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Status of zinc fractions in soils of Cooch Behar district, West Bengal, India

Sharmme Gogoi[1], G. C. Banik[1], A. Kundu[2], S. Mukhopadhyay[3] and D. Mukhopadhyay[1,*]

[1]Department of Soil Science and Agricultural Chemistry, and
[2]Department of Genetics and Plant Breeding,
Uttar Banga Krishi Viswa Vidyalaya, Pundibari 736 165, India
[3]National Bureau of Soil Survey and Land Use Planning (ICAR), Block DK, Sector-II, Salt Lake, Kolkata 700 091, India

A study was conducted on the distribution of different forms of zinc (Zn) in soils (0–20 and 20–40 cm depths) in different blocks of Cooch Behar district, West Bengal, India. The soils of the selected areas were acidic in reaction (pH) at both the depths, ranging from 4.23 to 6.96 (0–20 cm) and 3.89 to 6.45 (20–40 cm) and having sandy to sandy loam texture. The different fractions of Zn varied among the soils of all locations. The order of different zinc fractions was: exchangeable zinc (Ex-Zn) < organic matter-bound zinc (OM-Zn) < manganese oxide-bound zinc (Mn-Ox-Zn) < crystalline oxide-bound zinc (Cry-Ox-Zn) < amorphous iron oxide-bound zinc (Am-Ox-Zn). Am-Ox-Zn was relatively higher in the soils of Mekhliganj, i.e. 1.56 kg ha^{-1} at 0–20 cm depth and 0.92 kg ha^{-1} in the soils of Tufanganj-II at 20–40 cm depth respectively. Exch-Zn, OM-Zn, Mn-Ox-Zn and Am-Ox-Zn were positively correlated with CEC (r = 0.088, r = 0.105, r = 0.137, r = 0.103) at 0–20 cm depth, while at 20–40 cm depth, Exch-Zn, OM-Zn, Mn-Ox-Zn, Am-Ox Zn and Cry-Ox-Zn were positively correlated with CEC (r = 0.204, r = 0.168, r = 0.342, r = 0.123, r = 0.278). The influence of different soil properties on the distribution of Zn-fractions in the soils was apparent from this study.

Keywords: Acid soil, cation exchange capacity, terai region, zinc fractions.

THERE is continuous mining of not only the major plant nutrients like nitrogen, phosphorus and in some cases potash, but also secondary nutrients like sulphur, calcium and magnesium from the soils. In some regions of West Bengal (WB), India, the deficiency of micronutrients like zinc (Zn), boron and to a limited extent iron, manganese, copper and molybdenum in soils have been reported. This also occurs due to the use of high analysis fertilizers, increasing areas with high-yielding crop varieties or by increasing the cropping intensity which in turn affects the production and productivity of crops. Zn is essential for plant growth and development[1]. In sandy soil, the deficiency of micronutrients is prominent due to the low organic matter content and other available plant nutrients[2]. The different forms of zinc in soils are: primary and

*For correspondence. (e-mail: dibsm107@gmail.com)

