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To cite this article: Norfazrin Mohd Hanif *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **616** 012011

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Enhanced Chlorinated very Short-Lived Substances in South East Asia: Potential Source Regions and Source Types

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Abstract. Enhancements of the mixing ratios of short-lived halogenated gases were observed in air samples collected at Bachok Marine Research Station (BMRS), Peninsular Malaysia during Northern Hemisphere winters in 2013/2014 and 2015/2016. This study investigates the potential source regions and source types that influenced the variability in chlorinated very short-lived substances (Cl-VSLS) [dichloromethane, 1,2-dichloroethane, trichloromethane, tetrachloroethene] and methyl halides [methyl chloride and methyl bromide]. The UK Met Office's Numerical Atmospheric Modelling Environment (NAME) dispersion model, was used for tracking the origin of air masses arriving at BMRS. For the purpose of identifying possible sources of these compounds, carbon monoxide (CO) emission data taken from the Representative Concentration Pathway 8.5 were used along with NAME footprints to calculate modelled CO mixing ratios. A correlation analysis between the mixing ratios of measured compounds and the modelled CO from various emission sectors was performed to assess the extent to which emission sectors might be related to the mixing ratios of halogenated gases. The results show that the sectors of higher mixing ratios were associated with air masses, especially from East China. During the 2013/2014 campaign, the modelled CO from industrial, solvents and agriculture (waste burning on fields) were significantly correlated with the mixing ratios of Cl-VSLS ($R > 0.7$) and methyl halides ($R > 0.40$). During the 2015/2016 campaign, the strength of these correlations reduced for Cl-VSLS ($R > 0.5$) and with no significant correlations for methyl



halides. Instead, mixing ratios of methyl halides were correlated ($R=0.4$) with modelled CO from forest burning. This work provides evidence that East and South East Asia act as important sources of halogenated gases. This is of significant given the proximity of these regions to prevalent deep convection which can rapidly transport these halogen-containing gases into the stratosphere and impact the ozone layer.

1. Introduction

The Montreal Protocol's success in phasing out the use of ozone depleting substances has facilitated the gradual healing of the ozone layer. Recent work, however, has shown that rising emissions of very-short-lived chlorinated substances (chlorinated VSLs) threaten to delay such recovery. VSL is classified as trace gases whose local life is comparable to, or shorter than, inter hemispheric transport timescales [1]. VSLs were historically not considered damaging to the ozone layer as they have relatively short atmospheric lifetimes (less than six months) and are not expected to reach large amounts in the stratosphere. Their short lifetimes and corresponding low ozone depletion potentials (ODPs) has led them to be excluded from the Montreal Protocol [2]. However, chlorinated VSLs, which are primarily anthropogenic in origin, have been found to be increasing ($\sim 1.3 \pm 0.3$ ppt Cl yr⁻¹, 2008–2012) in contrast to the decline of long-lived controlled chlorinated substances (-13.4 ± 0.9 ppt Cl yr⁻¹) over the same period [1]. Increased anthropogenic emissions of VSLs containing chlorine, particularly from tropical sources, are an emerging issue for stratospheric ozone. The relative contribution of these emissions could become important as levels of ozone-depleting substances (ODSs) controlled under the Montreal Protocol decline [1]. Because of their short lifetimes, the potential impact of VSLs on stratospheric ozone depends heavily on the location of their sources, with emissions close to the major stratospheric input regions being of far greater significance for ozone depletion. This work focuses on the chlorinated VSLs most widely reported in the background atmosphere, dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃), tetrachloroethene (CCl₂CCl₂, shortened to C₂Cl₄), and 1,2-dichloroethane (CH₂ClCH₂Cl). Chlorinated VSLs are predominantly anthropogenic in origin, with the exception of CHCl₃ [2]. For CHCl₃, up to $\sim 50\%$ can be accounted for by anthropogenic sources [3]. This work aims to provide an assessment of the abundances of four chlorinated VSLs in the regions of East Asia and South East Asia. The findings from sampling station located in Bachok are presented. The overall aim of the multiyear regional measurements was to improve our knowledge on the tropospheric abundances of a wide range of halocarbon compounds including chlorinated VSLs. Specifically, this work aims:

- a. To assess the variability of chlorinated VSLs and identify any enhancement above background levels for the chlorinated VSLs.
- b. To investigate potential source regions and emission sectors that may contribute towards the variations in chlorinated VSL levels.

