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# Leaching Losses of Nutrient Cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) from Oxisol and Ultisol Under Different Rates of Acidic Deposition in Thailand

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Leaching losses of plant nutrients were estimated from two soil orders (oxisol and ultisol) under different rates of acidic deposition. Leaching experiments were conducted in the laboratory by applying {acidic (pH 5.0, 4.0, 3.5, 3.0, 2.5, 2.0) and non-acidic (7.0, control)} treatments to soil columns. The results showed that leaching losses of nutrients increased significantly (p value < 0.001) as the pH of applied solutions decreased. Quite high leaching losses of nutrient cations were found in both soils under moderately to highly acidic treatments. Leaching losses by acid rain from oxisol and ultisol depended not only on acid rain pH but also on weatherable minerals, original nutrient status, cation exchange capacity and soil texture. Leaching losses of plant nutrients were quantified by polynomial regression equations. There were very good correlations between acidic levels of treatments and leaching amount of nutrient cation in oxisol [$K^+$ ($R^2$ = 0.98), $Ca^{2+}$ ($R^2$ = 0.97) and $Mg^{2+}$ ($R^2$ = 0.96)] and ultisol [$K^+$ ($R^2$ = 0.97), $Ca^{2+}$ ($R^2$ = 0.92) and $Mg^{2+}$ ($R^2$ = 0.92)]. Significant losses of major plant nutrients from the plant root zone would affect soil quality, reduce soil productivity and degrade ground water quality.

**Keywords: Leaching losses, Acid rain, Nutrient cations, Highly weathered soils.**

## INTRODUCTION

Acid rain occurs when acidifying gases ($SO_2$ and $NO_x$) form acidic compounds in the atmosphere by reacting with water, oxygen and oxidants. Such acidic compounds ($H_2SO_4$ and $HNO_3$) acidify surface water bodies (lakes and streams), damage sensitive ecosystems and enhance the decaying process of buildings[1]. Acid deposition alters soil chemistry and causes acidification and mobilization of toxic elements in lakes and streams, which harm aquatic life[2]. Acidic deposition causes damaging effects on forest trees such as reduced tree growth, poor crown condition and high level of tree mortality[3]. Effects of acid deposition on soil system include depletion of base cations and nutrients[3] and dissolved organic matter[4]. Low soil pH increases mobility of toxic elements[5-8].

Leaching loss of nutrient cations caused by acid rain is a critical problem from agricultural and environmental point of view. Many studies showed the leaching impacts of acid rain[4,9-11], this study is focusing on the quantification of nutrients' leaching losses from oxisol and ultisol soils of Southeast Asian countries (*e.g.* Myanmar, Cambodia, Malaysia, Indonesia, Vietnam and Thailand). In this region, most of the soils' have formed by weathering of coarse-grained sediments having high quartz contents and were highly weathered at the time of deposition. Kaolinite is the most common mineral domain for the yellow and red oxisols and ultisols upland soils in the northeast. Soils having kaolinite can be categorized as Kandiustults, Paleustults, Kandiudults and Paleudults. Cultivation of paddy rice is common in the low-lying areas. Various cash crops, vegetables and fruit trees are cultivated on the higher areas of the flood plain[12].

Consequently, soils of this region have low weatherable mineral contents and plant nutrients[11,13-16]. The problem of acid deposition has been observed in Asian countries due to urbanization and rapid industrialization[10,17-22]. The main objective of this paper was to estimate the leaching losses of nutrient cations [potassium ($K^+$), calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$)] in agricultural soils (oxisol and ultisol) by simulated acid rain.

## EXPERIMENTAL

A laboratory experiment was conducted on two selected soil orders: Oxisol [Pak Chong (PC)] and Ultisol [Korat (Kr)] were selected from the Northeast region of Thailand. Collected soil samples (30 cm soil layers) were air dried under shade, ground, mixed thoroughly and sieved (2 mm mesh) to prepare soil columns. Selected properties of soil samples were determined including soil pH, particle size distribution by hydrometer method[23], soil organic matter by wet-oxidation method[24] and cation exchange capacity (CEC) by 1*N* ammonium acetate[25]. Soil columns were prepared using plastic cylinders (15 × 35 cm) having porous plate at the bottom with filtering material (Fig. 1). The experiments were carried out on 42 soil columns *i.e.* 2 soil types × 7 acid loading rates × 3 replications for each treatment.

