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MICROBIAL REMOVAL OF SELECTED VOLATILE ORGANIC COMPOUNDS FROM THE MODEL LANDFILL GAS

MIKROBIOLOGICZNE USUWANIE WYBRANYCH LOTNYCH ZWIĄZKÓW ORGANICZNYCH Z MODELOWEGO GAZU SKŁADOWISKOWEGO

Abstract: Landfills of municipal waste are an important source of BTEXs in the atmosphere. Biodegrability of these compounds implies that biological methods, such as oxidation in landfill covers, may be an effective way to mitigate emission of these gases. The aim of the study was to evaluate the efficiency of BTEXs removal from landfill gas by biofiltration method and to analyze the influence of methane on BTEXs oxidation rate. The experiments were carried out at laboratory scale continuous flow system (microcosms) and in batch tests. A mixture of municipal waste compost and expanded clay pellets (1:1 of volume) was used as a filter bed material. The model landfill gas (50% vol. of CH₄ and 50% vol. of CO₂) purged through the microcosms was enriched with toluene (series 1) and all the BTEXs (series 2). The results of 7-month continuous flow experiment showed that removal efficiency of BTEXs in experimental columns ranged from 91 to 100% when the individual trace gases loading rates in model gas were in the range of 0.1-0.2 g m⁻²d⁻¹. The rate of toluene removal, which followed the first order kinetics, depended on the presence of methane in treated gas. About 2-fold higher values of rate constant and 2.5-fold higher values of initial toluene removal rates were observed when no methane was present in the headspaces inside the vials used in the batch tests.

Keywords: biofiltration, BTEX, methane, landfill gas, air quality

Introduction

Waste landfilling is still one of the most popular methods of waste disposal. Deposited waste, containing about 50% of organic matter, undergoes anaerobic decomposition, which leads to landfill gas (LFG) production. Main components of landfill gas are methane (55-60% v/v) and carbon dioxide (40-45% v/v). Besides these major components, landfill gas contains also a high number of components such as bioaerosols, dusts and trace gases, of which many are toxic [1-3]. The trace components in landfill gas are mainly produced during microbial decomposition of organic materials deposited in the landfill or by vaporization of low boiling point liquids contained in the waste [4]. Non-methane organic compounds (NMOCs) constitute a numerous group of trace compounds, reaching up to 1% of gas volume [5, 6]. Volatile organic compounds (VOCs) comprise important group of the NMOCs in landfill gas. The most common VOCs found in LFG are benzene, toluene,

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ethylobenzene, and xylenes [7-9], called BTEXs. Benzene is a proven carcinogen, classified by International Agency for Research on Cancer to agents carcinogenic to humans (group 1). Ethylobenzene is classified as possibly carcinogenic to humans (group 2B), while toluene and xylenes are not classifiable in regard to their carcinogenicity to humans (group 3) [10-13].

Benzene concentrations in landfill gas usually range from 0.03 to 167 mg m⁻³ [9, 14, 15]; while toluene was found in higher concentrations, ranging from 0.2 to 953.5 mg m⁻³ [9, 14, 16, 17]. Concentrations of ethylobenzene in landfill gas are usually in the range from 0.1 to 117 mg m⁻³, whereas xylenes - from 0.2 to 440 mg m⁻³ [9, 14, 15, 18]. Concentrations of trace components in LFG depend mainly on waste composition. It is believed that domestic waste containing synthetic rubber, plastics, pesticides, paints, glues, furniture wax, detergents and cosmetics, is an important source of BTEXs in landfill gas. Another factor influencing the LFG composition is the age of a landfill. Davoli et al [19] noted differences in BTEXs concentrations among gases coming from young and old landfills. Higher concentrations of almost all BTEXs were observed in the gas produced inside old landfills. The same observation has been made in case of p-cymene, one of the terpenes which is regarded to be an indicator of waste age. Contrary to p-cymene, other terpene - limonene was found in higher concentration in the landfill gas generated inside young landfills. Similar observation had been made earlier by Termonia and Termonia [20].

