e-ISSN: 2687-6698

Research Article

Turkish Journal of
Analytical Chemistry
TurkJAC
https://dergipark.org.tr/tr/pub/turkjac

The effect of naphthalen-1-yl 2,4,6-trimethyl benzenesulfonate on micronutrient and elemental balance in *Zea mays* L. under cadmium stress

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Abstract

Cadmium (Cd) stress disrupts nutrient and elemental homeostasis in plants, thereby inhibiting growth and threatening food safety. Exogenous treatments can mitigate the adverse effects of Cd while enhancing the uptake of essential nutrients from the soil. Although the newly synthesized antioxidant naphthalen-1-yl 2, 4, 6-trimethylbenzenesulfonate (NTB) has demonstrated high free-radical–scavenging capacity in abiotic stress tolerance, studies of its effects remain limited; moreover, no research has examined NTB's impact on the elemental composition of plants under Cd stress. Therefore, this study aimed to evaluate for the first time NTB's potential to improve micronutrient efficiency and restore elemental homeostasis by assessing its influence on nutrient uptake and elemental balance in maize seedlings exposed to Cd stress. Three-week-old seedlings were pretreated with 0.25 mM NTB and then subjected to 100 µM Cd stress. Compared to Cd-stress, NTB+Cd treatment increased manganese (Mn) content by 85.4%, zinc (Zn) content by 43%, iron (Fe) content by 10.4% and copper (Cu) by 14.5%. Elemental analysis revealed that, NTB+Cd treatment exhibited a 5.5% increase in carbon (C) content and a 3% increase in hydrogen (H) content, alongside a 7.5% decrease in nitrogen (N) content; these shifts raised the C: N ratio by 12.7% and lowered the H: C ratio by 2.8% compared to the Cd stress. Notably, S content was detected only in NTB-treated seedlings, reaching 2.4% in the NTB-only treatment and 2.7% in the NTB+Cd. These findings demonstrate that 0.25 mM NTB treatment can effectively alleviate Cd toxicity by enhancing micronutrient uptake and restoring elemental balance.

Keywords: Cadmium stress, elemental status, maize, micronutrient, naphthalen-1-yl 2, 4, 6-trimethylbenzenesulfonate

1. Introduction

Heavy metal pollution, especially Cd, poses a serious threat to agricultural production and environmental health. Due to the high mobility of this toxic element in soils, cadmium rapidly accumulates in plant tissues (roots, leaves, and fruits) and can infiltrate groundwater [1]. Classified as a food contaminant in 1972, Cd is non-biodegradable and persistently accumulates in soils, posing long-term risks to plants, animals and human health [2,3]. This bioaccumulation is associated with chronic outcomes including kidney dysfunction, liver toxicity, bone demineralization, carcinogenesis and tissue necrosis [4,5].

Cd's effects are not limited to its direct toxicity. It also indirectly harms plants by disrupting the uptake of essential mineral elements. Cd enters via the same transporters as zinc (Zn) and copper (Cu), thereby outcompeting these micronutrients and also perturbing iron (Fe) and manganese (Mn) homeostasis. Consequently, enhanced oxidative stress and metabolic disturbances impair plant growth and vigor [6,7]. Nutrient uptake and assimilation must operate cohesively to support optimal plant growth. Cd stress disrupts these processes by inhibiting key enzymes and transporter proteins, leading to nutrient deficiencies and yield losses [8,9]. Therefore, it is essential to mitigate Cd stress and improve nutrient use efficiency for sustainable agriculture [10].

Exogenous compounds have shown promise in counteracting Cd-induced microelement deficits in diverse plant species. For example, foliar ascorbic acid application in barley seedlings suppressed Cd uptake and restored Fe, Mn, Zn and Cu levels [11]. In *Platycladus orientalis*, melatonin enhanced Fe, Mn, Zn, and Cu contents through increased mineral uptake and reduced Cd translocation.

Citation: A. Gümrükçüoğlu, C. Altuntaş, F. Yetişsin, M. Demiralay, The effect of naphthalen-1-yl 2,4,6-trimethyl benzenesulfonate on micronutrient and elemental balance in *Zea mays* L. under cadmium stress, Turk J Anal Chem, 7(3), 2025, 250–256.

