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 perform to assess the extent to which emission sectors might be related to the mixing ratios of halogenated gases. The results show that the events 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 VSLSs) threaten to delay such recovery. VSLS is classified as trace gases whose local life is comparable to, or shorter than, interhemispheric transport timescales [1]. VSLSs 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 VSLSs, which are primarily anthropogenic in origin, have been found to be increasing (~1.3 ± 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 VSLSs 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 VSLSs 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 VSLSs most widely reported in the background atmosphere, dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃), tetrachloroethene (CCl₂CCl₂, shortened to C₂Cl₄), and 1,2-dichloroethane (CH₂ClCH₂Cl). Chlorinated VSLSs are predominantly anthropogenic in origin, with the exception of CHCl₃ [2]. For CHCl₃, up to ~50% can be accounted for by anthropogenic sources [3]. This work aims to provide an assessment of the abundances of four chlorinated VSLSs 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 VSLSs. Specifically, this work aims:

a. To assess the variability of chlorinated VSLSs and identify any enhancement above background levels for the chlorinated VSLSs.

b. To investigate potential source regions and emission sectors that may contribute towards the variations in chlorinated VSLS levels.

2. Experimental

2.1. Sampling site
The measurements of chlorinated VSLSs 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 examining 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 VSLSs measured in Bachok, CH₂Cl₂ contributed the largest fraction (~70%) in both campaigns, followed by CH₂ClCH₂Cl, CHCl₃ and C₂Cl₄ (Table 1). The mixing ratios of the four chlorinated VSLSs were above the background levels (Table 1 and Figure 1). For instance, the median values of CH₂Cl₂ in 2013/2014 and 2015/2016 were 86.1 ppt and 70 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 VSLSs 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 VSLSs 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].

| Chlorinated VSLS | 1st campaign (2013/2014) | Median Range (ppt) | 2nd campaign (2015/2016) | Median Range (ppt) | MBL (WMO 2014) |
|------------------|--------------------------|---------------------|--------------------------|---------------------|-----------------|
| CH₂Cl₂           | 86.1                     | 66.4 - 352.2        | 70.0                     | 47.4 - 260.0        | 28.4            |
| CH₂ClCH₂Cl       | 40.6                     | 16.4 - 119.5        | 16.0                     | 8.5 - 78.2          | 3.7             |
| CHCl₃            | 15.2                     | 12.8 - 30.5         | 13.8                     | 9.7 - 35.4          | 7.5             |
| C₂Cl₄            | 2.0                      | 1.6 - 9.5           | 2.1                      | 1.3 - 7.9           | 1.3             |

Note:
* The WMO data are a compilation of all reported global measurements up to, and including, the year 2012.
* CH₂ClCH₂Cl was only analysed in 16 of the 28 samples during the 2013/2014 campaign.
* The CH₂ClCH₂Cl MBL data actually date back to the early 2000s. No recent data were reported.
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 VSLSs (table 2). It may potentially due to the air masses that transported the chlorinated VSLSs to Bachok originated or travelled across the same regions and so the chlorinated VSLSs are very likely to have similar source emissions.
Table 2. Correlation matrices for three chlorinated VSLSs, i.e. CH₂ClCH₂Cl, CHCl₃ and C₂Cl₄ measured in Bachok. The value presented is the correlation coefficient (R). Correlations that are significant (p<0.05) are in bold font.

|          | 2013/2014 |          |          |          |
|----------|-----------|----------|----------|----------|
| CH₂ClCH₂Cl | 1.00      |          |          |          |
| CHCl₃     | 0.94      | 0.93     | 0.94     | 0.95     |
| C₂Cl₄     | 0.85      | 0.95     | 0.90     |          |
| No. of data points | 26         | 26       | 26       | 26       |

|          | 2015/2016 |          |          |          |
|----------|-----------|----------|----------|----------|
| CH₂ClCH₂Cl | 0.93      |          |          | 0.93     | 0.79     |
| CHCl₃     | 0.93      | 0.84     | 0.93     | 0.90     |
| C₂Cl₄     | 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 VSLSs

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 CH₂Cl₂ 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 VSLSs emissions. The fact significant observed associations between CH₂Cl₂ and the other chlorinated VSLSs suggests that China is also a strong source of other observed chlorinated VSLSs. It is challenging at this point to determine which industrial sector(s) were responsible for emitting the chlorinated VSLS, 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/m³) from potential source regions 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 font.

| Sub-regions | Potential regions | 2013/2014 | 2015/2016 |
|-------------|------------------|-----------|-----------|
| China       | East China       | 0.87      | 0.68      |
|            | North China      | 0.61      | 0.56      |
|            | Northeast China  | -0.49     | 0.49      |
|            | Northwest China  | 0.86      | 0.61      |
|            | Southcentral China | 0.82    | 0.80      |
|            | Southwest China  | 0.76      | 0.70      |
| East Asia   | Taiwan           | 0.14      | 0.47      |
|            | Japan            | -0.86     | 0.20      |
|            | Korea            | -0.61     | 0.44      |
| South East Asia | Indochina    | 0.34      | 0.50      |
|            | Peninsula Malaysia | -0.05  | -0.22     |
|            | East Malaysia    | 0.42      | -0.53     |
|            | Philippines      | -0.50     | -0.65     |
| Oceanic regions | East China sea  | 0.47      | 0.46      |
|            | Japan Sea        | -0.90     | 0.38      |
|            | Pacific Ocean    | -0.70     | -0.57     |
|            | South China Sea  | -0.57     | -0.57     |

3.4. Effect of emission sources on chlorinated VLS mixing ratio

Table 4 presents the results of the correlation analysis between modelled CO due to each emission sector and chlorinated VLSs. 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 CH₂Cl₂ 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 CH₂Cl₂ 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 VLSs. 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 VLSs are consistently correlated with industrial and biomass burning emissions, the exact mechanism or process that leads the emission of chlorinated VLSs 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 CH$_2$Cl$_2$ 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 (VSLSs) 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 VSLSs suggests the significance of the regions as potential emitters of chlorinated VSLSs 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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