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室内濃度指針値候補物質の全国実態調査

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Nationwide survey of the candidate substances in guideline values for indoor air concentrations

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Indoor air quality (IAQ) is important for human health, and guideline values for indoor air concentrations (IAQ guidelines) in Japan have been set for 13 chemicals, including formaldehyde. Recently, three chemicals have been proposed as candidate substances for IAQ guidelines: 2-ethyl-1-hexanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. Continuous exposure assessments are required to properly set the IAQ guidelines for these candidates. In this survey, we investigated the pollution levels of three candidates at 28 houses in Japan four times a year. Consequently, three chemicals showed high concentrations during the hot season. The pollution sources of three chemicals originated from indoors. This is the first surveys on candidates in which seasonal influences in the same house were investigated. The results provide valuable scientific evidence for setting three candidates of IAQ guidelines in Japan.

Keywords: sick house syndrome, nationwide survey, guideline values for indoor air concentrations

1. Introduction

Sick Building Syndrome in housing, called Sick house syndrome is various health disorders, such as headache, rhinitis, pharyngitis, scintillating scotoma, asthma, dermatitis and dizziness, which are mainly caused by chemical substances emitted from buildings[1]. Poor ventilation in houses, lifestyle variation, and changes in chemical substances emitted from household products can have a significant impact on indoor air pollution. Therefore, continuous nationwide surveys of houses are essential for coping with sick house syndrome.

The Ministry of Health, Labour, and Welfare of Japan (MHLW) has set the guideline values for indoor air concentrations (IAQ guidelines) for 13 chemical substances, including formaldehyde, and provisional target values for total volatile organic compounds to prevent health deterioration due to indoor air pollution[2-3]. IAQ guidelines are founded on the latest scientific knowledge and the regulatory status in other countries, additional changes can be made if necessary.

Recently, three chemicals, 2-ethyl-1-hexanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TPMI), and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TPDI), have been proposed as candidate substances for IAQ guidelines by the Committee on Sick House Syndrome: Indoor Air Pollution[4], based on toxicological reports on 2-ethyl-1-hexanol for human sensory organs[5] and eye irritation[6], TPMI for skin irritation[7] and chronic toxicity[8], and TPDI for general toxicity[9]. Additional scientific evidence is required to set IAQ guidelines for these candidates.

Previously, we have investigated the pollution levels of three candidates at new office building of the National Institute of Health Sciences for three years and have reported to suggest the seasonal periodicity of 2-ethyl-1-hexanol and TPDI[10]. However, the pollution level at general residential housing in Japan is

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unknown.

In this survey, we focused on 2-ethyl-1-hexanol, TPMI, and TPDI as measurement targets, and investigated indoor air pollution status at houses across the country, as well as seasonal variations in these pollution levels.

2. Materials and Methods

2.1 Surveyed Houses and Survey Period

A survey was conducted at 28 randomly selected general residential housings across the country during the summer (July–August 2017), autumn (September–October 2017), winter (December 2017–January 2018), and spring (February–March 2018). The sampling map in Japan was shown in Fig. 1. Informed consent was obtained from all survey participants. Their personal data were strictly controlled, and the survey results and the participants' personal data were unconnectedly analyzed in anonymized form.

2.2 Sampling Methods

The survey was conducted following the "Manual for Measuring Indoor Air Chemical Substances" set by MHLW[11]. Briefly, active sampling method was used to collect indoor and outdoor air samples. Tenax TA SafeLok™ stainless steel thermal desorption tubes (Markes International Ltd., England, UK) were used for the sampling. Before sampling the air, the tubes were attached to TC-20 (Markes International Ltd., England, UK), heated at 100℃ for 1 h, then at 300℃ for 2 h, aerating with helium at 50 mL/min. According to the "Manual for Measuring Indoor Air Chemical Substances", the air collection time for sampling was 24 h while everyday life was going on. Two air samples were collected from the living room at 2 mL/min for 24 h (2.88 L) using an SP208-20 Dual II (GL Sciences Inc., Tokyo, Japan). Using a GSP-400FT (GASTEC Corporation, Kanagawa, Japan), one air sample was collected from outside the house in an equal volume of indoor air (2.9 L) at 50 mL/min for 58 min. The sampling start time was not specified. The height from the floor where the air samples were collected was specified as 1.2–1.5 m. Outdoor and indoor air samples were collected at the same time. The indoor air sampling pump records were observed, and samples below 90% of the target collection volume (2.88 L) due to high-frequency pulsating current were taken as missing data.