Zou et al [6] showed that not only the open cell landfills but also the landfills with a biocover layer were a source of VOCs emission to the atmosphere. They have analyzed the samples of ambient air from Datianshan landfill in Guangzhou (South China). They found that concentrations of benzene, toluene, ethylobenzene and (m+p) xylenes and o-xylene in the ambient air around the landfill ranged from 1.2 to 164 μ g m⁻³, 1.7 to 202 μ g m⁻³, 0.1 to 52 μ g m⁻³, 0.2 to 97 μ g m⁻³, and 0.1 to 72 μ g m⁻³, respectively. They stated that the quantitative and qualitative LFG composition was dependent on the season. Higher emissions and larger number of compounds were observed in summer. Sixty trace compounds were identified in summer, while only 38 compounds were detected in winter.

Due to hazardous or odorous properties of trace gases emitted from landfills, limitation of their emission to the atmosphere is recommended. The most efficient methods include recovery and combustion of LFG. However, even if LFG is used for energy production or flared off, significant amounts of this gas are still emitted to atmosphere from the landfill surface. Non-extracted landfill gas migrates upward inside the waste body and is released to the ambient air, thus becoming a source of numerous pollutants, eg BTEXs. Different physical, chemical and biological methods can be used for mitigation of BTEXs emission from anthropogenic sources. However, taking into the account the technical and economic aspects, most of them are not feasible under the existing landfill conditions. The main technical barrier is related to the recovery and channeling of the gas stream at landfill, especially during the operation phase. Landfills equipped with a degassing system cause the least troubles in this area, but large volume of gas creates an economic barrier for the use of advanced chemical methods. Because many trace gases are susceptible to biodegradation, biological methods seem to be the most useful for the mitigation of BTEXs emission from landfills. They are cheap, waste-free and energy-efficient. Among these methods, biofiltration consisting in purging the gas through a packed bed inhabited by relevant microorganisms which are able to degrade organic compounds, has the important application potential for residual landfill gas treatment [21-24].

The aim of the study was to evaluate the efficiency of BTEXs removal from landfill gas by means of biofiltration method and to analyze the influence of methane - which is always present in landfill gas - on BTEXs oxidation rate. Experiment was conducted in a laboratory scale continuous flow system, in PVC columns filled with a mixture of municipal waste compost and expanded clay pellets. The model LFG used in the experiment was enriched with BTEXs. The kinetics studies were performed in batch tests.

Materials and methods

Column experiment

The experimental set-up consisted of 6 columns made of plexiglas (1 m high with the internal diameter of 0.15 m). It was simulating a landfill top cover soil matrix, through which the model mixture imitating landfill gas was passed. Each column was equipped with a gas valve, placed at the bottom part, allowing gas inlet. Two rows of sampling ports were made along each column. The ports were distributed in 10 cm intervals. Holes placed in the first row were plugged with a septum providing gas samples taking off. Three holes in the second row were occupied by sensors for moisture, temperature and soil conductivity measurement (Decagon Devices Inc type 5TE) and two manometers (Fig. 1).



Fig. 1. The scheme of a single laboratory column

The bottom of each column formed a funnel which allowed to drain the excess water outflow. The lower parts of the columns were filled with a 15 cm layer of expanded clay pellets (8-20 mm in diameter) in order to enable regular gas distribution and to prevent the leakage of filter bed material. Plastic mesh (4 mm \times 4 mm) was placed on the expanded clay pellets layer. The 80 cm filter bed material layer consists of the mixture of mature

municipal waste compost and expanded clay pellets (1 : 1 v/v) placed on the mesh. Municipal waste compost was chosen because of its high nutrient content and high water holding capacity. Expanded clay pellets were used as a support material, allowing to maintain gas permeability. Main parameters of the mixture components are presented in Table 1.

Parameter	Unit	MSW compost	Expanded clay pellets
Moisture	[%]	30.71	n.a.
Organic dry mass	[% of dry mass]	18.10	0.1
Total organic carbon	[% of dry mass]	11.40	n.a
Kjeldahl nitrogen	[%]	1.17	n.a
C:N ratio	[-]	9.74	-
Total phosphorus	[mg/kg]	0.85	n.a.
Carbonate	[%]	6.02	0.39
pH	[-]	8.34	8.73
Fraction size	[mm]	< 20	8-20

Properties of filter bed components

n.a. - not analyzed

Properties of filter bed material (mixture of municipal waste compost and expanded clay pellets) were as follows: bulk density 0.53 g cm⁻³, density of solid phase 2.39 g cm⁻³, porosity 78.7%, total water retention 92.7% of weight, oxygen diffusion coefficient $0.0769 \text{ cm}^2 \text{ s}^{-1}$.

