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論　文　名	「Development of Simultaneous and Continuous Measurements of Formaldehyde in the Atmosphere and Rain and Role of Photoproduction and Microorganism for Formaldehyde Concentration（大気と雨中のホルムアルデヒドの同時連続測定の開発とホルムアルデヒド濃度に対する光生成及び微生物の役割）」
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論文要旨

Formaldehyde (HCHO) is well-known as an important chemical species in term of atmospheric chemistry and toxicology. It exists in most of medias in the atmosphere, including gaseous phase, aqueous phase and particle phase as the result of oxidation of volatile organic compounds (VOCs). HCHO is an essential component of the reactivity of the atmosphere, a providing source of radicals that drive important chemical processes of atmosphere such as ozone formation. Due to its high solubility in water and interactions with other, HCHO participates in aqueous chemistry in clouds. The chemistry of HCHO is an indicator of our overall understanding of atmospheric chemistry. Understanding the production and decay of HCHO will enable us to consider the effect of technology development and policies on air quality. Besides, HCHO is a hazardous air pollutant suspected as a carcinogenic risk for human and well-known as one of sick house gases. Therefore, studying on HCHO in the environment is necessary and brings many benefits, but the existing barrier is a measuring method. In considering of the role, the importance of good

understanding and the lacuna in knowledge of HCHO in atmosphere, this thesis approached issues as following steps:

In Chapter 1, the introduction to the nature of HCHO in the environment, the formation, important role, motivation, and difficulty in HCHO research field are summarized.

In Chapter 2, the developed continuous and selective determination method of formaldehyde (HCHO) in gas phase using the chemiluminescence method is described. The concentration of HCHO in the ambient air is low and the conventional determination method of aldehyde (2, 4-DNPH-HPLC method) requires long time for sampling. Furthermore, there are some difficulties to measure HCHO continuously and selectively with high time resolution. The chemiluminescence method by using gallic acid and H_2O_2 can measure HCHO continuously with high time resolution, but the interference is still a problem. To solve these problems, the improved chemiluminescence method was developed. The counter current flow tube was used to collect and concentrate gaseous formaldehyde. The air sample was passed through the (id 6 mm×100 cm length) counter current flow tubes (CCFT) that comprises a 6 mm outer diameter helical glass wire that was inserted inside a glass tube. The absorption solution containing HCHO was introduced to the iodoform reaction section to remove the interferences from other aldehydes. Subsequently, the sample was introduced to the sample analysis section by the chemiluminescence. The chemiluminescence produced from the reaction of HCHO, gallic acid, H_2O_2, and KOH was detected by a photo-diode detector. The limit of detection (S/N = 3) was 4.5 ppbv (v indicates volume ratio) in the air with a linearity up to 6.25 ppmv. The effect of ions and heavy metal ions are negligible in which the effect of ferrous ion was totally removed. The removal of interference makes this method suitable for measuring in the air and rainwater with good time resolution and reliability. HCHO concentration measured by the present method showed good agreement with that obtained by the 2,4-Dinitrophenylhydrazine method.

In Chapter 3, the developed method was applied to measure HCHO in the ambient air and rainwater to investigate the characteristic of HCHO in the environment. In this study, the HCHO in the ambient air in a residential area (Sakai City, Japan) and polluted area (Ho Chi Minh City, Vietnam) and that in rainwater in Sakai City were investigated. In Sakai City, the measurement of HCHO in the ambient air was conducted continuously from December 2017 to January 2018. The diurnal average of HCHO concentration varied within 8 to 23 ppbv. The HCHO concentration in the nighttime was persistent approximately 12 ppbv and slowly increased to 14 ppbv in the morning (around 9 AM). The variation of HCHO in Sakai City was reflected by the pattern characterized for clean environment and affected by meteorological conditions but less affected by stationary emission. In contrast to Sakai City, in Ho Chi

Minh City, HCHO pattern seems to be strongly affected by rush hours, and high peaks were clearly observed. The high peak (up to 65 ppbv) appeared in the morning rush hours is the evidence for direct emission from the vehicles.

The concentration of HCHO in rainwater, its variation and the processes that might be expected to occur in rainwater were also investigated. The concentration of HCHO in 20 rain events including typhoons in 2018 Baiu season in Sakai City, Osaka, Japan, ranged from below detection limit (3σ) of 0.08 μM to 9.91 μM, and the average of each rain event varied from 0.13 to 2.75 μM. The average concentration observed in this study was lower than the reported in the previous studies and between the range of the marine value and urban value. The high concentration was mainly observed during the nighttime that contrast with the ambient HCHO that is usually high in day time due to the photoproduction. Based on observation, the variation patterns of HCHO during rain events were divided into four types. The concentration and observed patterns could be the result of complex processes relating to sources and processes during rainfall. However, no relations were observed for HHO concentration in rainwater with rainfall intensity and local HCHO gas phase concentration. That implies the concentration of HCHO in rainwater might be controlled before falling by aqueous photolysis of dissolved organic compounds (DOCs) and other processes.