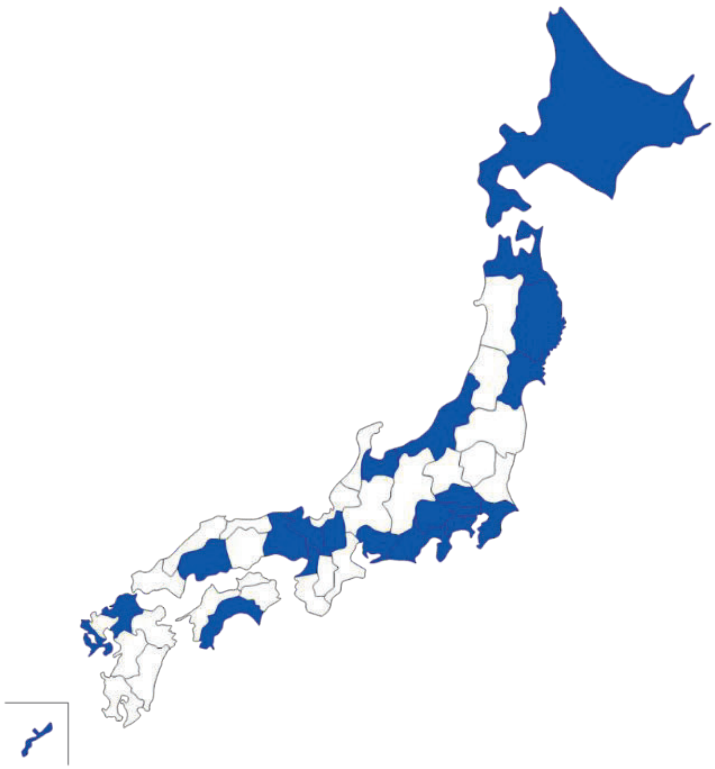

Fig. 1. Sampling Map in Japan.
The *Blue* area indicates the location of air collection by prefecture.

2.3 Analytical Methods

Thermal desorption (TD)-GC/MS was used to measure volatile organic compounds using TD-20 and GCMS-QP2010 Ultra (Shimadzu Co., Kyoto, Japan). The main measurement conditions were as follows. Targeted compounds were measured using Fast Automated Scan/Selected Ion Monitoring (SIM) Type, which switches between scan mode and SIM mode at high speed, and quantified based on internal standard methods using toluene-d_8. The concentration range of the calibration curve was 0.5–100 ng. Values below the lower limit of the calibration curve (0.17 μg/m^3) were counted as 0. TPMI was quantified as the overlapping peaks of two isomers. The details of the measurement conditions were as follows.

[Thermal Desorption]
Desorption: 300℃, 8 min, 50 mL/min
Cold Trap: −20℃
Trap Desorption: 280℃, 5 min
Line and Valve Temperature: 250℃

[GC]
Column: Rtx®-1 (0.32 mm i.d. × 60 m, 1 μm)
Carrier Gas: He, 40 cm/s at constant linear velocity
Split Ratio: 20:1
Oven Temperature: 40℃ − (5℃/min) − 280℃ (4 min)

[MS]
Interface Temperature: 250℃
Ion Source Temperature: 200℃
Scan Range: *m/z* 35–400
Scan Rate: 10 Hz

Target and qualifier ions are as follows.
2-Ethyl-hexanol: *m/z* 57 (target ion), *m/z* 41, 43 (qualifier ion)
TPMI: *m/z* 71 (target ion), *m/z* 43, 56 (qualifier ion)
TPDI: *m/z* 71 (target ion), *m/z* 43, 56 (qualifier ion)
Toluene-d_8: *m/z* 98 (target ion), *m/z* 70, 100 (qualifier ion)

3. Results and Discussion

3.1 Surveyed houses

28 houses were surveyed four times a year (112 houses in total). There were 17 detached houses and 10 multifamily houses (one unknown). Among the 17 detached houses with a known completion date, 8 had completed the construction before the revision of the Japanese Building Standards Law (before June 2003), whereas 9 houses were completed after the revision (after July 2003).