The operational conditions of two stages of column experiment

Table 2

Stage	Model gas composition	Particular column volumetric gas flow [cm ³ min ⁻¹]	Surface load [g m ⁻² d ⁻¹]	EBRT [h]
Ι	CH_4 : CO_2 (1 : 1 vol.), toluene (average concentration 281 mg m ⁻³)	10	methane: 290 toluene: 0.34	28
п	 CH₄: CO₂ (1 : 1 vol.), benzene (average concentration 221 mg m⁻³) toluene (average concentration 212 mg m⁻³), ethylbenzene (average concentration 197 mg m⁻³), o-xylen (average concentration 167 mg m⁻³), m,p-xylens (average concentration 167 mg m⁻³). 	10	methane: 290 benzene: 0.18 toluene: 0.29 ethylobenzene: 0.16 o-xylene: 0.13 m,p-xylenes: 0.12	28

Methane (99.5%) and carbon dioxide (99.7%) taken from the 50 dm³ gas tanks (Linde Gas Polska), were mixed in a gas mixer. Mixture containing CH_4 and CO_2 in 1:1 volumetric ratio was introduced to a trace gases vapor generator. It was a sealed steel chamber in which the glass vials with liquid phase of particular trace gases, equipped with capillary closure, were placed. Temperature in the gas generator was maintained at a constant level of $35\pm1^{\circ}$ C. The model gas enriched with trace gases going out from generator was introduced to 6 columns through gas valves placed on their bottoms with a constant rate (10 cm³ min⁻¹). In the first stage of column experiment (5 months), toluene was used as the only trace compound. In the second stage of experiment (2 months), benzene, toluene, ethylobenzene and xylenes were added to the stream of model gas. Digital gas flow

Table 1

controllers (Brooks Instruments) were used in order to maintain the gas mixture composition homogeneity and the gas flow rate. Scheme of gas supply to the experimental set-up is presented in Figure 2.

The experiment was carried out under laboratory conditions. The temperature inside the laboratory ranged from 21 to 23°C. The operational conditions of the study are presented in Table 2.

Upper parts of biofilters were kept open for the atmosphere and gas was introduced into the columns under pressure which created conditions similar to these in landfill cover soils. The degradation process was conducted in a methane and oxygen counter-gradient system. The experimental set-up was working for 7 months at stable gas flow rate.

> R5 R6 R7 R8 83 Trace gases vapor generator R2 CO, tank CH₄ tank

Fig. 2. Scheme of model gas supply system: R1-R8 - gas flow controllers

Batch tests

Batch tests were conducted in order to examine the influence of methane on toluene biodegradation rate. At the end of column experiment, 0.1 kg samples of filter bed material were taken from three depths of one column, from which 5 g of subsamples were separated. Subsamples were placed in glass vials with the volume of 80 cm³. Vials were sealed by means of plastic caps with rubber stoppers. Methane and toluene vapors were introduced into the vials by a gas-tight syringe wherein additional needle was driven into the rubber stoppers in order to prevent the build-up of excessive pressure. Gas samples (5 mm³ of volume) withdrawn from the vials headspace were sampled periodically and analyzed chromatographically. The decrease in the concentration of considered gases in time was analyzed. Particular gases oxidation rates were calculated in relation to filter bed material mass. Examinations were carried out at temperature of $22 \pm 1^{\circ}$ C, in three repetitions. Batch experiment description is presented in Table 3.



Table 3

Sample characteristic and experiment conditions	Initial conditions
Material: mixture of municipal waste compost and expanded clay pellets collected from three depths of a column (15, 45 and 75 cm) at the end of continuous flow experiment Wet sample mass: 5 g Process temperature: 22 ±1°C Experiment duration: 72 h	Samples were incubated in atmosphere enriched with - only toluene (series 1). Initial toluene concentration: 89 ± 9 mg m ⁻³ - methane and toluene (series 2). Initial methane concentration: 16.8 ±2.1%. Initial toluene concentration: 78 ±11 mg m ⁻³

Initial conditions of batch experiment

Determination of soil gas concentration profiles in the experimental columns

Methane and BTEXs concentrations on various depth of columns (0, 20, 40, 60, 80, 90 cm) were measured twice a week. In order to determine CH_4 concentration, the gas samples of 50 mm³ volume were taken through rubber septa by a gas-tight syringe (Hamilton) and analyzed chromatographically. For the purpose of BTEXs concentration evaluation the solid-phase microextraction (SPME) method was used (15 minutes SPME fibres exposition to the gas inside the columns). Gas samples were then analyzed using chromatograph. The column inlet gases concentration were measured before the gas valve in a gas sampling port placed in the tube.

