of these spherical particles is an indicator of material melting under oxidizing conditions. The origin of these particles is closely related to processes that involve the condensation of vapors in the atmosphere once they have been emitted by industries such as iron foundry, in this way, an important contribution in the generation of spherical ferrite particles, are steel companies or steel mills (Aragón, 2011). The EDS analysis shows a higher content of O, Fe and Si, which confirms the presence of ferrites.

Results

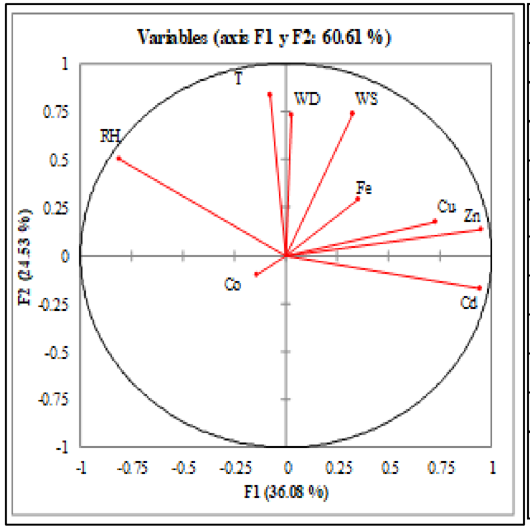
Statistical Analysis.

The table shows a Pearson's correlation analysis, where a strong correlation was observed between Zn with Cd and Zn with Cu (0.84 and 0.66 respectively).

	Zn	Cd	Fe	Cu	Co	WS	WD	T	RH
Zn	**1**								
Cd	**0.84**	**1**							
Fe	0.50	0.19	**1**						
Cu	0.66	**0.57**	0.08	**1**					
Co	-0.39	-0.01	-0.50	0.008	**1**				
WS	0.31	0.26	0.15	0.23	0.32	**1**			
WD	-0.003	-0.04	0.007	0.27	0.37	0.60	**1**		
T	0.130	-0.21	0.13	0.05	-0.45	0.48	0.34	**1**	
RH	-0.66	**-0.90**	0.04	-0.44	-0.12	-0.02	0.26	0.50	**1**

Values in bold are different at a significant level of alfa=0.05; WS: Wind speed; WD: Wind direction; T: Temperature; RH: Relative humidity

These metals are associated with industrial emissions. Cd had a moderate correlation with Cu (0.57), these elements are mainly produced by incineration waste, electricity generation plants and industrial sources (Barratt, 1988).



Square cosines of the variables			
Variables	F1	F2	F3
Zn	**0.908**	0.018	0.062
Cd	**0.893**	0.029	0.014
Fe	0.125	0.087	0.351
Cu	**0.533**	0.030	0.032
Co	0.020	0.010	**0.905**
WS	0.104	**0.543**	0.159
WD	0.001	**0.538**	0.261
T	0.006	**0.700**	0.103
RH	**0.658**	0.252	0.046

Values in bold correspond to those who were significant at a level of significance of alfa=0.05

It can be seen in the bi-plot, two factors (F1 and F2) were needed to explain 60.61% of the variability of the data. 3 groups and variables could be identified where F1 represents the metals (Cd, Cu and Zn) associated with industrial sources, especially Zn that is generated by mobile sources, in road sediments and soil in an area of high vehicular density (Machado et al., 2008). The second group of variables F2, included the meteorological parameters, while the third group F3 included only cobalt, indicating that this metal could have its origin in a different source.

Results

Health risk assesment.

Risk Cancer Coefficient (CR)	Metal	Adult population	Child Population
	Cadmium	4.56 x 10^{-7}	1.14 x 10-7
	Cobalt	9.65 x 10^{-7}	2.41 x 10^{-7}

Average values of carcinogenic risk coefficients of metals.
Source: Own elaboration from calculated data.

Non-cancer Risk Coefficient (Hazard Quotient: HQ)	Metal	Adult population	Child Population
	Cadmium	0.0439	0.205
	Cobalt	0.0310	0.144

Average values of non-carcinogenic risk coefficients of metals.
Source: Own elaboration from calculated data.

The risk coefficients (CR) of suffering cancer in the life time for Cadmium and Cobalt presenting values lower than those established by the WHO (1 x 10^{-6}), however, they are only one order of magnitude below the acceptable limit, so if emissions of particles containing these metals are not reduced, in the future carcinogenic effects related to the inhalation of these metals in PM10. Cancer risk coefficient values were higher for the adult population compared to the child population. These differences may be due to the greater mobility of the adult population due to their work and occupations

The values results for the non-carcinogenic risk (THQ) for cadmium and cobalt must be <1 in order not to present a health risk, as is evident, although the Cd value in infants is higher than in adults, neither of the two metals exceeded this parameter. The above suggests that the child population is at greater risk of suffering some negative effect related to the respiratory tract, however, the risk is low, taking into account that it does not exceed the value established by the WHO of 1.0.

Conclusions

1. The gravimetric concentrations of PM10 in the study site exceeded the maximum permissible limits established by the Mexican Regulations (NOM-025-SAA1-2014: 75 µg m^{-3}) and by the World Health Organization (50 µg m^{-3}).

2. The results of the analysis of the content of heavy metals (Cd, Co, Cu, Fe and Zn) in the collected PM10 particles showed that the dominant metal was Fe, followed in order of importance by Zn during the study period. This finding was to be expected since because these metals are abundant in the earth's crust. Cu and Co were found in lower proportions, Cd was the one that presented the lowest concentrations of all the metals measured.

3. The bi-variate analysis (Pearson's correlation matrix) and the multivariate analysis (Principal Component Analysis) confirmed the anthropogenic origin of Cd, Cu and Zn and their common source (burning of fossil fuels). Co was probably originated from production of batteries, industrial processes of metal refining and the expulsion of smoke and gases from these processes.

Conclusions

4. The results of the health risk assessment showed that the cancer risk coefficients values (CR) did not exceed the threshold value established by the EPA of 10^{-6} for Cd and Co during the sampling season. The non-cancer risk coefficients (HQ) were higher for the child population in both Cadmium and Cobalt, although neither of the two metals exceeded the maximum allowable limit established by the WHO and the EPA.

5. The SEM-EDS analysis of selected particles allowed to study the morphology and content of the main metals in the PM10 samples. From the morphological analysis of the studied particles it was possible to deduce their possible origin. It was confirmed that Fe was the dominant metal in the collected particles with spherical and irregular shapes, so this metal could have its origin beyond natural sources (the earth's crust) and it could be influenced by re-suspension processes, mining, smelting and welding activities.

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