3.2 2-Ethyl-1-hexanol

The indoor 2-ethyl-1-hexanol concentrations were the highest in summer, with a maximum concentration of 42.31 μg/m^3 and a 95th percentile concentration of 20.88 μg/m^3. The median indoor concentration was the highest (6.30 μg/m^3) in summer and the lowest (1.95 μg/m^3) in winter. Follin T. reported indoor 2-ethyl-1-hexanol concentrations of 1–86 μg/m^3 in 150 rooms of an apartment building[12-13], supporting the results of this survey. 2-Ethyl-1-hexanol was reported to show a seasonal periodicity[10, 13-14], with low concentrations in the cold season followed by high concentrations in the hot season. This is because that compounds with 2-ethylhexyl groups, such as DEHP, were decomposed by the strong alkaline moisture in the concrete and the rise in outside temperature and humidity[15]. In this survey, 2-ethyl-1-hexanol concentrations were high in the hot season and low in the cold season (Fig. 2A), supporting previous reports on the seasonal periodicity of 2-ethyl-1-hexanol. Furthermore, 2-ethyl-1-hexanol was detected in all of the houses.

To evaluate the influence of outdoor air, the indoor to outdoor concentrations ratios (I/O ratio) were calculated, resulting in the I/O ratios of all houses being >1 in four measurements (Fig. 2B). Furthermore, the median indoor concentrations were higher than outdoor concentrations in four measurements. These findings indicated that the pollution sources of 2-ethyl-1-hexanol originated from indoors, such as carpets[16-17], computers[18], books[19-20], food wrappings[21], cosmetics[22], bedding products[23], gypsum boards[24], wall papers[25], paints[26], polyvinyl chloride floorings[27], and adhesives[28].

3.3 TPMI

The indoor TPMI concentrations were the highest in summer, with a maximum concentration of 86.37 μg/m^3 and a 95th percentile concentration of 53.14 μg/m^3. The median concentrations were 6.46 μg/m^3 in summer, 5.06 μg/m^3 in autumn, 2.90 μg/m^3 in

