



Methyl chloride and methyl bromide emissions from baking: an unrecognized anthropogenic source



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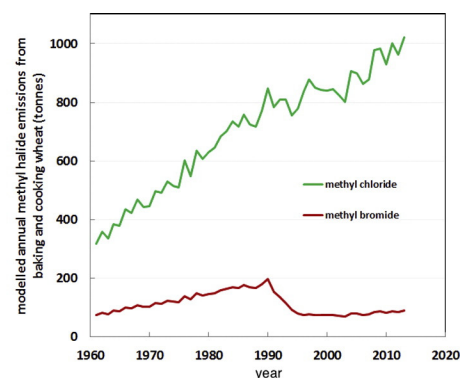
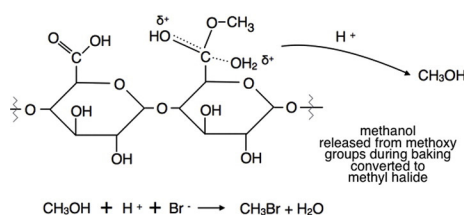
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HIGHLIGHTS

- First report of methyl halides produced during breadbaking
- New, unrecognized anthropogenic source of ozone depleting gases
- Methyl bromide from baking has decreased with restrictions of potassium bromate use.

GRAPHICAL ABSTRACT



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ABSTRACT

Methyl chloride and methyl bromide (CH_3Cl and CH_3Br) are the largest natural sources of chlorine and bromine, respectively, to the stratosphere, where they contribute to ozone depletion. We report the anthropogenic production of CH_3Cl and CH_3Br during breadbaking, and suggest this production is an abiotic process involving the methyl ester functional groups in pectin and lignin structural polymers of plant cells. Wide variations in baking styles allow only rough estimates of this flux of methyl halides on a global basis. A simple model suggests that CH_3Br emissions from breadbaking likely peaked circa 1990 at approximately 200 tonnes per year (about 0.3% of industrial production), prior to restrictions on the dough conditioner potassium bromate. In contrast, CH_3Cl emissions from breadbaking may be of similar magnitude as acknowledged present-day CH_3Cl industrial emissions. Because the mechanisms involve functional groups and compounds widely found in plant materials, this type of methyl halide production may occur in other cooking techniques as well.

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1. Background

Methyl chloride (CH_3Cl) is the largest natural contributor to stratospheric ozone destruction, responsible for 16.4% of total tropospheric chlorine in 2012 (Carpenter et al., 2014). Methyl chloride is principally produced naturally, though there is a known anthropogenic component. Industrial production emitted 1200 tonnes (1000 tonnes = 1 Gg) in 2004, though more is used as chemical feedstock and not released to the environment (UNEP, 2007). Unintentional production via other human activities, such as rice paddies and fossil fuel burning, also contribute large quantities of CH_3Cl to the atmosphere (Santee et al., 2013). Total natural and anthropogenic emissions total about 4400–5700 Gg year⁻¹, and the troposphere contained about 540 ppt per volume in 2012 (Carpenter et al., 2014). The budget of CH_3Cl production and loss is not balanced (Carpenter et al., 2014), though many natural sources have been identified in recent years. The production and use of CH_3Cl is not controlled under the Montreal Protocol or its successor amendments, nor is it likely to be due to the relative dominant magnitude of its natural sources.

Similarly, methyl bromide (CH_3Br) is the largest natural source of bromine to the stratosphere. It was present at approximately a 1:77 ratio with CH_3Cl in the troposphere in 2012 (Carpenter et al., 2014). As with CH_3Cl , though many natural sources and sinks of this gas are known, the total budget remains somewhat unbalanced, although recent work has suggested that the imbalance in the CH_3Br budget is due to missing natural, not anthropogenic sources (Yvon-Lewis et al., 2009). Historically, CH_3Br was produced and used as a fumigant, especially in quarantine and pre-shipment (QPS) fumigation. Unlike CH_3Cl , most CH_3Br use is controlled under the Copenhagen amendment to the Montreal Protocol (though not QPS uses), and its production and use in most countries and for most purposes has dramatically decreased since the 1990s (Carpenter et al., 2014).

Both CH_3Br and CH_3Cl are principally lost by hydroxyl (OH) radical reactions in the troposphere, and have lifetimes of 0.8 and 0.9 years, respectively (Carpenter et al., 2014). Importantly, a portion of the gases emitted at the surface will reach the stratosphere, and contribute to stratospheric ozone loss. As the acknowledged industrial production of CH_3Br decreases, understanding all remaining natural and anthropogenic sources is important, as CH_3Cl and CH_3Br will become the dominant halogen gases to the stratosphere in the second half of the 21st century due to decreases in chlorofluorocarbons (Law et al., 2007). Because they are the largest natural sources of chlorine and bromine to the stratosphere, understanding all current sources and sinks is vital to predicting how stratospheric chemistry and the ozone layer will respond to future changes in the earth's atmosphere, both human-induced and natural.