Table 1. Geographical locations of the collected soil samples

Serial no.	Block	Gram Panchayat	Latitude	Longitude
S_1	Mathabhanga-I	Pachagarh	26°20′11.87″	89°12′23.4″
S_2		Sikarpur	26°20′18.3″	89°09′56.3″
S_3		Nayarhat	26°24′52.8″	89°07′21.0″
S_4		Jorpatki	26°15′58.67″	89°12′21.87″
S_5	Mathabhanga-II	Unishbisha	26°23′50.7″	89°18′10.0″
S_6		Ghokshadanga	26°24′59.4″	89°18′48.7″
S_7		Nishiganj-I	26°19′08.0″	89°17′34.9″
S_8		Nishiganj-II	26°21′20.6″	89°15′56.7″
S_9	Tufanganj-I	Nakkatigachh	26°18′18.3″	89°39′19.7″
S_{10}		Balarampur-II	26°13′23.1″	89°33′27.1″
S_{11}		Maruganj	26°18′09.9″	89°33′48.4″
S_{12}		Chilakhana-I	26°17′50.9″	89°36′48.9″
S_{13}	Tufanganj-II	Barokodali-I	26°18′47.4″	89°43′00.9″
S_{14}		Barokodali-II	26°18′06.2″	89°42′52.3″
S_{15}		Bhanukumari-I	26°21′49.7″	89°46′27.4″
S_{16}		Bhanukumari-II	26°20′41.9″	89°45′59.2″
S_{17}	Dinhata-I	Bhetaguri-I	26°12′01.4″	89°29′49.1″
S_{18}		Bhetaguri-II	26°11′34.1″	89°29′01.6″
S_{19}		Petla	26°07′54.9″	89°24′56.5″
S_{20}		Gosanimari-I	26°08′22.7″	89°22′17.3″
S_{21}	Dinhata-II	Burirhat-I	26°11′06.3″	89°32′05.8″
S_{22}		Sahebganj	26°06′57.1″	89°32′43.8″
S_{23}		Nazirhat-I	26°10′11.0″	89°34′34.3″
S_{24}		Nazirhat-II	26°10′03.3″	89°35′05.3″
S_{25}	Sitalkuchi	Bara Koimari	26°13′15.8″	89°11′55.2″
S_{26}		Gosairhat	26°12′17.8″	89°12′18.5″
S_{27}		Sitalkuchi	26°09′35.87″	89°11′31.97″
S_{28}		Golenaohati	26°09′21.2″	89°10′54.5″
S_{29}	Cooch Behar-I	Ghughumari	26°17′23.3″	89°26′40.3″
S_{30}		Panishala	26°16′47.3″	89°30′34.4″
S_{31}		Haribhanga	26°13′39.4″	89°28′24.3″
S_{32}		Moamari	26°15′12.9″	89°30′58.6″
S_{33}	Cooch Behar-II	Khagrabari	26°21′50.8″	89°26′074.7″
S_{34}		Madhupur	26°21′55.5″	89°23′05.6″
S_{35}		Pundibari	26°23′56.9″	89°23′32.5″
S_{36}		Patlakhawa	26°27′13.8″	89°22′08.3″
S_{37}	Mekhliganj	Changrabandha	26°27′10.9″	88°56′55.5″
S_{38}		Ranirhat	26°30′16.5″	88°58′0.89″
S_{39}		Jamaldaha	26°26′39.77″	89°0.1′34.97″
S_{40}		Uchalpukuri	26°28′32.0″	89°01′05.6″
S_{41}	Haldibari	Uttar Bara Haldibari	26°22′23.3″	88°46′09.6″
S_{42}		Daxin Bara Haldibari	26°19′22.5″	88°47′48.6″
S_{43}		Dewanganj	26°19′18.5″	88°49′51.4″
S_{44}		Per Mekhliganj	26°19′43.5″	88°50′11.9″
S_{45}	Sitai	Adabari Ghat	26°07′19.0″	89°19′15.7″
S_{46}		Sitai-I	26°04′17.0″	89°18′30.1″
S_{47}		Sitai-II	26°04′10.0″	89°17′31.4″
S_{48}		Brahmattar Chhatra	26°06′11.4″	89°21′22.17″

secondary minerals, insoluble inorganic and organic precipitates, soluble organic complexes, exchangeable and adsorbed forms and soil-solution zinc. The labile zinc pool[3] is influenced by the amount and rate of transformation of zinc fractions, the availability of which is often characterized by soil properties such as the extent to which each fraction is present and its equilibrium between the fractions is influenced by soil properties like pH, cation exchange capacity (CEC), presence of metal oxides and soil organic matter[4], etc. Among the fractions, residual Zn and oxide-bound Zn are more stable than exchangeable Zn (Ex-Zn) and water-soluble Zn (ref. 5) and are influenced by the farming systems[6]. It has been observed that pH and organic carbon in soils affect the variation in extractable cations under Terai (areas prone to heavy rainfall (3000 mm/annum), acidic and light textured soils) conditions of WB[7], although, the distribution of Zn in its various chemical forms may differ in response to changing soil properties[8,9]. Based on the above perspectives, the objective of the present study is to assess the distribution of different forms of zinc in some soils of the Terai region of WB with the hypothesis that the soil properties can play a significant role on the availability of zinc fractions.