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Received: April 10, 2025 **Accepted:** July 8, 2025
doi https://doi.org/10.51435/turkjac.1673423

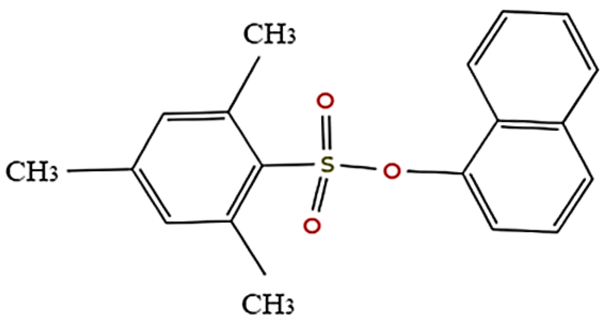

Figure 1. 2D structure of naphthalen-1-yl 2, 4, 6-trimethyl benzenesulfonate (NTB)

Similarly, salicylic acid application in Lemna minor alleviated Cd toxicity by preserving microelement levels and bolstering antioxidant defenses [12]. Furthermore, silicon treatment in Brassica chinensis suppressed Cd uptake and enhanced antioxidant capacity, reinforcing microelement homeostasis [13].

NTB is a recently synthesized naphthalene-sulfonate hybrid compound. Its hydrophobic naphthyl ring and polar sulfonate moiety confer strong affinity for plant biomolecules (Fig. 1). This dual structure enables NTB to attenuate oxidative damage by reducing hydrogen peroxide (H_2O_2) and thiobarbituric acid reactive substances (TBARS) accumulation under abiotic stress [14].

Beyond its basic structural characteristics, NTB offers several advantages compared to traditional sulfur-containing compounds used in mitigating abiotic stress. For instance, reduced glutathione (GSH) is a well-characterized antioxidant known to alleviate cadmium-induced oxidative stress in plants by directly scavenging reactive oxygen species and supporting phytochelatin synthesis [15]. However, the thiol (-SH) group in GSH is highly susceptible to oxidation, which limits its persistence and efficacy under prolonged stress conditions. Similarly, thiourea has demonstrated effectiveness in reducing lipid peroxidation and H_2O_2 levels in Brassica species exposed to heat or cadmium stress, but its protective capacity also diminishes with sustained oxidative pressure [16].

In contrast, NTB's sulfonate group is chemically stable and resistant to oxidation, allowing it to remain functionally active over longer durations [17]. Moreover, the amphiphilic nature of NTB, owing to its combination of a hydrophobic aromatic ring and hydrophilic sulfonate group, facilitates better membrane interaction, potentially enhancing its absorption and systemic distribution within plant tissues [17]. Amphiphilic sulfonates have previously been shown to act as surfactants that improve the foliar penetration and systemic mobility of agrochemicals [18]. Recent evidence supports NTB's superior antioxidant performance in plants. In a study on maize seedlings, certain naphthalene-sulfonate derivatives including NTB significantly reduced oxidative stress biomarkers such as H_2O_2 and TBARS under abiotic conditions, suggesting a promising protective role [14]. Taken together, these features indicate that NTB may provide more stable, efficient, and bioavailable protection compared to conventional thiol-based agents under cadmium-induced stress.

We hypothesize that NTB's unique dual structure combining hydrophobic and hydrophilic properties will enhance micronutrient uptake and restore elemental balance in maize seedlings exposed to cadmium stress. To test this hypothesis, we evaluated NTB's ability to mitigate Cd-induced disruptions in three-week-old maize seedlings under controlled conditions. Specifically, we quantified leaf tissue concentrations of essential micronutrients (Mn, Zn, Fe, and Cu), macronutrient elements (total C, H, N, and S), and calculated the C: N and H: C ratios as indicators of metabolic status. By elucidating NTB's capacity to restore nutrient uptake and maintain elemental balance under cadmium stress, this study provides insights for developing biochemical strategies to enhance crop resilience and sustainability in heavy metal contaminated environments.

