（ 続紙 1 ）

京都大学	博士（地球環境学）	氏名	Sathiyamurthi Ramasamy
論文題目	A quantitative approach on understanding emission and removal of trace gases and atmospheric oxidation chemistry in remote and suburban forest		

（論文内容の要旨）

The continuous increasing trend in photochemical oxidants (surface O_3) has been observed for a long time in Japan, even though the precursors volatile organic compounds (VOCs) and nitrogen oxides (NO_X = NO + NO_2) have decreased from 1990-2010 after several strict regulations for anthropogenic emission. Although anthropogenic VOCs can be controlled, a vast amount of biogenic VOCs from plants is still continuously emitted in Japan, because of 67 % forest coverage. Despite, BVOCs are important; there is substantial uncertainty in their contribution to the oxidant formation. To understand the involvement of BVOCs in photochemical formation of O_3 in the absence and the presence of anthropogenic sources, comprehensive measurements of atmospheric OH loss rate and trace species such as VOCs, NO_X, O_3, CO, etc. were conducted in the remote and suburban forest and interpretation of destribution of biogenic and anthropogenic species with other forest and urban area were discussed. This dissertation contains 5 chapters as follows.

1. Introduction

In this chapter primary emission sources from biogenic and anthropogenic region and further photochemical products and secondary products formation were discussed. Contrasting behaviour of decreasing trends in primary air pollutants but increasing trend in photochemical oxidants trend in Japan is shown. Several research questions are raised that are why photochemical O_3 increasing, how to improve knowledge about distribution of biogenic and anthropogenic precursors to understand photochemical O_3 formation, which combination of instruments explain more about primary emission and secondary products and which place will give clear picture about primary sources distribution. To understand more details about biogenic VOCs remote forest (Wakayama Forest Research Station–WFRS) with unique characteristics such as larger area, predominant coniferous tree species coverage, clean air flow from Ocean was selected. Additionally to understand biogenic and anthropogenic sources distribution and photochemical O_3 formation suburban area near Tokyo (Field Museum Tama) was selected.

2. Identification and characterisation of VOCs in Wakayama forest

In this chapter distribution of BVOCs and nature of emission are discussed. Additionally to get more details BVOCs in WFRS are compared with that in Boreal forest. (Station for Measuring Ecosystem-Atmospheric Relations (SMEAR-II)). With improved recently developed BVOCs detection method several BVOCs were measured. The majority of the monoterpenes showed night-time maximum because the forest is dominated by coniferous trees which are reported to

emit a copious amount of monoterpene from their storage structures depending on the ambient temperature. Interestingly monoterpenes measured in WFRS have shown similar diurnal cycle and mixing ratio with representative boreal forest. However, the average mixing ratio of BVOCs in WFRS was substantially higher than that of boreal forest due to the lower oxidant level.

3. Total OH reactivity measurements in Wakayama forest

In this chapter measured OH reactivity and calculated OH reactivity and origin missing sinks are discussed. The average measured OH reactivity was (7 s^{-1}) and comparable with that made in similar environments (e.g. boreal forest 9 s^{-1} and coniferous pine forest 10 s^{-1}). During the cleaner period of this campaign most of the abundant species were measured because missing OH reactivity only 11 %. BVOCs accounted for 44 % especially larger fraction (30-40 %) of monoterpenes in the night-time, due to temperature dependency and shallow boundary layer. Higher missing OH reactivity was observed during transported pollution event. Linear regression analysis of missing OH reactivity with several other species have shown secondary products are most likely contribute to the missing OH reactivity.

4. OH reactivity and trace species measurement in a suburban forest near Tokyo during AQUAS-TAMA campaign

In this chapter, the anthropogenic and biogenic VOCs composition and sources in suburban forest, measured and calculated OH reactivity comparison and O_3 formation potential are discussed. Similar trend of AVOCs with nearby suburban and lower mixing ratio was observed that indicates same sources and urban air outflow. However, mixing ratio is 2-3 times lower than that of suburban especially reactive alkenes are multifold lower which indicates urban air outflow and photochemical removal during transportation. OH reactivity was much lower but O_3 formation comparable with urban area. From the larger fraction of isoprene (28.2 %) to overall reactivity in the summer time, it is clear that biogenic VOCs potentially involved in O_3 production. Additionally, estimation shows that unmeasured species were also significantly accounted for photochemical O_3 formation.

5. Conclusion

VOCs trend includes both highly reactive species and less reactive species. Even though biogenic VOCs contribution is less for the overall mixing ratio, due to their higher reactivity they contribute much for O_3 formation. For example, in suburban forest measurement, AVOCs mixing ratio 15.40 ppb and BVOCs 1.13 ppb. But for OH reactivity AVOCs contribution is only 12.3 % BVOCs 28.6 %. Additionally, remote forest measurement showed several BVOCs supplied to the atmosphere. Therefore, BVOCs emission and anthropogenic interaction is one of the candidates for increasing of O_3. However, presence of unknown sinks indicates further development is needed for more details.

（ 続紙 2 ）

（論文審査の結果の要旨）

我が国のオキシダントレベルはその前駆物質の濃度が斬減しているにもかかわらず明確な増加トレンドを示しており、その原因解明が急がれている。前駆物質としては揮発性有機化合物(VOC)が重要となるがその重要な発生源としては人為起源および植物起源が考えられている。人為起源由来のVOCは明確に削減が進んでいることから、植物起源のVOCの相対的な重要性が増加していると考えられている。本論文では植物起源のみで記述できる清浄な大気が観測できる京都大学和歌山演習林と人為起源および植物起源物質が混在する東京農工大学FM多摩での反応性物質およびOH反応性の総合観測を行い、清浄大気の場合は未知なる反応性として10%程度であることを報告している。しかし、近畿地方から汚染空気が流入した場合、未知なるOH反応性は28.5%まで増加していることを明らかとした。この事実は酸化剤であるオゾンが大気に供給されたことにより酸化反応が進み、２次的に生成した化学物質が未知なる反応性として検出されたという合理的な解釈を可能としている。

OHラジカル反応性という新たな指標を駆使しまた、ユニークな環境を提供する場所で観測を進め未知なる反応性物質の性状について重要な示唆を与えた論文であると判断される。今後、オキシダントの戦略的な制御を構築するためには本論文の知見が極めて重要であると考えられられることから、地球環境学の発展に大きく貢献した。

よって本論文は博士（地球環境学）の学位論文として価値あるものと認める。また、平成 28 年 8 月 4 日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

要旨公開可能日：　　年　　月　　日以降