2. Experimental

2.1. Sampling site

The measurements of chlorinated VSLs were carried out at the atmospheric observation tower established at the Bachok Marine Research Station, Kelantan, Peninsular Malaysia. The station was built as part of the Institute of Ocean and Earth Sciences (IOES) at the University of Malaya (UM). The station is extremely well positioned for studies on the outflow of the rapidly developing Southeast Asian countries. The measurement campaigns were carried out during the Northern Hemisphere winter months. The first campaign was from the 20th January 2014 to the 5th February 2014. The second campaign was conducted from the 19th November 2015 until 27th January 2016.

2.2. Sample collection and analysis

Air samples were collected in stainless steel canisters. Analysis of the all air samples was conducted using gas chromatography mass spectrometry.

2.3. Dispersion modelling

The UK Met Office's Numerical Atmospheric Modelling Environment (NAME) dispersion model was used for tracking and understanding the origin of air masses arriving at sampling station. The identification of the origin air masses that arrived at Bachok was conducted by examine the NAME footprints. For NAME particle distribution, the analysis was started by dividing the area into countries using shapefiles generated from ArcGIS and then extracting the time integrated particle density (g s m^{-3}) for each region. The NAME footprints were used along with emissions data of carbon monoxide (CO) taken from RCP 8.5 (Representative Concentration Pathway 8.5) for the year 2010 to calculate the concentration of CO above background at the Bachok.

3. Results and Discussions

3.1. Observation of chlorinated VSLs mixing ratios

When comparing each chlorinated VSLs's contribution to the total chlorinated VSLs measured in Bachok, CH_2Cl_2 contributed the largest fraction (~70%) in both campaigns, followed by $\text{CH}_2\text{ClCH}_2\text{Cl}$, CHCl_3 and C_2Cl_4 (Table 1). The mixing ratios of the four chlorinated VSLs were above the background levels (Table 1 and Figure 1). For instances, the median values of CH_2Cl_2 in 2013/2014 and 2015/2016 were 86.1 ppt and 70.0 ppt, respectively, three and 2.5 times higher than the background value (28.4 ppt, range = 21.8 – 34.4 ppt).

Some unusual enhancements in the mixing ratios of all chlorinated VSLs were observed on certain days throughout the campaigns (examples are labelled (a), (c), (d), (e) and (f) in Figure 1). It appears that the variation of chlorinated VSLs measured at Bachok could have been influenced by the pathway along which the air masses had travelled prior to reaching Bachok.

Table 1. Summary of the chlorinated VSLs data obtained from measurement campaigns in Bachok. For comparison, also shown are the approximate median background concentrations and ranges for each chlorinated VSLs in the remote marine boundary layer (MBL), taken from the most recent WMO ozone assessment [1].

| | 1 st campaign (2013/2014) | | 2 nd campaign (2015/2016) | | MBL (WMO 2014) ^a | |
|-------------------------------------|---|----------------|---|----------------|--------------------------------|-------------------------|
| | Median (ppt) | Range (ppt) | Median (ppt) | Range (ppt) | Median (ppt) | Range (ppt) |
| CH_2Cl_2 | 86.1 | 66.4 - 352.2 | 70.0 | 47.4 - 268.0 | 28.4 | 21.8 - 34.4 |
| $\text{CH}_2\text{ClCH}_2\text{Cl}$ | 40.6 ^b | 16.4 - 119.5 | 16.0 | 8.5 - 78.2 | 3.7 | 0.7 - 14.5 ^c |
| CHCl_3 | 15.2 | 12.8 - 30.5 | 13.8 | 9.7 - 35.4 | 7.5 | 7.3 - 7.8 |
| C_2Cl_4 | 2.0 | 1.6 - 9.5 | 2.1 | 1.3 - 7.9 | 1.3 | 0.8 - 1.7 |

Note:

^a The WMO data are a compilation of all reported global measurements up to, and including, the year 2012.

^b $\text{CH}_2\text{ClCH}_2\text{Cl}$ was only analysed in 16 of the 28 samples during the 2013/2014 campaign.

^c The $\text{CH}_2\text{ClCH}_2\text{Cl}$ MBL data actually date back to the early 2000s. No recent data were reported.

