1 Introduction

Iodine is the heaviest stable halogen element with atomic number 53. It has an average atomic weight of 126.904 u and forms a semi-lustrous solid under standard conditions (here 273.15 K and 1 bar, see Calvert (1990)) (Kaiho, 2015). Its melting and boiling points are 114 °C and 184 °C, respectively, and its vapour pressure is 0.031 kPa and 9.17 kPa at 25 °C and 113.6 °C, respectively (Kaiho, 2015). The atomic radius of iodine is 140 pm and its first ionisation energy is 1015 kJ mol^{-1} (Kaiho, 2015). Iodine is important in the enviornment: in the atmosphere, it influences the chemistry of ozone and important radical species, and it may be cause the formation of particles that may act as nuclei for aerosol or clouds (Saiz-Lopez, Plane, et al., 2012). The former is important for the capability of the atmophere to oxidise and remove species emitted to it, while the latter is important because of its effect on radiative equilibrium of Earth.

1.1 Iodine in the environment

Iodine is litophilic and incompatible in Earth's astenosphere, and therefore concentrated in oceans and surface sediments (Kendrick, 2024). Marine sediments constitute the largest iodine reservoir (Kendrick, 2024) with much higher concentrations of 20…600 mg kg^{-1} compared to soil- (0.5…20 mg kg^{-1}) or rock (0.08…0.5 mg kg^{-1}) concentrations (Whitehead, 1984). Sedimented iodine may be recycled into the oceans through sedimentary brines (Muramatsu, Fehn, et al., 2001; Muramatsu, Yoshida, et al., 2004) around techtonically active subduction zones (Carrano et al., 2020) through diagenesis processes involving thermal decompostion or microbiological reduction of buried organic matter (Kendrick, 2024; Muramatsu, Fehn, et al., 2001). Consequently, iodine concentrations in the oceans are approximately 45…60 µg L^{-1} (Whitehead, 1984), mostly in the form of iodate (IO_3^-), the thermodynamically most stable state of iodine in aqueous solution (Fuge et al., 2015). However, iodate exhibits a nutrient-like profile (Carrano et al., 2020) being depleted at the surface, whereas iodide (I^-) is enriched in the surface (Elderfield et al., 1980). Similarly, organic matter is enriched in the surface, so that the existence of some iodinated organics may be presumed (Saiz-Lopez, Plane, et al., 2012). Within the oceans, iodine is incorporated preferrentially in organic matter (Kendrick, 2024) by micro- and macroalgae, and aerobic bacteria (L. Carpenter, 2015): through faciliated diffusion (see detailed descriptions in Küpper et al. (2008), Winter et al. (2009), and Amachi (2008)), cells store iodine as I^-(aq) or associated to organic molecules (Küpper et al., 2008; Amachi, 2008). Iodide within the cell interior may act as an antioxidant (Küpper et al., 2008): upon oxidative stress, the iodide reservoir is mobilised and cells emit I^-(aq) and a range of volatile organic iodine compounds (VOICs) (Küpper et al., 2008; L. Carpenter, 2015) that may volatilise to the atmosphere. Analogously, when oxidative stress occurs during air exposure at low tide, the hetergeneous surface reaction of iodide and ozone (O_3) at the sea-water interface produces hypoiodous acid (HOI), molecular iodine (I_2) and iodine monoxide radicals ($IO^\bullet$) directly emitted to the atmosphere (L. Carpenter, 2015; Palmer et al., 2005; Liu et al., 2001; Sakamoto et al., 2009; Hayase et al., 2010; He et al., 2021). It is currently thought that the biggest source of inorganic iodine to the atmosphere is hypoiodous acid produced via the same pathway, exceeding the emissions of molecular iodine by one order of magnitude (L. J. Carpenter et al., 2013). Nevertheless, the atmospheric iodine budget is currently not well-constrained (Saiz-Lopez, Plane, et al., 2012). VOICs (notably CH_3I) and inorganic iodine species (HOI, I_2, $IO^\bullet$) emitted from the oceans constitute the biggest source of iodine to the atmosphere (L. Carpenter, 2015; L. J. Carpenter et al., 2013), with estimated input $\approx$ 550 Gg yr^{-1} (Saiz-Lopez, Plane, et al., 2012). Most VOICs are photolabile with lifetimes on the order of minutes