The concentration of out-going gases was measured in the given volume of closed headspace over the filter bed material. In order to determine it, the columns were closed for 10 minutes using the PVC plugs.

The gases concentrations measured in the gas stream entering and leaving the columns were the basis for calculating the removal efficiencies.

Methane and BTEXs removal efficiencies and oxidation rates

Gases oxidation rates in experimental columns were defined as the amount of gas oxidized in a filter bed material in relation to the surface unit, in a unit of time. Particular gas load and its flux from the filter surface were the basis for these calculations.

Gas load was calculated using inlet gas concentration. The gas flux from the surface was evaluated on the basis of gas concentration measured in the closed headspace of column.

Activity of toluene oxidation (q_t) in batch tests was defined as the amount of gas oxidized in a filter bed material in relation to its mass in a unit of time. These values were determined on the basis of time-dependent decrease in toluene concentrations, according to equation:

$$q_t = \frac{\Delta C \cdot V}{M \cdot \Delta t} \cdot \rho_t \tag{1}$$

where: q_t - activity of toluene oxidation [µg g⁻¹d⁻¹], ΔC - decrease in toluene concentrations measured at t_0 and t [cm³cm⁻³], V - volume of vials [cm³], M - soil sample mass [g], Δt - time between the measurements [d], ρ_t - toluene density at 20°C [g cm⁻³].

Two chromatographs were used for the measurement of particular compounds concentrations: 1) gas chromatograph Thermo GC/MS Trace Ultra (with mass spectrometer Polaris Q, ion trap and Rtx Dioxin column of initial temperature 45°C and temperature growth rate of 8°C min⁻¹. The carrier gas was helium, with a flux rate of 1.2 cm³ min⁻¹. Peak areas were determined using computer integration program Xcalibur ver. 2.0 and 2)

Thermo GC Trace Ultra gas chromatograph (equipped with TCD RESTEK thermal conductivity detector, Rt-Q-Bond 30 m, 0.32 mm ID, 10 μ m, initial temperature 35°C, temperature growth rate of 35°C min⁻¹) and with FID flame ionization detector (RESTEK Rtx®-5MS 30 m, 0.25 mm ID, 1 μ m, initial temperature 40°C, temperature growth rate of 15°C min⁻¹). The carrier gas was helium with a flux rate of 40 cm³ min⁻¹.

Results and discussion

BTEXs and methane soil concentration profiles in experimental columns

In the first stage of column experiment, a gradual decrease of toluene and methane concentrations from the bottom part of the column, where the gas mixture was introduced, toward filter bed material surface, was observed. It was showed that in the case of toluene the higher decline in its concentration, which is revealed in the slope of the curves on Figure 3a, occurred in lower part of columns, on the depth of 80-90 cm, while the more evident decrease in methane concentration was observed in the upper part of the columns (Fig. 4a). It could have been caused by different requirements for oxygen which is needed for the biodegradation of toluene and methane.

Taking into account the differences in methane and BTEXs concentrations in treated gas mixture, the oxygen demand for methane oxidation is many times higher than for toluene and other BTEXs oxidation. Thus, the process of methane removal occurred in an extensively aerated area. Methanotrophs belong to microaerophiles, and the process of methane oxidation is strongly oxygen-dependent. The increase of O_2 concentration from 2.5 to 21% in air contained in pores of sandy soil material exposed for high methane concentration caused a 6-fold growth in the rate of CH₄ uptake [25]. Lower location of the zone of intensive toluene biodegradation can be also explained by a flexible metabolism of heterotrophs responsible for toluene biodegradation. They can respire aerobically or anaerobically using nitrate or sulfate [26, 27].