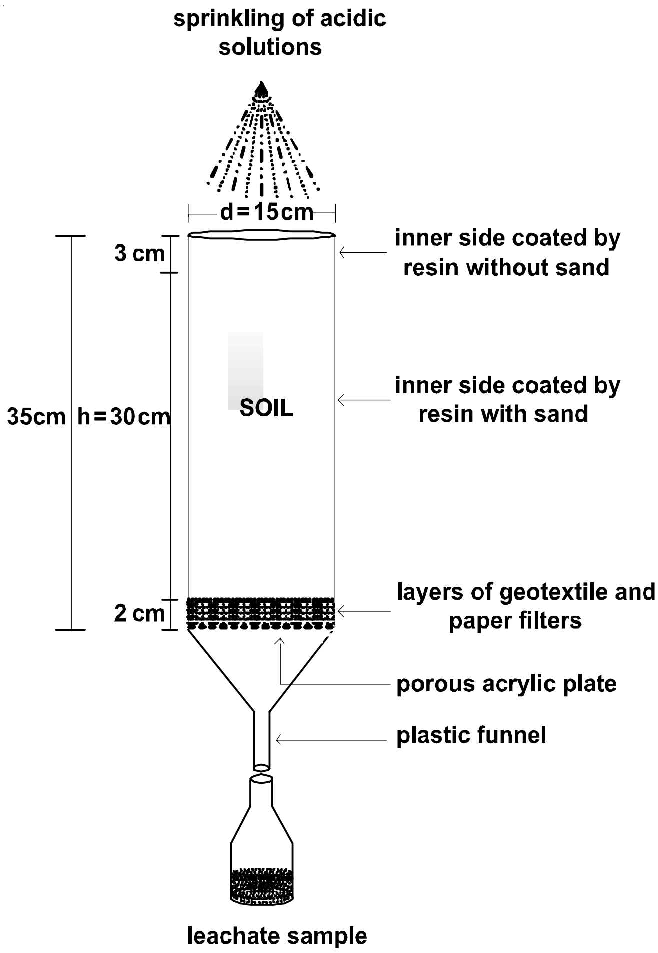


Fig. 1. A schematic sketch of experimental setup. It represents sprinkling of simulated acid rain on the soil columns (15 × 30 $cm^2$) prepared in plastic pipes with filtering mechanism and leachate collection system

Acidic solutions were prepared in the laboratory using nitric acid and sulfuric acid having pH 5 (T2), 4 (T3), 3.5 (T4), 3 (T5), 2.5 (T6) and 2 (T7). Deionized water having pH 7 (T1) was used as control treatment (unpolluted rain). The total volume of applied solution (24.38 L) was calculated using an equation ($V = \pi r^2 h$); where, V is the total volume of applied solution, r is radius of the soil columns and h is average annual rainfall (1379.1 mm). The prepared solutions were sprayed on the upper surface of the soil columns for a period of 45 days representing average annual rainfall in the study area.

**Analysis of leachate and soil samples:** Soil leachate (effluent) samples were collected at regular intervals analyzed for nutrient cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) using inductively coupled plasma-optical emission spectrometry (ICP-OES). After the leaching experiments, the soil was removed carefully from the columns. Samples were prepared for extraction of residual nutrient cations and analysis by ICP-OES. Soluble and exchangeable forms of nutrient cations were extracted from soil samples by water[26] and 1N ammonium acetate[27], respectively. F-test was performed for all the obtained data from leachate analysis with a statistical significance at $\alpha$ = 0.01.

## RESULTS AND DISCUSSION

The selected soil properties are given in Table-1. Pak Chong soil with clayey texture has higher CEC due to higher clay and organic matter contents as compared to Korat soil (ultisol) having sandy texture. Clayey soil (oxisol) also has higher amounts of total exchangeable bases (TEB) contributing to its higher base saturation (BS) and lowering sensitivity to acid deposition. However, both soils are slightly acidic in nature.