A survey was conducted in different blocks of Cooch Behar district, WB (Table 1). A total of 48 composite soil samples from two different depths, i.e. 0–20 and 20–40 cm were collected. These were stored in properly labelled polythene bags and taken to the laboratory for analyses, dried in air, ground using a porcelain pestle and mortar, and passed through a 2 mm sieve and stored. The important physico-chemical properties of the selected soil samples were determined (texture, organic carbon (OC), pH, CEC, etc.) using the standard methods[10]. The zinc fractions from soils were estimated by sequential extraction method[11]. The data obtained were analysed using GenStat version 11.1.0.1504 (VSN International Ltd, Oxford, UK) and GIS-mapping was done using the Arc GIS (version 10.1) software.

The soils in different blocks of Cooch Behar were mostly acidic in reaction, with ranging pH from 4.23 to 6.96 at 0–20 cm and 3.89 to 6.45 at 20–40 cm depth respectively. The native organic carbon (g/kg) in soils varied from 5.03 to 15.13 and 3.42 to 13.58 at 0–20 and 20–40 cm depths respectively.

The exchangeable zinc was maximum in the soils of Dinhata-II with a mean value of 0.81 kg ha^{-1} at 0–20 cm depth and lowest value of 0.13 kg ha^{-1} in Cooch Behar-II soils (Figure 1 *a*). Similarly, at 20–40 cm depth, the soils of Dinhata-II had the higher exchangeable zinc (0.31 kg ha^{-1}) compared to those of Cooch Behar-II, Mathabhanga-I and Sitai (Figure 1 *b*). The buffering capacity of soils for zinc could have a low amount of water-soluble + exchangeable zinc[12]. Similar findings were reported elsewhere by other researchers[13,14]. The soil pH could influence zinc precipitation, thus lowering Ex-Zn in soils[15]. It was observed that Ex-Zn in most of the soils at both depths was less than the critical limit (0.66 mg kg^{-1}), and hence the crops (rice in particular) would face zinc deficiency in such areas. Similar results have been reported elsewhere for rice[16].

The organic matter bound zinc (OM-Zn) at 0–20 cm depth was found maximum in soils of Tufanganj-II (0.87 kg ha^{-1}) and minimum in Cooch Behar-II (0.14 kg ha^{-1}) (Figure 1 *a*). However, at 20–40 cm depth, OM-Zn in the soils of Dinhata-II was found to be maximum (0.34 kg ha^{-1}) and minimum (0.11 kg ha^{-1}) was observed in the soils of Mathabhanga-1 (Figure 1 *b*). The concentration as well as per cent contribution of this zinc fraction was next to that of Ex-Zn. Thus OM-Zn could play a significant role in zinc nutrition of lowland rice[17]. Similar trend of organically complexed (0.3–6%) zinc has been reported[18]. It has been observed that the phyto-available parts (Ex-Zn + OM-Zn) are associated with the geochemical characteristics like CEC and OC of soils.

The manganese oxide-bound zinc (Mn-Ox-Zn) was recorded highest in the soils of Dinhata-II (0.98 kg ha^{-1}) and lowest (0.32 kg ha^{-1}) in Cooch Behar-II at 0–20 cm depth (Figure 1 *a*). At 20–40 cm depth, Mekhliganj soils showed higher value (0.41 kg ha^{-1}) while soils of Mathabhanga-I (0.21 kg ha^{-1}) showed lower Mn-Ox-Zn (0.21 kg ha^{-1}) (Figure 1 *b*). The contribution of manganese oxide bound zinc fraction was next to crystalline iron oxide-bound Zn. This finding is in agreement with that of Shuman[11], who showed that[11] Zn in the crystalline iron oxide fraction was higher than in the manganese oxide fraction.

Among the zinc fractions studied, amorphous iron oxide-bound zinc (Am-Ox-Zn) with the mean of 1.56 kg ha^{-1} (Figure 1 *a*) was observed in the soils of Mekhliganj at 0–20 cm depth and 0.92 kg ha^{-1} in the soils of Tufanganj-II (Figure 1 *b*) at 20–40 cm depth respectively. At 0–20 cm depth, in the soils of Cooch Behar-II, Am-Ox-Zn was found to be lower (0.80 kg ha^{-1}) while at 20–40 cm depth, the soils of Sitai showed the lowest value (0.43 kg ha^{-1}) than the other blocks of Cooch Behar district. The Am-Ox fraction of zinc was relatively higher among the other four Zn fractions in soils, which might be due to the greater ability of amorphous sesquioxide to adsorb Zn with its high specific surface area.