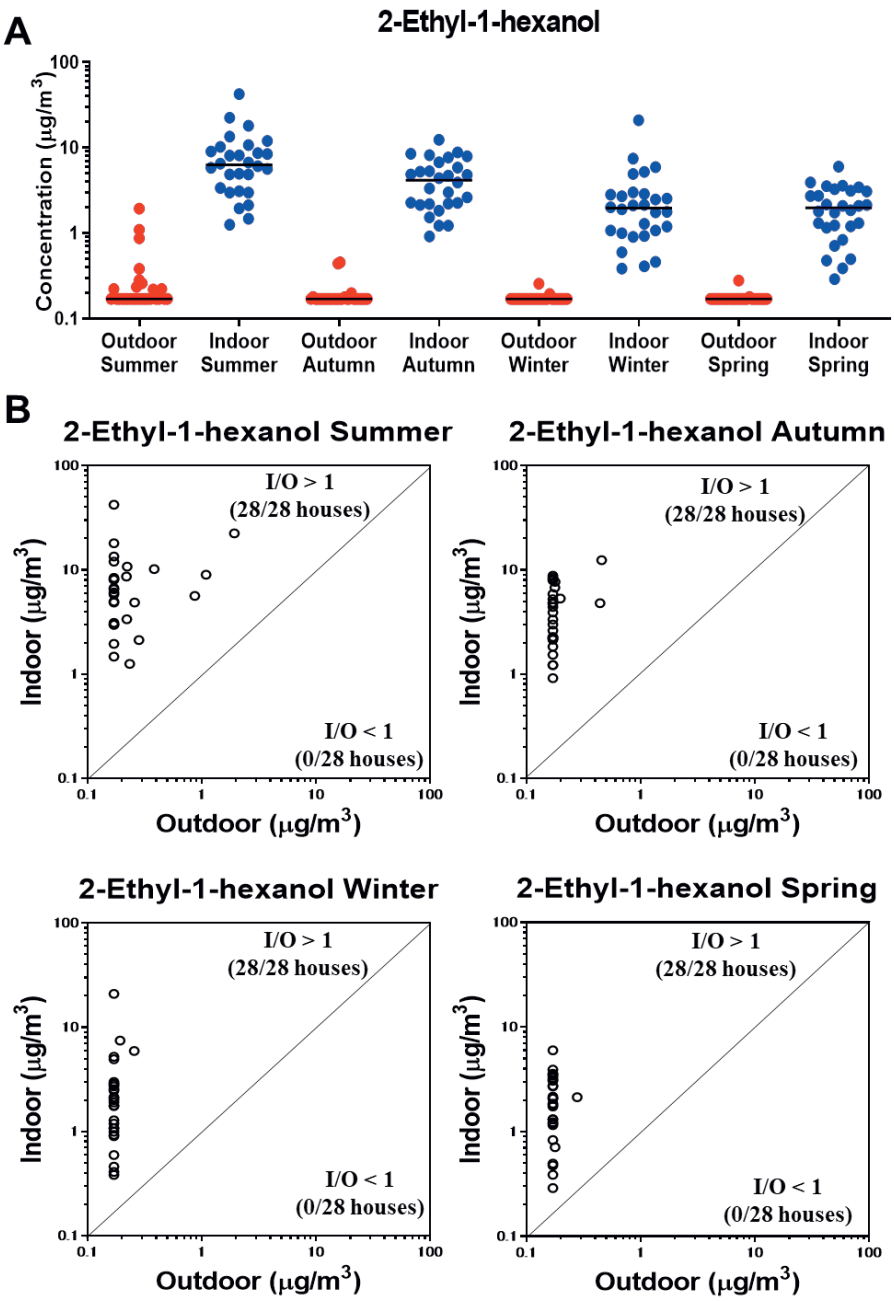

Fig. 2 . Survey results for 2-ethyl-1-hexanol.

A; Outdoor and indoor concentration distribution. The median values are represented by the black bars.

B; Correlation between outdoor and indoor concentrations.

winter, and 2.80 μg/m^3 in spring (Fig. 3A) indicating a seasonal change with high concentrations during the hot season. The cause of the high indoor TPMI concentrations in the summer was considered to be the accelerated hydrolysis of TPDI due to the higher outdoor temperatures. TPMI was detected in all 28 houses. I/O ratios of all houses were greater than 1 in four measurements (Fig. 3B), revealing that the pollution sources of TPMI originated from indoors, such as latex paint[29-30].

3. 4 TPDI

Indoor TPDI concentrations were the highest in summer, with a maximum concentration of 87.64 μg/m^3 and a 95th percentile concentration of 32.08 μg/m^3. TPDI was detected in almost all of the houses (98 houses/112 houses = 88%) (Fig. 4A). The median of indoor concentration was the highest (1.52 μg/m^3) in summer and lowest (0.53 μg/m^3) in winter, supporting our previous study on the seasonal periodicity of TPDI[10].