2. Materials and methods

2.1. Plant material, growth conditions, and NTB/stress treatments

Seeds of *Zea mays* L. (cv. ADA 523) were obtained from the Sakarya Maize Research Institute. Four seeds were sown in each soil-filled pot. Seedlings were grown for 21 days in a chamber maintained at 60-65 % RH, 400 μmol m^{-2} s^{-1} PPFD, 25 °C ± 2, and a 16:8 h light: dark photoperiod. When seedlings reached the three-leaf stage, their aerial parts were trimmed to a 2 cm length and the roots were placed in tubes of distilled water for 1 h to alleviate transplant shock. Cd (100 μM) and NTB (0.25 mM) concentrations were selected based on previous studies [14,19]. Four treatment groups were established: (i) Control: 18 h DW; (ii) Cd stress: 6 h DW pre-treatment followed 12 h in 100 μM Cd, (iii) NTB: 6 h in 0.25 mM NTB, then 12 h DW, (iv) NTB + Cd: 6 h in 0.25 mM NTB followed by 12 h in 100 μM Cd. After the 18 h treatment period, samples were collected and stored at -20 °C for later analysis. All treatments were replicated in three independent biological replicates (n = 3).

2.2. Measurements of micronutrients by ICP-MS analyzer

2.2.1. Instrument

Elemental concentrations were determined on an Agilent 7900 inductively coupled plasma mass spectrometer configured with a radio frequency power of 1550 watts, a plasma gas flow rate of 15 L/min, an auxiliary gas flow rate of 1 L/min, and a carrier gas flow rate of 1.1 L/min. The spray chamber temperature was maintained at 2 °C, the sample depth set to 8 mm, the sample introduction flow rate adjusted to 1 µL/min, and the nebulizer pump speed operated at 0.1 revolutions per second. All measurements were performed in three replicates. Samples were digested in polytetrafluoroethylene vessels using an Anton Paar microwave reaction system (Germany).

2.2.2. Reagents and solutions

Unless otherwise specified, all reagents were analytical MS grade used. Nitric acid (65%, Merck, Germany) and hydrogen peroxide (35%, Merck, Germany) were used to digest the maize seedlings.

2.2.3. Analytical determination

After acid digestion with microwave assistance, contents of micronutrients (Mn, Zn, Fe, and Cu) were examined using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). Prior to digestion, approximately 1 g of each oven-dried leaf sample (to constant weight at 65 °C) was accurately weighed and recorded. First, each sample was digested in PTFE vessels with 8 mL of 65% (v/v) HNO_3 and 1 mL of 35% (v/v) H_2O_2. The vessels were heated to 185 °C for 20 min, held for 15 min, then cooled to 60 °C over 21 min. Each digest was quantitatively transferred and diluted to 50 mL with deionized water. During ICP-MS analysis, the instrument method included input of each sample's exact dry weight and the dilution factor. Calibration curves were constructed using multi-element standards at known concentrations (0-500 ppb). The ICP-MS software automatically corrected for weight and dilution to report final micronutrient concentrations in mg/kg dry weight (ppm).

2.3. Estimation of carbon, hydrogen nitrogen and sulphur by CHNS (O) analyzer

Leaf samples were dried, ground to powder, and analyzed for C, H, N, and S contents. Organic elemental analysis was performed with a Thermo Fisher Flash Smart CHNS/O analyzer (Thermo Fisher Scientific). Samples were combusted at 950 °C with 240 mL/min O_2 flow during analysis. The combustion gases (CO_2, H_2O, N_2, SO_2) were separated by gas chromatography at 65 °C using helium as the carrier gas (flow rate 250 mL/min) [20].

2.4. Statistical analysis

Experiments were arranged in a randomized complete block design with at least three biological replicates. Data were analyzed using SPSS version 27 (IBM Corp., USA). Duncan's multiple range test was used to identify statistically significant differences ($p< 0.05$). In each analysis, $p< 0.05$ was used to signify statistical significance.

3. Results

3.1. Effects of exogenous NTB on the contents of micronutrients under Cd stress

Table 1 shows micronutrient levels in maize seedlings under each treatment. Mn content increased from 1.09 mg/kg DW in the control to 1.45 mg/kg DW under Cd stress, representing a 24.8% increase ($p< 0.05$). NTB-only treatment elevated Mn to 6.5 mg/kg DW, an 83.2% increase compared to the control ($p< 0.05$), and NTB+Cd treatment further boosted it to 9.93 mg/kg DW, equating to an 85.4% increase compared to Cd stress ($p< 0.05$). Zn content declined from 1.95 mg/kg DW in the control to 1.91 mg/kg DW with Cd stress, corresponding to a 2.1% decrease ($p< 0.05$).