**Leaching losses of potassium from soils:** Figs. 2 and 3 show the leaching losses of $K^+$ from both the investigated soils under different treatments. Leaching losses increased significantly (p value < 0.001) with a decrease in pH of the applied solution, particularly as the pH of simulated rain dropped to 3.5 or less. Solution with pH 3.5 caused significant leaching, amounting 3.43 and 3.45 mg $K^+$ per kg of soil from oxisol and ultisol, respectively. Acidic treatment with pH 2.5 caused quite high leaching losses of potassium *i.e.* 13.6 and 9.5 mg per kg of soil from oxisol (Pak Chong) and ultisol (Korat), respectively. However, maximum depletion of potassium was found under acidic treatment with pH 2, amounting 18.6 mg per kg of soil in Pak Chong soil (oxisol). Acid rain increases $H^+$ ions in the soil system and causes soil acidity[28]. These $H^+$ ions displace $K^+$ ions from the negative sites by the phenomenon of cation exchange. A very good correlation has been found between pH of acid rain and amount of $K^+$ leached in both soils, oxisol ($R^2$ = 0.98) and ultisol ($R^2$ = 0.97). These leaching losses of $K^+$ are much higher than those found in other studies

TABLE-1
SELECTED PROPERTIES OF THE INVESTIGATED SOILS

| Soil | Depth (cm) | Bulk density (Mg $m^{-3}$) | Particle size distribution (%) | | | Soil texture | pH (1:1) | SOM (%) | TEB (cmol $kg^{-1}$) | CEC (cmol $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Sand | Silt | Clay | | | | | |
| Pc | 0-30 | 1.18 | 34.30 | 18.43 | 47.27 | Clay | 6.31 | 2.94 | 17.23 | 17.72 |
| Kr | 0-30 | 1.53 | 80.30 | 12.43 | 7.27 | Loamy sand | 5.82 | 0.19 | 2.23 | 2.75 |

Where, Pc = Pak Chong soil (Oxisol), Kr = Korat soil (Ultisol)

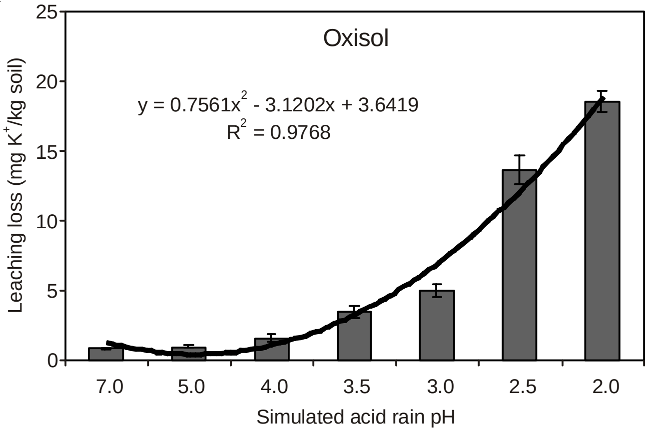


Fig. 2. Leaching losses of potassium from oxisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

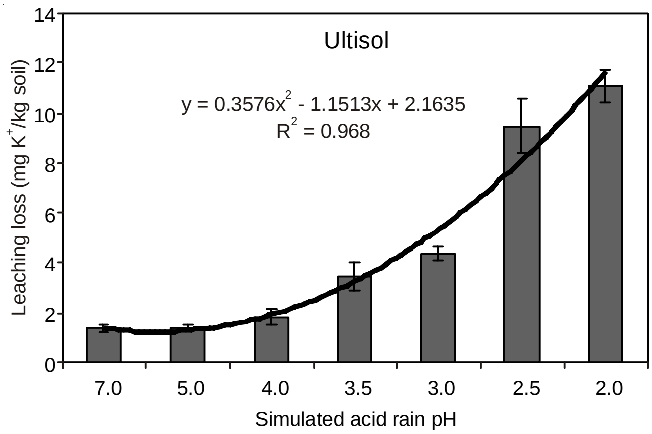


Fig. 3. Leaching losses of potassium from ultisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