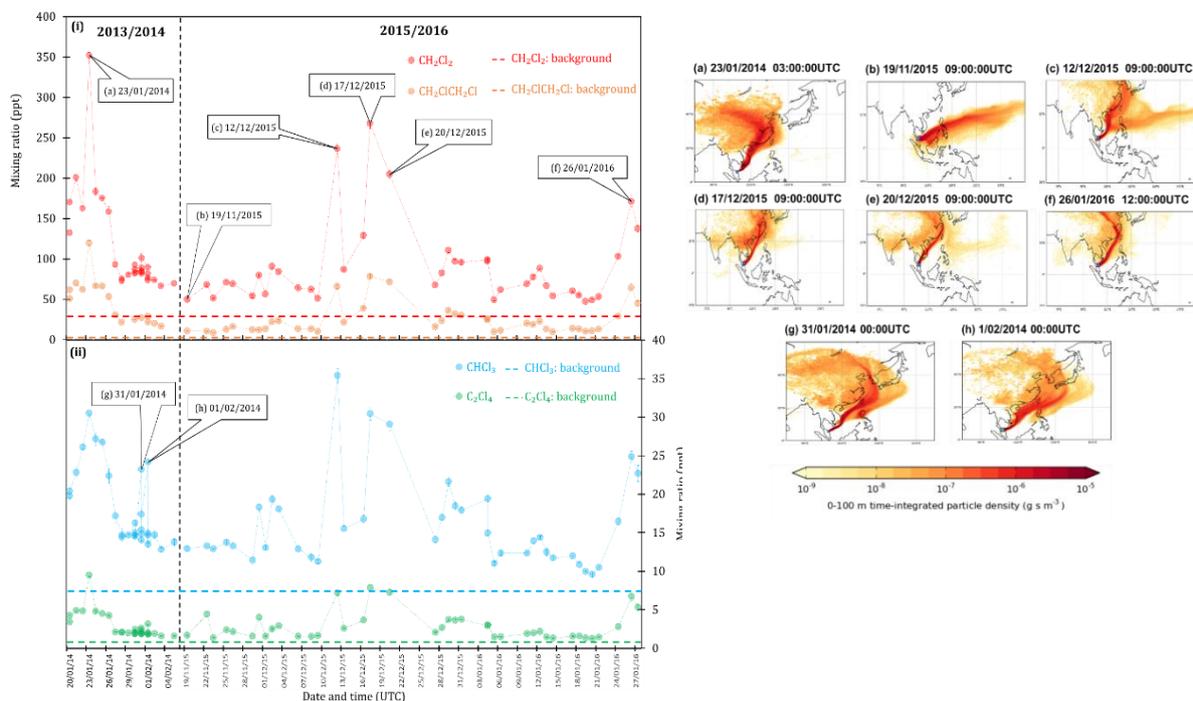


Figure 1. Left panel, Mixing ratios (ppt) of the four chlorinated VSLs in 68 air samples collected at Bachok during the Northern Hemisphere winters, 2013/2014 and 2015/2016. Right panel, (a) to (f): NAME footprint maps generated from a back-trajectory analysis indicating the likely origin of the air sampled at Bachok, with the darker colours indicating greater influence.

3.2. Interspecies correlations of chlorinated VSLs

The temporal patterns of all compounds in Bachok over the entire campaign cycles (Figure 1) appear comparable, indicating that the compounds are co-emitted, or at least coming from same source location(s). The findings of the interspecies correlation indicate very strong associations ($R > 0.8$, $p < 0.05$) between all four measured chlorinated VSLs (table 2). It may potentially due to the air masses that transported the chlorinated VSLs to Bachok originated or travelled across the same regions and so the chlorinated VSLs are very likely to have similar source emissions.

Table 2. Correlation matrices for three chlorinated VSLs, i.e. $\text{CH}_2\text{ClCH}_2\text{Cl}$, CHCl_3 and C_2Cl_4 measured in Bachok. The value presented is the correlation coefficient (R). Correlations that are significant ($p < 0.05$) are in bold font.

| | 2013/2014 | | | |
|-------------------------------------|--------------------------|-------------------------------------|-----------------|-------------------------|
| | CH_2Cl_2 | $\text{CH}_2\text{ClCH}_2\text{Cl}$ | CHCl_3 | C_2Cl_4 |
| $\text{CH}_2\text{ClCH}_2\text{Cl}$ | 1.00 | | 0.94 | 0.95 |
| CHCl_3 | 0.94 | 0.93 | | 0.90 |
| C_2Cl_4 | 0.85 | 0.95 | 0.90 | |
| No. of data points | 26 | 26 | 26 | 26 |

| | 2015/2016 | | | |
|-------------------------------------|--------------------------|-------------------------------------|-----------------|-------------------------|
| | CH_2Cl_2 | $\text{CH}_2\text{ClCH}_2\text{Cl}$ | CHCl_3 | C_2Cl_4 |
| $\text{CH}_2\text{ClCH}_2\text{Cl}$ | 0.93 | | 0.93 | 0.79 |
| CHCl_3 | 0.93 | 0.84 | | 0.90 |
| C_2Cl_4 | 0.90 | 0.90 | 0.90 | |
| No. of data points | 40 | 40 | 40 | 40 |