Furthermore, the formation and sink of HCHO in rainwater were investigated. Series of irradiation experiments was carried out to confirm that HCHO was produced by photolysis of DOCs in rainwater. The samples were exposed under various kinds of light sources including room light, sunlight and UV lamp, and the results were compared with control samples. The result showed that HCHO concentrations increased in all irradiated samples. The formation rates were calculated in the range of 0.05 to 2.43 $\mu M\ h^{-1}$ and faster than the decomposition rate by radical in aqueous phase. These results proved the photoproduction of HCHO. Besides the HCHO formation by photolysis of DOCs, the role of microorganism in rainwater was also investigated. The loss in dark samples indicated the activity of microorganisms in the samples. Microbial activity in the cloud and droplet could be one important factor to control the concentration of HCHO with digestion rate observed up to 3.2 $\mu M\ h^{-1}$ in normal rainwater and 0.27 and 0.15 $\mu M\ h^{-1}$ in typhoon rainwater.

In Chapter 4, the sources of HCHO indoor was focused. Incense stick burning is one of casual household activity especially in east and southeast Asian countries, including Vietnam, but the emission profile carbonyls has not been studied properly. In this study, the target is HCHO and other carbonyl compounds emitted from burned incense stick. Nine incense stick types were collected from Vietnam and

investigated the carbonyl emission profile. The incense sticks were burned in a chamber, and aldehydes were collected by 2,4-dinitrophenylhydrazine cartridge (2,4-DNPH) and analyzed by HPLC. The concentration of HCHO was also measured by the developed chemiluminescence method. The result showed that in ten analyzed carbonyl compounds, propionaldehyde (3-84 %, avg. 32 %), acetaldehyde (8-90 %, avg. 30 %), and acetone (0-38 %, avg. 9 %) were the most abundant in term of total weight emitted carbonyls, respectively. The fourth abundant aldehyde was HCHO (1-26 %, avg. 8 %). The concentration of HCHO in released smoke was ranged from 46.65 ± 4.44 to 596.89 ± 279.17 $\mu g/m^3$ (38.02 ± 3.62 to 486.46 ± 242.19 ppb). Tested samples showed HCHO concentrations higher than the value according to the World Health Organization (WHO) guideline (WHO 2010) and Vietnam National standard for indoor air quality (QCVN-2009). Therefore, in this chapter, the personal risk assessment of HCHO inhalation exposure was carried out by the burning simulation in a small unventilated room. The risk calculation showed the cancer risk is 1.81×10^{-5} which is 24% higher than the base risk. However, the number of the day people burning incense could be more than the estimation. Therefore, the cancer risk they can get must be much higher, especially for the women who are the most frequently use incense.

In Chapter 5, the obtained results were summarized and discussed future study for aldehydes especially role of HCHO in the environment.

審査結果の要旨

本論文は、大気中及び雨中のホルムアルデヒド(HCHO)の新規連続測定法の開発と環境測定への応用についてまとめたものである。HCHO は毒性物質、発がん物質、シックハウス症候群の原因物質としても知られており、また、大気環境中での種々の反応により生成したり、種々の反応に関与するなど重要な役割を果たしている。しかし、HCHO の測定には一般には誘導体化して測定する必要があるなど、連続測定が難しい物質の一つである。本研究では、HCHO だけを選択的に高時間分解能で測定する簡易な方法を新たに開発し、環境測定に適応した結果をまとめたもので、次のような興味深い新たな結果を得ている。

(１) 簡易的な連続測定法である化学発光法を改良し、従来は全てのアルデヒドが検知されていた方法を、ヨードホルム反応が HCHO は起こらないが、アセトアルデヒドとアセトンが反応することに着目し、HCHO だけを連続測定できる方法を確立した。気液接触型の向流管を用いることで大気中の HCHO を吸収液に吸収させ、大気の連続測定に用いることができることを明らかにした。本法を堺市及びホーチミンの大気観測に用い、それぞれの都市の大気中

HCHO の濃度変動の違いを示し、その原因を推定した。

(２) 開発した方法を改良し、大気と雨中の HCHO の同時連続測定に応用した。その結果、雨の中 HCHO 濃度は従来考えられていたように大気の濃度に影響を受けているわけではなく、雨の中の有機物の光化学生成が重要であることを明らかにした。また、微生物による分解も雨中の濃度に影響を与えている可能性を示した。

(３) 線香の燃焼から放出されるアルデヒド類濃度を従来の方法で測定すると同時に開発した測定法で HCHO の連続測定を行い、線香を使用した後の室内の濃度変動を明らかにした。その結果をもとにシミュレーションを行い、家庭生活で生涯にわたって線香を使用した際の HCHO による健康リスクを評価した。

以上の結果は、従来の測定法では困難であった高時間分解能の HCHO の動態を解明したもので、大気環境分野で非常に貴重な研究結果である。大気化学や室内環境で重要であると認識されている HCHO の濃度及び動態に新たな知見を加え、今後の発展に期待できる結果を示したもので、大気環境の研究領域で多大な貢献がある。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを示したものである。