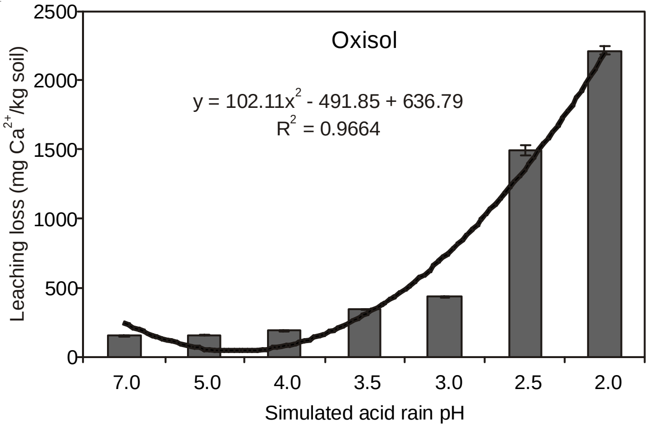


Fig. 4. Leaching losses of calcium from oxisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

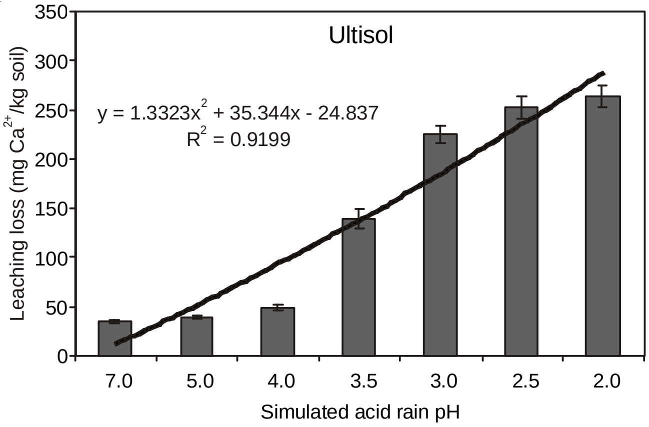


Fig. 5. Leaching losses of calcium from ultisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

conducted by Zhang *et al.*[10] and Ling[4]. The leaching of $K^+$ out of the root zone from the oxisol and ultisol would reduce soil productivity and affect groundwater quality.

**Leaching losses of calcium from soils:** Leaching losses of $Ca^{2+}$ from both soils are presented in Figs. 4 and 5. Quite high and significant (p value < 0.001) leaching losses occurred with higher acidic treatments. Highly acidic treatment (pH 2) depleted high amounts of $Ca^{2+}$ *i.e.* 2215.2 (oxisol) and 263.1 mg $kg^{-1}$ (ultisol). Moderately acidic solution (pH 3.5) also depleted significant amount of $Ca^{2+}$ from both the soils. Higher losses were found in Pak Chong (341.4 mg per kg of soil) as compared to that of Korat soil (139.45 mg per kg of soil). Higher depletion losses were observed from clayey soil (Pak Chong) because of high initial content of $Ca^{2+}$, as shown in Table-1. A good correlation has been found between pH of acid rain and amount of $Ca^{2+}$ leached in both soils, oxisol ($R^2$ = 0.97) and ultisol ($R^2$ = 0.92). Negative charges on soil particles are involved in controlling retention and removal of calcium from soils. The investigated soils contain Kaolinite, which belongs to 1:1-type silicate clays with higher pH-dependent negative charges[29]. Any rain having pH lower than that of soil, would increase $H^+$ ions in the soil system and consequently there would be accelerated leaching of $Ca^{2+}$ from the soils[10]. Due to leaching of $Ca^{2+}$, soil acidity would become severe in oxisol and ultisol[28], decreasing the availability of nitrogen, phosphorus and sulfur and affecting the activities of microbes (bacteria and actinomycetes) in soil system[30].