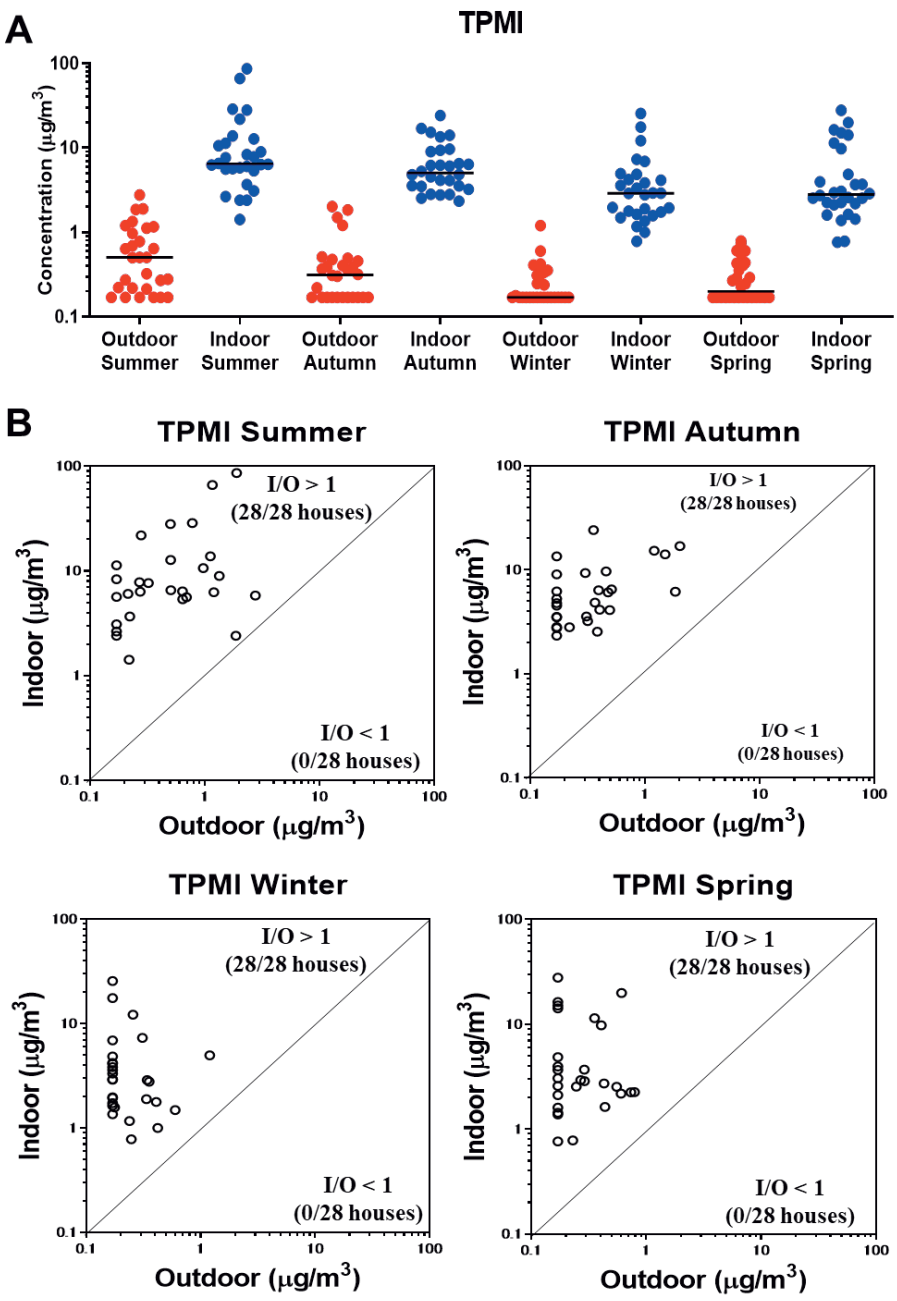

Fig. 3 . Survey results for TPMI.

A; Outdoor and indoor concentration distributions.The median values are represented by the black bars.

B; Correlation between outdoor and indoor concentrations.

I/O ratios of TPDI were calculated, resulting that the number of houses with indoor concentrations higher than outdoor concentrations (I/O ratio > 1) was 28 (100.0%) in summer, 28 (100.0%) in autumn, 28 (100.0%) in winter, and 25 (89.3%) in spring (Fig. 4B). Therefore, the pollution sources of TPDI were also detected indoors such as polyvinyl chloride materials[27].

Japanese IAQ guidelines are set so that, according to currently available scientific knowledge, no adverse health effects would be expected to occur in humans even if exposures to the chemicals at the levels decided to continue throughout life[4]. Furthermore, the IAQ guidelines should be reviewed regularly to ensure the safety of constantly changing the IAQ. Therefore, it is essential to conduct nationwide surveys that can monitor the IAQ of houses. In this survey, we investigated the indoor air in the same house four times throughout the year. Because these chemicals have been used in various materials such as