Fig. 3. Toluene concentration profile in the columns (average value and standard deviations, n = 3) in the stages: a) I and b) II of the experiment

In the second stage of the experiment, when other BTEXs were added to the treated gas, methane oxidation process shifted upwards the columns (Fig. 4b). The share of the 0-20 cm zone in total methane removal was more evident compared with the results obtained in stage I (Fig. 4a). The highest declines of benzene, ethylobenzene and xylenes

concentration in the profiles were observed in lower part of columns, on the depth of 80-90 cm, similarly as in the case of toluene (Fig. 5).



Fig. 4. Methane concentration profile in the columns (average value and standard deviations, n = 3) in the stages: a) I and b) II of the experiment



Fig. 5. Concentration profile of: a) benzene, b) ethylobenzene, c) m, p-xylenes and d) o-xylene in the columns (average value and standard deviations, n = 3) in the stage II of the experiment

BTEXs and CH₄ oxidation rates and removal efficiencies

Analyzed filter bed material showed a high capacity for toluene oxidation resulting in a very high oxidation rates from 0.11 to 0.35 g m⁻² d⁻¹, which corresponded to the toluene removal efficiency between 85 and 100%. In the first seven weeks of experiment duration, with the average toluene loading rate of 0.13 g m⁻² d⁻¹, removal efficiency ranged from 86.3 to 100%. In the 8th week of experiment, after toluene loading rate was increased to 0.35 g m⁻² d⁻¹ (by raising toluene concentration in gas mixture), a decrease of toluene removal efficiency to 85.3% was observed. With the highest toluene loading rate (0.4 g m⁻² d⁻¹), noted in 11th week, its removal efficiency amounted to 90%, which can indicate microorganisms adaptation to conditions inside the filter bed material (Fig. 6). In the stage II when all the BTEXs were present in the gas mixture, the toluene removal efficiency ranged from 99.8 to 100% (at loading rates from 0.16 to 0.18 g m⁻² d⁻¹).



Fig. 6. Toluene loading rate and its removal efficiency during the stages: a) I and b) II of the column experiment



Fig. 7. The correlation of toluene oxidation and loading rates

On the basis of the results obtained in the stage I of the experiment, where only one trace gas was introduced to the model landfill gas, it was stated that the toluene oxidation rate is positively correlated with its loading rate, which ranged from 0.11 to 0.4 g m⁻² d⁻¹ (Fig. 7). The dependence was statistically significant ($\alpha = 0.05$).

Removal efficiencies of the other trace components examined in stage II, at its individual loading rates from 0.1 to 0.2 g m⁻² d⁻¹, ranged from 99.5 to 100% (Fig. 8). Oxidation rates for benzene, toluene, ethylobenzene, o-xylene and m,p-xylenes were in the range: 0.16 to 0.20 g m⁻² d⁻¹, 0.16 to 0.18 g m⁻² d⁻¹, 0.14 to 0.18 g m⁻² d⁻¹, 0.10 to 0.15 g m⁻² d⁻¹ and 0.10 do 0.14 g m⁻² d⁻¹, respectively.



Fig. 8. Loading rates and removal efficiencies of: a) benzene, b) ethylobenzene, c) m, p-xylenes and d) o-xylene in the columns (average value and standard deviations, n = 3) in the stage II of the column experiment

Methane loading rate maintained an almost steady level of 287 ± 17 g m⁻² d⁻¹ during the both stages of the experiment, which resulted from a slight variability in methane concentration in the filtered gas mixture. Average concentration of methane introduced to column was about 48.6%. Filter bed material was characterized by high methane removal efficiency, ranging from 90 to 100%. A slight decrease in removal efficiency was observed starting from the 9th week of the experiment. From that time, methane oxidation rate oscillated at 270 g m⁻² d⁻¹ and did not show visible changes during the end of the stage I (Fig. 9a). Maintaining methane oxidation rate at an almost steady level can result from a low susceptibility of the mixture of compost and expanded clay pellets on subsidence affecting stability of air and aqueous conditions of filter bed material. High stability in the efficiency of microbial methane removal in biofilter beds composed with compost and different mineral components was obtained by Pawlowska et al [28].