**Leaching losses of magnesium from soils:** Figs. 6 and 7 present the leaching losses of $Mg^{2+}$ from both soils. $Mg^{2+}$ losses increased significantly (p value < 0.001) with an increase in acidity of applied solutions. Higher acidic treatments (pH 2.5 and 2.0) depleted quite large amounts of $Mg^{2+}$ from both the soils. Under acidic treatment with pH 2.5, higher leaching losses of $Mg^{2+}$ were found in Pak Chong soil (221.4 mg/kg), as compared to that of Korat soil (145.3 mg/kg). This is because of differences in the original content in both soils. Highly acidic treatment (pH 2) induced profound leaching losses of $Mg^{2+}$ *i.e.* 291.9 and 63.6 mg per kg from Pak Chong and Korat soil, respectively. These losses are higher than those found by Walna *et al.*[31] and Zhang *et al.*[10]. A very good correlation has been found between pH of acid rain and amount of $Mg^{2+}$ leached in both soils, oxisol ($R^2$ = 0.96) and ultisol ($R^2$ = 0.92). Acidic treatments caused higher leaching losses of all the nutrient cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) from Pak Chong (oxisol) soil as compared to those of Korat (ultisol) soil. This is because of more pH-dependent negative charges in Pak Chong soil due to higher organic matter and kaolinite. High leaching of $Mg^{2+}$ from oxisol and ultisol would reduce soil quality and consequently soil productivity.

TABLE-2
CONTENTS OF NUTRIENT CATIONS IN OXISOL AND ULTISOL BEFORE AND AFTER DIFFERENT ACIDIC TREATMENTS

| Soil | Form | Nutrient | Mean nutrient content (mg/kg soil) under different treatments | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Original | pH = 7 | pH = 5 | pH = 4 | pH = 3.5 | pH = 3 | pH = 2.5 | pH = 2 |
| Pak Chong (Oxisol) | Exchangeable form | K | 94.2 | 90.6 | 93.1 | 92.1 | 83.7 | 80.3 | 69.3 | 59.3 |
| | | Ca | 2914.1 | 3107.9 | 3100.3 | 3182.7 | 2605.2 | 2455.2 | 1789.4 | 852.5 |
| | | Mg | 279.1 | 289.7 | 290.5 | 301.5 | 268.1 | 226.6 | 149.5 | 72.5 |
| | Soluble form | K | 94.2 | 90.6 | 93.1 | 92.1 | 83.7 | 80.3 | 69.3 | 59.3 |
| | | Ca | 2914.1 | 3107.9 | 3100.3 | 3182.7 | 2605.2 | 2455.2 | 1789.4 | 852.5 |
| | | Mg | 279.1 | 289.7 | 290.5 | 301.5 | 268.1 | 226.6 | 149.5 | 72.5 |
| Korat (Ultisol) | Exchangeable form | K | 52.4 | 46.0 | 46.7 | 44.3 | 40.7 | 36.9 | 33.0 | 32.9 |
| | | Ca | 343.2 | 316.2 | 317.1 | 320.2 | 211.8 | 153.8 | 106.8 | 71.4 |
| | | Mg | 33.6 | 34.5 | 35.0 | 35.8 | 21.6 | 13.9 | 13.4 | 10.9 |
| | Soluble form | K | 16.6 | 22.6 | 21.9 | 24.3 | 27.4 | 29.8 | 30.2 | 26.8 |
| | | Ca | 38.4 | 48.0 | 47.6 | 40.2 | 52.6 | 73.1 | 59.0 | 57.3 |
| | | Mg | 11.1 | 14.5 | 13.4 | 14.4 | 11.9 | 8.1 | 7.2 | 6.7 |

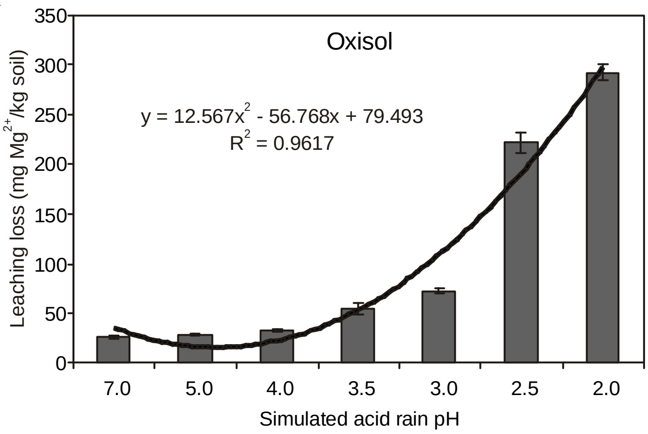


Fig. 6. Leaching losses of magnesium from oxisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