Table 1. The effects of exogenous NTB on micronutrients under Cd stress (mg/kg DW)

Treatments	Mn	Fe	Zn	Cu
Control	1.09 ± 0.01^d	1.95 ± 0.02^c	5.41 ± 0.04^c	1.07 ± 0.02^b
NTB	6.5 ± 0.3^b	2.16 ± 0.3^b	5.85 ± 0.04^b	1.19 ± 0.01^a
Cd	1.45 ± 0.03^c	1.91 ± 0.01^d	5.32 ± 0.03^d	1.00 ± 0.03^c
NTB + Cd	9.93 ± 1.4^a	3.35 ± 0.7^a	5.94 ± 0.01^a	1.17 ± 0.02^a

Mn: manganese; Fe: iron; Zn: zinc; Cu: copper. The difference between the bars with the same letters on the columns is insignificant ($p < 0.05$)

NTB-only treatment raised Zn to 2.16 mg/kg DW, a 9.7% increase compared to control, while NTB+Cd treatment increased it to 3.35 mg/kg DW, a 43% improvement compared to the Cd stress ($p< 0.05$). Fe content fell from 5.41 mg/kg DW in the control to 5.32 mg/kg DW under Cd stress, marking a 1.6% decrease ($p< 0.05$). NTB-only treatment increased Fe to 5.85 mg/kg DW, a 7.5% rise ($p< 0.05$), and NTB+Cd treatment further

Table 2. The effects of exogenous NTB on CHNS analysis of biomasses, based on dry weight (in wt. %)

Treatments	C (%)	H (%)	N (%)	S (%)	C:N	H:C
Control	45.86 ± 0.3^b	6.06 ± 0.04^a	2.74 ± 0.1^c	N/D	16.71 ± 0.2^b	0.132 ± 0.01^c
NTB	46.65 ± 0.3^a	6.02 ± 0.09^a	2.37 ± 0.3^c	2.36 ± 0.21^b	19.71 ± 0.3^a	0.129 ± 0.02^c
Cd	41 ± 0.2^d	5.82 ± 0.02^b	3.05 ± 0.03^a	N/D	13.44 ± 0.12^d	0.142 ± 0.002^a
NTB+Cd	43.41 ± 0.5^c	6.00 ± 0.03^a	2.82 ± 0.02^b	2.74 ± 0.12^a	15.4 ± 0.35^c	0.138 ± 0.001^b

C: carbon; H: hydrogen; N: nitrogen; S: sulfur. The difference between the bars with the same letters on the columns is insignificant ($p < 0.05$). N/D: Not detected

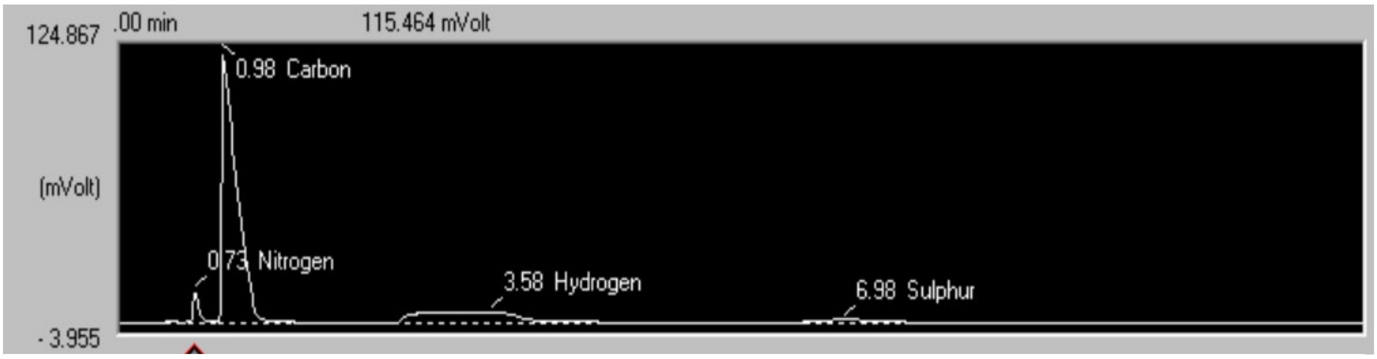

Figure 2. Chromatogram of carbon (C), hydrogen (H) and nitrogen (N) in the optimum CHNS analyzer conditions.