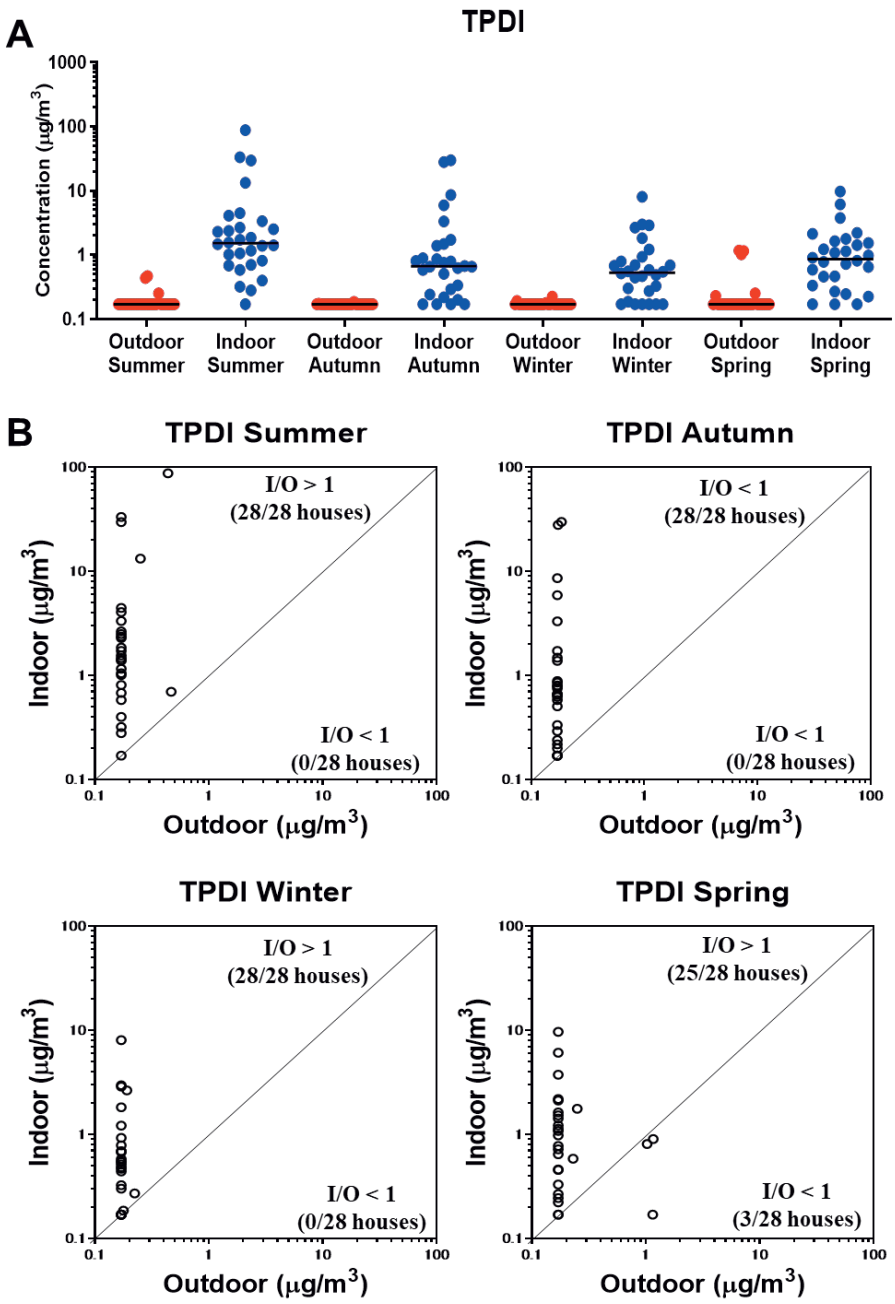

Fig. 4 . Survey results for TPDI.

A; Outdoor and indoor concentration distributions. The median values are represented by the black bars.

B; Correlation between outdoor and indoor concentrations.

paints, plasticizers and household products, and were detected in almost all of the houses, three candidates can be considered persistent indoor pollutants. These chemicals should be closely monitored in the future.

4. Conclusion

In this study, we investigated the pollution levels of three candidates in 28 houses throughout the year, including 2-ethyl-1-hexanol, TPMI, and TPDI which are potential chemicals for health risks. This survey revealed that three chemicals were detected in almost all of the houses, and that these pollution sources originated indoors. These results provide valuable scientific evidence for properly setting new IAQ guidelines.

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