The crystalline iron oxide-bound zinc (Cry-Ox-Zn) was found to be highest in the surface soils of Mekhliganj (1.26 kg ha^{-1}) and lowest in the soils of Cooch Behar-II (0.65 kg ha^{-1}) (Figure 1 *a*). However, at 20–40 cm depth, both Tufanganj-I and Tufanganj-II soils recorded higher crystalline iron oxide-bound zinc of 0.61 kg ha^{-1} (Figure 1 *b*) compared to other blocks. This fraction was dominant

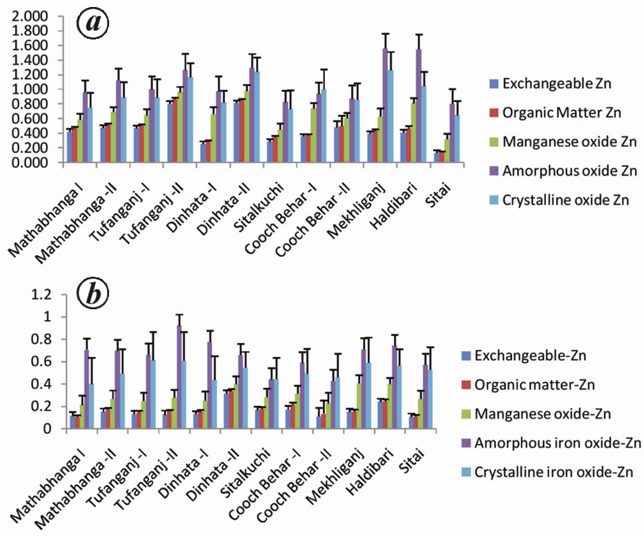

Figure 1. Distribution of zinc fractions in different blocks of Cooch Behar at (***a***) 0–20 cm and (***b***) 20–40 cm depth. The error bars indicate the standard deviation (SD) at $P = 0.05$ level of significance.

Table 2. Correlation coefficient between physico-chemical properties and zinc fractions at 0–20 cm depth

Soil properties	pH	EC	OC	CEC	Clay	Available phosphorus	Exchangeable zinc	Organic matter-bound zinc	Manganese oxide-bound zinc	Amorphous iron oxide-bound zinc	Crystalline iron oxide-bound zinc
pH	1.000	–0.219	–0.001	–0.059	–0.207	0.032	–1.000	0.008	–0.115	–0.218	–0.161
EC		1.000	0.046	–0.148	0.101	0.032	–0.120	–0.117	0.089	0.0262	–0.038
OC			1.000	–0.118	0.142	–0.073	–0.120	–0.109	–0.0854	–0.114	–0.127
CEC				1.000	0.148	0.253	0.088	0.105	0.138	0.104	–0.019
Clay					1.000	0.076	0.023	0.038	–0.018	–0.019	–0.046
Available phosphorus						1.000	–0.056	–0.065	–0.029	–0.112	–0.079
Exchangeable zinc							1.000	0.994****	0.836****	0.633****	0.762****
Organic matter-bound zinc								1.000	0.837****	0.643****	0.742****
Manganese iron oxide-bound zinc									1.000	0.722****	0.757****
Amorphous iron oxide-bound zinc										1.000	0.834****
Crystalline iron oxide-bound zinc											1.000

****Significant at 0.1% level of probability. EC, Electrical conductivity; OC, Organic carbon; CEC, Cation exchange capacity.

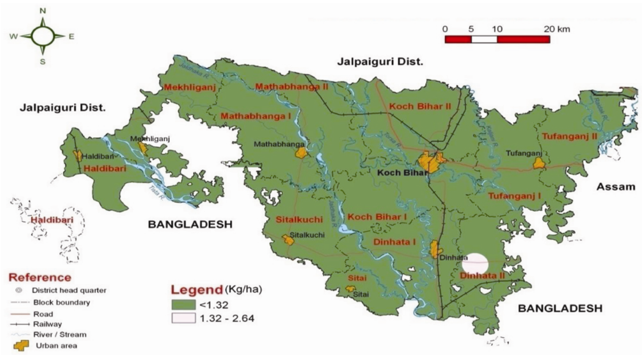

Figure 2. Location map of soil sampling sites and exchangeable zinc (kg/ha) at 0–20 cm depth.