3.3. Identification and quantification of possible geographical source region(s) of chlorinated VSLs

During the Northern Hemisphere winters, the air flow was usually dominated by south-eastward movement of cold air in the high pressure Siberian-Mongolian High. The cold air then passed the East Asia region and travelled to the northern South China Sea and as far as the tropics. Table 3 indicates that China is the primary source region of CH_2Cl_2 observed at Bachok. The findings from this study are consistent with recent publications (e.g. [4], [5]) and provide further evidence that the East Asia region is responsible for the chlorinated VSLs emissions. The fact significant observed associations between CH_2Cl_2 and the other chlorinated VSLs suggests that China is also a strong source of other observed chlorinated VSLs. It is challenging at this point to determine which industrial sector(s) were responsible for emitting the chlorinated VSL, and whether the emissions were from single or multiple industrial applications. The challenge arises due to limited knowledge of Chinese emissions and a lack of official usage reports to regulating bodies [6].

Table 3. Association of particle concentrations (g s/m^3) from potential source regions with the observed mixing ratios of CH_2Cl_2 in Bachok. The values indicate the Spearman correlation coefficients (R), significant correlations ($p < 0.05$) are in bold font.

| Sub-regions | Potential regions | 2013/2014 | 2015/2016 |
|-----------------|------------------------|-------------|-------------|
| China | 1. East China | 0.87 | 0.68 |
| | 2. North China | 0.61 | 0.56 |
| | 3. Northeast China | -0.49 | 0.49 |
| | 4. Northwest China | 0.86 | 0.61 |
| | 5. Southcentral China | 0.82 | 0.80 |
| | 6. Southwest China | 0.76 | 0.70 |
| East Asia | 7. Taiwan | 0.14 | 0.47 |
| | 8. Japan | -0.86 | 0.20 |
| | 9. Korea | -0.61 | 0.44 |
| South East Asia | 10. Indochina | 0.34 | 0.50 |
| | 11. Peninsula Malaysia | -0.05 | -0.22 |
| | 12. East Malaysia | 0.42 | -0.53 |
| | 13. Philippines | -0.50 | -0.65 |
| Oceanic regions | 14. East China sea | 0.47 | 0.46 |
| | 15. Japan Sea | -0.90 | 0.38 |
| | 16. Pacific Ocean | -0.70 | -0.57 |
| | 17. South China Sea | -0.57 | -0.57 |

3.4. Effect of emission sources on chlorinated VSLs mixing ratio

Table 4 presents the results of the correlation analysis between modelled CO due to each emission sector and chlorinated VSLs. The modelled CO due to emissions from industrial, solvents and agriculture (waste burning on fields) were significantly associated ($R > 0.69$, $p < 0.05$) with CH_2Cl_2 observed at Bachok for both the 2013/2014 and the 2015/2016 campaign. In the 2013/2014 campaign, the association between modelled CO due to forest burning emissions and observed CH_2Cl_2 was found to be negligible but significant in the 2015/2016 campaign, suggesting that biomass burning may also have been a potential emitter of chlorinated VSLs. This could be true because a substantial part of biomass burning activities occur in tropical regions and may therefore be the primary source of trace gas in these areas with otherwise only relatively small manmade emissions [7]. However, little information is known on the contribution of biomass burning as a potential emission source. Overall, while it is evident from this analysis that chlorinated VSLs are consistently correlated with industrial and biomass burning emissions, the exact mechanism or process that leads the emission of chlorinated VSLs to the atmosphere is still uncertain. This work was restricted to a limited number of compounds and further analysis (e.g. associations with other tracers) may enable detailed source pinpointing and provide concrete conclusions as to the possible emission sources of each gas.

Table 4: Association of modelled CO mixing ratios derived from various emission types with the observed mixing ratios of CH₂Cl₂ in Bachok. The values indicate the Spearman correlation coefficients (R). Significant correlations ($p < 0.05$) are in bold.

| Emission type | 2013/2014 | 2015/2016 |
|--|-------------|-------------|
| 1. Industry (combustion and processing) | 0.80 | 0.69 |
| 2. Solvent | 0.83 | 0.71 |
| 3. Agriculture (waste burning on fields) | 0.71 | 0.70 |
| 4. Forest burning | 0.27 | 0.45 |

4. Conclusion

Overall, the sources of chlorinated very-short-lived substances (VSLs) may just be co-located with emission activities generated from industry, solvent production, waste burning on agricultural fields found in the East Asia and South East Asia regions. The fact that both regions contain multiple sources of chlorinated VSLs suggests the significance of the regions as potential emitters of chlorinated VSLs to the atmosphere. This highlights the importance of carrying out more regional studies not only as few measurements have been made so far but also the proximity of this region to prevalent deep convection, which escalates the chance of pollutants emitted from here being transported into the stratosphere and impacting the ozone layer.

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