Fig. 9. Methane loading rate and its removal efficiency during the stages: a) I and b) II of the column experiment

When the benzene, ethylbenzene and xylenes were added to model landfill gas, the methane removal efficiency slightly dropped, and it ranged from 91 to 97%. Methane oxidation rate was in the range from 251 to 281 g m⁻² d⁻¹.

Influence of methane on toluene biodegradation

The results of batch test showed that biodegradation of toluene was influenced by methane. Toluene was consumed with lower rate when the methane (17% v/v) was in the headspace. After *ca.* 2 days, toluene was not detected in the headspace in any of the samples incubated without the methane (series 1), while in the samples incubated in the atmosphere enriched with methane (series 2) the toluene was still present even after 3 days from the start of the experiment (Fig. 10a, b).



Fig. 10. Toluene concentration drop in the headspace of materials, taken at the end of the experiment from three depths of column, incubated in atmosphere enriched with toluene only (a), and toluene and methane (b)

The results of batch test showed that toluene oxidation in all analyzed samples followed first-order kinetics. When toluene was the only supplement of the air inside the vials (series 1), the highest differences in toluene oxidation rate with course of the

experiment were observed, in comparison to the results obtained in series 2. The lower initial reaction rates r_t and reaction rate constants k were noticed in the samples incubated in toluene-containing atmosphere. For example, the k and r_t values measured in series 2 in the soil samples taken from the depth of 15 cm, incubated in very similar initial toluene concentration, were about 50% lower than relevant values determined in series 1 (Tables 4 and 5).

The activity of toluene oxidation by microorganisms inhabiting the soil samples, calculated on the basis of initial toluene reaction rates r_t ranged from 1.35 to 3.4 µg g⁻¹ d⁻¹ in series 1, and from 0.78 to 0.97 µg g⁻¹ d⁻¹ in series 2 (Fig. 11).



Fig. 11. Initial activity of toluene removal in soil materials taken from the depths of 15, 45 and 75 cm of the experimental column

Table 4

Depth of sample collection [cm]	Toluene initial concentration C ₀ [ppm]	Toluene reaction rate constant <i>k</i> [min ⁻¹]	Toluene initial removal rate r_t [ppm min ⁻¹]	Correlation coefficient <i>R</i> [-]
15	81.8	0.00092	0.075	0.9981
45	99.7	0.00125	0.126	0.9989
75	85.3	0.00112	0.096	0.9999

Kinetic parameters of toluene oxidation in series 1 (incubated in toluene)

The depth the samples were taken from influenced the kinetic parameters. In both series, the lowest reaction rate constants k were noticed in the samples taken from upper part of the columns (15 cm), while the highest ones were observed in samples taken from the depth of 45 cm. This observation in discordant with the results of column experiment, where the most intensive removal of toluene was noticed in the bottom part. The discrepancy can be explained by different oxygen accessibility for microorganisms in batch and continuous flow studies. The increase in oxygen concentration in the headspaces in batch tests did not raise the rate of toluene oxidation in samples taken from the depth of 75 cm. It suggests that the process of toluene removal in the lower part of the column may have anoxic character.

Table 5

Depth of sample collection [cm]	Toluene initial concentration C ₀ [ppm]	Toluene reaction rate constant k [min ⁻¹]	Toluene initial removal rate <i>r_t</i> [ppm min ⁻¹]	Correlation coefficient <i>R</i> [-]
15	82.7	0.00051	0.042	0.9571
45	61.5	0.00060	0.035	0.9833
75	75.1	0.00058	0.041	0.9604

Kinetic parameters of toluene oxidation in series 2 (incubated in toluene and methane)

Conclusions

The results of 7-month continuous flow experiment on BTEXs removal from model landfill gas showed that the mixture of municipal waste compost and expanded clay pellets (1:1 by volume) is a very forgiving biofilter bed material, ensuring the long-lasting efficient BTEXs removal from the gas emitted from landfills. Removal efficiency of BTEXs from the experimental columns ranging from 91 to 100% was observed when the individual trace gases loading rates in model gas were from 0.1 to 0.2 g m⁻² d⁻¹. On the basis of the outcomes of the batch test it was stated that the rates of traces gases removal depends on the presence of methane in treated gas. About twice as high values of first-order kinetics parameters of toluene oxidation process (initial toluene removal rates and rate constants) were observed when no methane was present in the headspaces inside vials used in the batch tests.

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