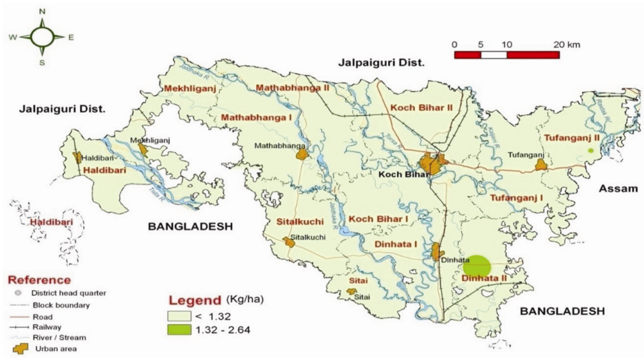

Figure 3. Location map of soil sampling sites and organic matter-bound zinc (kg/ha) at 0–20 cm depth.

compared to (solution + exchangeable) and organically-bound zinc fractions, which may be due to the chemical affinity or specific adsorption of Zn in soil[14]. A negative correlation of the Zn fractions (Mn-Zn, Am-Ox-Zn and Cry-Ox-Zn) with clay content was obtained. This might be due to the varying degree of crystallization of these fractions, which supports the contention of the importance of soil properties affecting Zn-mobilization to plants[19].

A GIS-based map showed that the exchangeable zinc was <1.32 kg ha^{-1} (critical limit for DTPA-Zn for rice) in the blocks of Mathabhanga-I, Mathabhanga-II, Tufanganj-I, Tufanganj-II, Dinhata-I, Sitalkuchi, Cooch Behar-I, Cooch Behar-II, Sitai, Haldibari and Mekhliganj while the same at Dinhata-II varied from 1.32 to 2.64 kg ha^{-1} at 0–20 cm depth (Figure 2). The organic matter-bound zinc, manganese oxide-bound zinc and amorphous iron oxide-bound zinc at 0–20 cm depth of soil were <1.32 kg ha^{-1} in the blocks of Mathabhanga-I, Mathabhanga-II, Tufanganj-I, Tufanganj-II, Dinhata-I, Sitalkuchi, Cooch Behar-I, Cooch Behar-II, Sitai, Haldibari and Mekhliganj (Figures 3–5). In Dinhata-II, the extractable-Zn varied from 1.32 to 2.64 kg ha^{-1}, while the amorphous iron oxide-bound zinc and the extractable-zinc (0–20 cm) were <1.32 kg ha^{-1} in the blocks of Mathabhanga-I, Mathabhanga-II, Tufanganj-I, Dinhata-I, Sitalkuchi, Sitai and Cooch Behar-I and Cooch Behar-II. The blocks of Haldibari, Mekhliganj, Dinhata-II and Tufanganj-II had crystalline zinc varying from 1.32 to 2.64 kg ha^{-1} (Figure 6).

The correlation matrix indicated that pH of the soil had no significant correlation with the different zinc fractions at 0–20 cm depth (r = –0.0003, r = 0.0084, r = –0.1152,

Table 3. Correlation coefficient between physico-chemical properties and zinc fractions at 20–40 cm depth

Soil properties	pH	EC	OC	CEC	Clay	Available phosphorus	Exchangeable zinc	Organic matter-bound zinc	Manganese oxide-bound zinc	Amorphous iron oxide-bound zinc	Crystalline iron oxide-bound zinc
pH	1.000	–0.075	–0.122	–0.143	0.078	–0.073	–0.187	–0.234	–0.444	–0.126	–0.178
EC		1.000	0.076	–0.014	0.055	–0.027	–0.134	–0.074	0.074	–0.095	0.028
OC			1.000	–0.221	0.104	–0.159	0.186	–0.183	–0.194	–0.170	–0.137
CEC				1.000	0.141	0.178	0.205	0.168	0.342	0.123	0.278
Clay					1.000	–0.012	–0.116	–0.097	–0.142	–0.282	–0.063
Available phosphorus						1.000	0.076	0.089	0.083	–0.074	–0.125
Exchangeable zinc							1.000	0.966****	0.813****	0.224	0.638****
Organic matter-bound zinc								1.000	0.828****	0.216	0.651****
Manganese oxide-bound zinc									1.000	0.372**	0.800****
Amorphous iron oxide bound zinc										1.000	0.465****
Crystalline iron oxide bound zinc											1.000