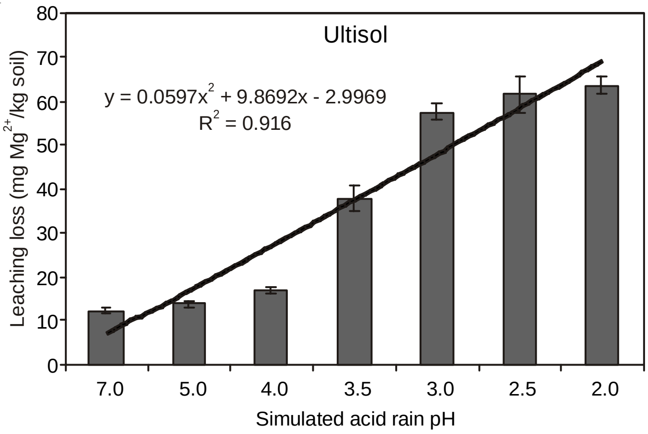


Fig. 7. Leaching losses of magnesium from ultisol under different treatments. Error bars represent the standard deviation of replicate (n = 3) leachate samples

**Status of nutrient cations in soils after acidic treatments:** Table-2 shows the status of soluble and exchangeable forms of potassium, calcium and magnesium in both the investigated soils after leaching with different solutions. Exchangeable forms of target nutrient cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) did not experience significant change in their amounts in control (T1) and slightly acidic treatments (T2 and T3), however quite high reduction in their amounts were observed in moderately to highly acidic treatments (T4, T5, T6 and T7) in both the soils due to profound leaching losses of nutrient cations, as presented in Figs. 2-7.

The amounts of soluble forms of all the nutrient cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) increased in Pak Chong (oxisol) soil as the pH of the applied solutions decreased. This is because of weathering of soil material and conversion of exchangeable forms to soluble ones induced by acidic treatments. In case of Korat soil, similar changes in soluble forms of $K^+$ and $Ca^{2+}$ were observed. However, soluble $Mg^{2+}$ decreased under higher acidic treatments, probably due to lower content of original exchangeable $Mg^{2+}$ (33.6 mg $kg^{-1}$) and lower cation exchange capacity of Korat soil. The low contents in soils are because of nutrient leaching due to precipitation[32]. This would result to increased extractable aluminum and iron as the soil pH drops to 5 or low particularly in the surface-soil, due to antagonistic relation between acid and basic cations[33]. This is unfavorable and would cause rhizotoxicity and groundwater contamination.

## Conclusions

Laboratory experiments were carried out to quantify the leaching losses of nutrient cations by acid rain with pH levels (2 to 7) over a period of 45 days from oxisol and ultisol. The important findings from the study are summarized below;

- Results showed that leaching of nutrient cations ($K^+$, $Ca^{2+}$ and $Mg^{2+}$) increased significantly as pH of acid rain decreased. A strong correlation ($R^2 > 0.90$) existed between pH of the acid rain and leaching amounts of all the nutrient cations investigated in oxisol and ultisol.
- Oxisols and ultisols are highly susceptible and vulnerable against acid rain in terms of nutrient cations leaching and depletion due to their low cation exchange capacity and limited weatherable minerals.
- Acid rain causes higher leaching losses of nutrient cations from the soils having more pH-dependent negative charges. Higher acidic treatments depleted nutrient cations from the exchange sites of oxisol and ultisol due to profound leaching.
- Higher levels of acidic deposition depleted nutrient cations from the plants' root zone, which in turn would develop acidification in soils. These changes in the soils decreased their quality from agricultural production and environmental perspectives. The leaching of nutrient cations would also degrade groundwater quality.

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