raised it to 5.94 mg/kg DW, representing a 10.4% increase compared to the Cd stress ($p< 0.05$). Cu content decreased from 1.07 mg/kg DW in the control to 1.00 mg/kg DW under Cd stress, corresponding to a 6.5% decrease. NTB-only treatment raised Cu to 1.19 mg/kg DW, a 10% increase ($p< 0.05$), and NTB+Cd treatment elevated it to 1.17 mg/kg DW, a 14.5% increase compared to the Cd stress ($p< 0.05$).

3.2. Effects of NTB on CHNS elemental composition under Cd stress

A representative CHNS chromatogram and elemental composition percentages are shown in Fig.2.

As shown in Table 2, C content increased from 45.86% in the control to 46.65% in the NTB-only treatment, corresponding to a 1.7 % increase ($p< 0.05$), while Cd stress lowered C content to 41%, resulting in an 11% decline ($p < 0.05$). H content did not differ significantly between control (6.06 %) and NTB treatment (6.02%) ($p < 0.05$), but decrease to 5.82 % under Cd stress, but declined to 5.82% under Cd stress, a decrease of 3.9% ($p< 0.05$). N content did not differ significantly between control (2.74%) and NTB treatment, (2.37%), reflecting a 13.5% reduction, but increased to 3.05% under Cd stress, a 10.2% rise ($p< 0.05$). In the NTB+Cd treatment, C reached 43.41% and H reached 6.02%, representing increases of 5.5% and 3%, respectively, compared to the Cd stress (both $p < 0.05$), while N fell to 2.82%, marking a 7.5% reduction ($p< 0.05$). S was undetectable in both control and Cd treatments but appeared at 2.4% with NTB-only treatment and 2.7% with NTB+Cd. The C: N ratio increase from 16.71 in the control to 19.71 under NTB-only treatment, a 15.2 rise, and declined to 13.44 under Cd stress, a 19.6% decrease ($p< 0.05$). The NTB+Cd treatment produced a C: N ratio of 15.4%, which is 12.7 % higher than Cd stress ($p< 0.05$). The H: C ratio remained at 0.132 in the control and 0.129 with NTB-only treatment, increased to 0.142 under Cd stress ($p< 0.05$), representing a 7.04% rise, and then declined to 0.138 with NTB+Cd, representing a 2.8% decrease ($p< 0.05$).

4. Discussion

Cd contamination in agricultural soils poses serious risks to plant, animal, and human health [21]. Soil-accumulated Cd competes with essential micronutrients at membrane transporters, disrupting ion homeostasis and reducing nutrient uptake. This competition ultimately leads to nutrient deficiencies [22,23]. Many studies have revealed that exogenous treatments can effectively reverse Cd's inhibitory impact on micronutrient uptake, restore ionic homeostasis, and substantially mitigate Cd toxicity, offering a promising strategy to enhance plant resilience and productivity in heavy metal contaminated soils [24–27].

Naphthalene and sulfonate derivatives have a wide range of biological activities: anticancer, antibacterial, anti-HIV, anti-inflammatory, antiarrhythmic, enzyme inhibition, abiotic stress tolerance, and metal chelation [28,29]. NTB is a newly synthesized compound that can alleviate drought stress by decreasing oxidative stress level in plants [14 To date, only one study has examined NTB's role in alleviating drought-induced oxidative stress [14]. To our knowledge, no studies have examined NTB's effects on nutrient uptake and elemental composition under Cd stress. Accordingly, to evaluate NTB's protective efficacy under Cd stress, micronutrient (Mn, Zn, Fe, Cu) concentrations and elemental composition (total C, H, N, S, and C: N and H: C ratios) were measured in maize seedlings.