1.1. Natural production pathways of methyl halides

It is known that natural biotic production pathways to both CH_3Br and CH_3Cl via enzymatic reactions exist (Harper, 1985; Wuosmaa and Hager, 1990; Attieh et al., 1995; Saini et al., 1995; Schmidberger et al., 2010). In addition, a number of natural abiotic methyl halide production mechanisms have also been described. CH_3Cl production from biomass burning is thought to proceed from a different path via methanol production during pyrolysis (Aries et al., 1988). Methanol production is more efficient at lower pyrolysis temperatures, and produced methanol readily reacts with available chloride (Reinhardt and Ward, 1995). Biomass burning in 2012 was estimated to produce 468 and 23 Gg of CH_3Cl and CH_3Br respectively (Carpenter et al., 2014).

A second abiotic CH_3Cl production path was later suggested for senescent plant material, where a methoxy moiety ($-\text{O}-\text{CH}_3$) directly reacts with halides (Hamilton et al., 2003) via a nucleophilic displacement reaction, producing a methyl halide (e.g. Horst et al., 2014, Fig. 1). This process was suggested to operate at moderate temperatures as low as 30 °C. The methoxy moieties are part of the methyl esters in pectin

and lignin, two structural polymers common in plants. Further work on this process has suggested that the abiotic formation of CH_3Cl from chloride and pectin is a pseudo first order, $\text{S}_{\text{N}}2$ type reaction (Sailaukhanuly et al., 2014). The pectin-chloride reaction was observed to have substantial production at 100 °C, and peaked at 210 °C, with much lower rates at 50 °C; this was attributed to the larger release of methoxy moieties from pectin or lignin as the temperature was increased (McRoberts, 2011).

It has been suggested that this second abiotic production pathway may be the largest source of CH_3Cl to the atmosphere (Keppler et al., 2005; Saito and Yokouchi, 2008). Searches for similar processes with bromide ions led to a study which incubated a variety of plant materials and bromide-enriched pectin and found CH_3Br production to be dependent on incubation temperature and bromine content of the plant, and concluded that CH_3Br production could also be abiotic (Wishkerman et al., 2008). Both lignin and pectin provide large amounts of methoxy moieties for this process. More recently, the emissions of CH_3Br from *Salicornia frutescens*, a halophytic plant, and the common plant cell-wall material pectin were studied under incubation temperatures from 30 to 300 °C; efficient uptake of potassium bromide (KBr) by pectin at 300 °C was noted (Horst et al., 2014).

A third abiotic production path from pectin and lignin is also conceivable. Protonation of the methyl ester would liberate a methanol molecule from the pectin or lignin. This shares a similarity with the pyrolysis pathway, in that the liberated methanol then reacts with available halide ions. It seems difficult to distinguish between this mechanism and the direct nucleophilic displacement reaction (Hamilton et al., 2003; Keppler et al., 2004, 2005; Sailaukhanuly et al., 2014) with experiments carried out to date; however, the third process does not include direct halide attack on the methyl carbon of the direct nucleophilic displacement reaction (B). Such direct attack as in reaction (B) is an energetically unfavourable reaction. These three abiotic pathways for producing methyl halides from plant materials are shown in Fig. 1. In these mechanisms, bromide is shown; the bromide+methanol substitution reaction is known to be faster than the chloride+methanol substitution reaction under acidic conditions (all common bread doughs are acidic). Reactions similar to these are thus expected to occur for production of CH_3Cl from pectin and inorganic chloride; as well as reactions where lignin is substituted for pectin.

1.2. Chloride and bromide in baked foods

Chloride, from sodium chloride or other sources, is ubiquitous in foods. Bromine can be present in some foods naturally, and in foods that are grown or produced near bromine sources, such as the ocean; the use of sea salt in cooking also adds bromide. However, historically and presently in some nations, a source of bromine was intentionally added to many baked goods. The bromine is added in the form of potassium bromate (KBrO_3) as a dough conditioner. KBrO_3 is a slow-acting oxidant during both the preparation and baking of bread dough; it speeds the formation of large glutenin polymer proteins (Wieser, 2007). KBrO_3 is expected to be transformed to potassium bromide (KBr) in the baking process. However, numerous reports (e.g. Himata et al., 1997) have noted that residual KBrO_3 often remains in finished baked goods. Another possible source in some cooked foods is added pectin; incubations of pectin alone at 180 °C resulted in 118 μg CH_3Cl /g pectin and 0.16 μg CH_3Br /g pectin; this was attributed to chloride and bromide added during industrial separation of pectin (Horst et al., 2014).

Concerns about the carcinogenicity of potassium bromate (Kurokawa et al., 1990; DeAngelo et al., 1998) led to its removal from foods in many countries beginning in 1990 in the UK. In the United States, "brominated flour" is still available, and though the FDA has recommended against its use since 1991 and most American bakeries have switched to other dough conditioners, it is not banned. In the European Union, potassium bromate is given the E-number E924. Potassium

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