**Significant at 1% level of probability. ****Significant at 0.1% level of probability.

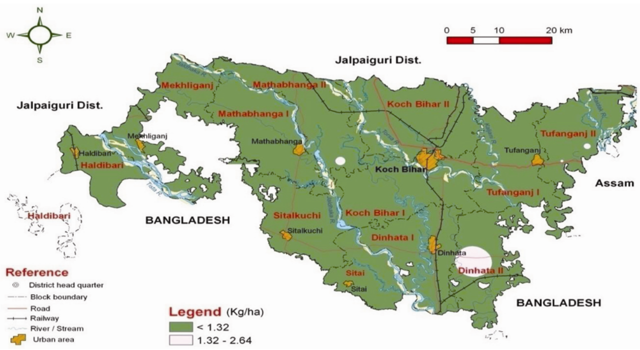

Figure 4. Location map of soil sampling sites and manganese oxide-bound zinc (kg/ha) at 0–20 cm depth.

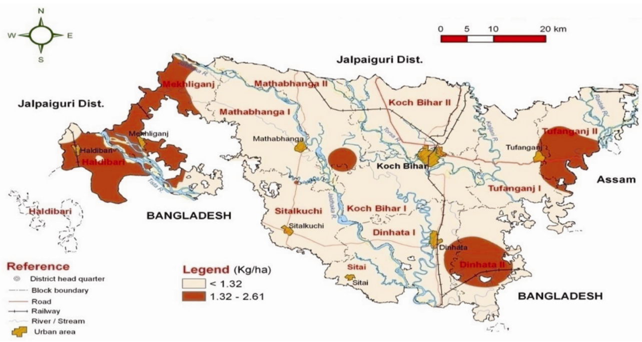

Figure 5. Location map of soil sampling sites and amorphous iron oxide-bound zinc (kg/ha) at 0–20 cm depth.

$r = –0.2179$ and $r = –0.1615$), i.e. Exch-Zn, OM-Zn, Mn-Ox-Zn, Am-Ox-Zn and Cry-Ox-Zn (Table 2) and at 20–40 cm depth ($r = –0.1871$, $r = –0.2340$, $r = –0.4435$, $r = 0.1263$, $r = –0.1782$) (Table 3), but had a positive correlation with CEC (20–40 cm) and negative correlation

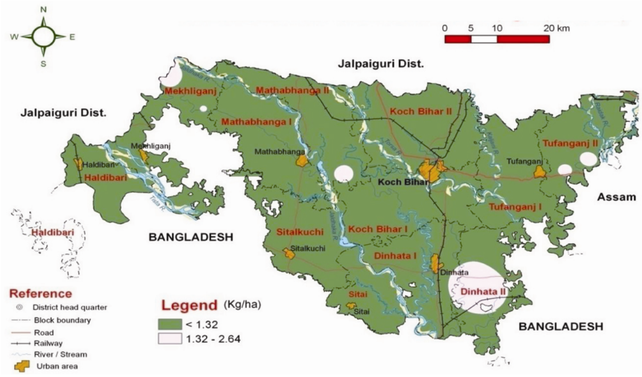

Figure 6. Location map of soil sampling sites and crystalline iron oxide-bound zinc (kg/ha) at 0–20 cm depth.

with clay (Table 3). Similar results were also obtained in other experiments[20]. Among the different zinc fractions, pH showed negative and lowest correlation with exchangeable zinc at 0–20 and 20–40 cm soil layers. This might be due to the fact that at higher pH, the formation of insoluble calcium zincate or higher oxides of zinc reduces the solution concentration[21].

Hence, it can be concluded that the chemical distribution of zinc pools in soils is in the order amorphous iron oxide-bound zinc > crystalline oxide-bound zinc > manganese oxide-bound zinc > organic matter-bound zinc > exchangeable zinc at both soil-depths, i.e. 0–20 and 20–40 cm respectively. Furthermore, zinc mobilization is regulated by different soil properties as reflected during the extraction processes. In this regard, more attention is needed on the phyto-availability of Zn from the Zn-deficient areas with due consideration to the influencing soil properties.

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