Cd stress competes with root transporters, reducing Fe, Mn, Zn and Cu uptake [22,23]. In the present study, NTB+Cd treatment significantly higher Mn, Zn, and Cu accumulations under Cd stress, highlighting NTB's ability to counteract Cd-induced micronutrient deficiency (Table 1), rebalancing metal homeostasis and alleviating toxicity. Similar benefits have been reported for other exogenous agents: for example, ascorbic acid in wheat reversed Cd-induced losses of Fe, Mn, Zn and Cu, enhanced antioxidant enzyme activities and maintained membrane integrity [25]. Melatonin treatment in *Platycladus orientalis* under Cd stress elevates Fe, Mn, Zn, and Cu levels by 20-50% via upregulation of metal-transporter genes and enhancement of antioxidant defenses [11]. NTB's amphiphilic structure, which features a hydrophobic naphthyl ring and a polar sulfonate group, appears to stabilize cell membranes and sustain transporter activity. Moreover, NTB likely competes with Cd for binding sites, facilitating the movement of essential micronutrients. Together, these dual actions restore metal uptake pathways and bolster antioxidant systems, fully reinstating ionic homeostasis and surpassing the recovery achieved by single antioxidants or mineral supplements.

Cd stress reduces C accumulation and restricts plant growth by inhibiting photosynthetic CO_2 fixation and related enzyme activities. Cd also disrupts nitrate uptake and sulfate assimilation, disturbing N and S metabolism. This reduces tissue N content and depletes S-containing thiol defenses [30]. Moreover, Cd-induced stomatal closure and osmotic stress further reduce leaf hydration, adversely affecting tissue H content [31]. In the present study, NTB treatment reversed these imbalances: C and H were restored and N and S levels normalized (Table 2). NTB likely improved C retention by preserving photosynthetic function and promoting C-rich osmolyte accumulation. It balanced tissue N%, and stimulated S assimilation to replenish thiol pools. Numerous studies demonstrate that exogenous antioxidants and S donors restore elemental balance and bolster defense systems in Cd-stressed plants. Melatonin enhances S assimilation and raises glutathione and phytochelatin levels under Cd stress [32]. Thiourea provides bioavailable S and boosts antioxidant capacity under heavy-metal stress [33]. Salicylic acid reactivates N and S metabolism, boosting stress-related metabolites [34]. NTB's amphiphilic structure, which consists of a hydrophobic naphthyl ring and a polar sulfonate group, may stabilize lipid membranes and scavenge reactive oxygen species, potentially restoring C, H, N, and S homeostasis disrupted by Cd.

5. Conclusion

In this study, we showed that cadmium stress severely impairs maize seedling performance by disrupting micronutrient uptake and altering elemental composition. The exogenous application of NTB reversed these effects. Under Cd stress, NTB pretreatment restored Mn, Zn, Fe, and Cu levels to match or exceed those of untreated controls, thereby reestablishing metal balance. NTB also corrected Cd-induced shifts in C and H contents and normalized the C: N and H: C ratios. S became detectable only in NTB-treated plants, indicating activation of thiol-based defense mechanisms.

Overall, NTB alleviates Cd-induced micronutrient deficiencies by enhancing essential metal uptake and preserving elemental integrity. By preserving membrane transporter function and homeostasis of C, H, N, and S, NTB significantly enhances maize seedling tolerance to heavy-metal stres. These findings suggest that NTB offers a promising biochemical approach for improving plant growth and nutrient efficiency in contaminated soils.

Future study should elucidate NTB's molecular mechanisms by examining its effects on metal-transporter gene expression, thiol metabolite synthesis and photosynthetic performance, with transcriptomic and metabolomic analyses guiding the discovery of its protective pathways.

Acknowledgments

Thanks to PhD Adem KORKMAZ, who synthesized the NTB, and Sakarya Maize Research Institute, Türkiye that supplied the maize seeds, cultivar ADA-523.

Ethical approval

Not applicable

Consent to participate

Not applicable

Consent to publish

The study described has not been published before, that it is not under consideration for publication anywhere else, and that its publication has been approved by all co-authors.

Authors contributions

FY and MD conceived and designed the present study and have supervised this study. CA and AG performed the experiments. The analysis and interpretation of the results were carried out by CA and AG. The drafting of the manuscript was carried out by CA with the assistance of AG. All the authors contributed and reviewed the results and approved the final manuscript.

Funding

This study was not financially supported by anybody or any organization.

Competing interests

The authors declare no competing interests.

Data availability

All data analyzed during the study are included in this article.

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