to days (Bloss et al., 2001). Other natural sources of iodine to the amtosphere include soils and plants (Whitehead, 1984; L. Carpenter, 2015; Fuge et al., 2015), terrestrial water systems (Whitehead, 1984), and volcanoes or salt lakes (L. Carpenter, 2015). The additional input from terrestrial sources into the atmosphere is $\approx 80 \ldots 110\,\mathrm{Gg\,yr^{-1}}$ (Saiz-Lopez, Plane, et al., 2012). Anthropogenic sources include direct emissions from fossil fuel burning (Fuge et al., 2015) and pesticide use (Zheng et al., 2003; Whitehead, 1984). There are indirect anthropogenic effects as well: ice core data indicates that the sea-air flux of iodine has tripled between 1950 and 2010 as a consequence of increased anthropogenic ozone pollution of the troposphere (Cuevas et al., 2018). Sinks of atmospheric iodine include wet- and dry deposition (Fuge et al., 2015), and direct uptake through plants (Fuge et al., 2015). Overall, this leads to boundary layer mixing ratios of $\chi_{\mathrm{I_2(g)}} \leq 93\,\mathrm{pptv}$ (L. Carpenter, 2015), $\chi_{\mathrm{IO^{\bullet}(g)}} \leq 3 \ldots 20\,\mathrm{pptv}$ (L. Carpenter, 2015), $\chi_{\mathrm{HOI(g)}} \leq 1\,\mathrm{pptv}$ (He et al., 2021) and $\chi_{\mathrm{I^{\bullet}(g)}} \leq 0.1 \ldots 22\,\mathrm{pptv}$ (L. Carpenter, 2015; He et al., 2021).

1.2 Iodine Chemistry in the Atmosphere

The importance of the marine iodine source is likely also reflected in aerosol composition: above marine areas, aerosol is enriched in iodine relative to seawater content by a factor of 100…1000 (L. Carpenter, 2015). Iodine may be transported into the aerosol phase through bubble-bursting of iodine-rich surface ocean waters (Saiz-Lopez, Plane, et al., 2012), or through the formation of aerosol via iodine oxide particles (IOPs) (O'Dowd et al., 2002). Likely, low-volatility iodinated organics may also condense into the aerosol phase. Overall, various iodinated species may be present in aerosol including iodide, iodate, hypoiodous acid and soluble organic iodine (SOI) (Saiz-Lopez, Plane, et al., 2012). Saiz-Lopez, Plane, et al. (2012) and Gilfedder et al. (2008) report that SOI is very frequent in aerosol and may constitute the largest reservoir of iodine in aerosol. There appear to be two principal pathways of SOI accomodation: direct accumulation from sea spray enriched in iodinated organics, and the reaction of hypoiodous acid with aerosol organics. Hypoiodous acid may also be highly reactive towards other species, likely due to its affinity for nucelophilic attacks on susceptible species. In general however, hypoiodous acid or other likewise reduced iodine species such as iodide should be oxidised to iodate (Gilfedder et al., 2008), the thermodynamically most stable form of iodine in aqueous solution. Consequently, the accumulated form of iodine in condensed aerosol phases is often thought to be iodate (Gilfedder et al., 2008; Saiz-Lopez, Plane, et al., 2012). However, observations in the troposphere indicate higher aerosol contents of iodide than iodate (Gilfedder et al., 2008), or high variability in the iodide/iodate ratio (Saiz-Lopez, Plane, et al., 2012). This indicates the presence of a mechanism reducing iodate in the troposphere.

Hetergeneous aerosol chemistry of iodine is closely linked to homogeneous chemistry of iodine through many iodine species. Generally, atmospheric iodine chemistry is initiated mostly through reactive iodine species (RIS) such as iodine radicals ($\mathrm{I^{\bullet}}$) or iodine monoxide radicals. Briefly, homogeneous iodine chemistry involves catalytic destruction of troposheric ozone via various pathways involving hydrogen oxide radicals (HO_x) and nitrous oxides (NO_x) as well as other halogen atoms in the atmosphere (Saiz-Lopez and Von Glasow, 2012). This process is photochemically driven and initiated with $\mathrm{IO^{\bullet}}$ and $\mathrm{I^{\bullet}}$. Saiz-Lopez and Von Glasow (2012) have outlined the mechanism: the intial step is the production of iodine radicals from VOICs (RI_n) or molecular iodine. The iodine radicals react with ozone to produce iodine monoxide radicals that in turn recombine to again produce iodine radicals:

$$\mathrm{RI(g)} + h\nu \longrightarrow \mathrm{R^{\bullet}(g)} + \mathrm{I^{\bullet}(g)} \quad \text{[R1.2.1]}$$

$$\mathrm{I_2(g)} + h\nu \longrightarrow 2\,\mathrm{I^{\bullet}(g)} \quad \text{[R1.2.2]}$$

$$\mathrm{I^{\bullet}(g)} + \mathrm{O_3(g)} \longrightarrow \mathrm{IO^{\bullet}(g)} + \mathrm{O_2(g)} \quad \text{[R1.2.3]}$$

$$2\,\mathrm{IO^{\bullet}} \longrightarrow 2\,\mathrm{I^{\bullet}(g)} + \mathrm{O_2(g)} \quad \text{[R1.2.4]}$$

The net outcome is ozone destruction with $2\,O_3(g) \longrightarrow 3\,O_2(g)$, although reaction 1.2.4 has other channels that may involve HO_x and NO_x cycles. Importantly, the iodine monoxide radical has a lifetime against photolysis in the boundary layer on the order of seconds (Bloss et al., 2001). Likewise, the effective lifetime of iodine radical species (I_x) against uptake in aerosol is on the order of hours (Dix et al., 2013): sustained presence of iodine monoxide radicals in the atmosphere therefore requires an effective recycling mechanism for $IO^{\bullet}$.
Additionally, iodine may be involved in the oxidation of atmospheric organic molecules or mercury, allowing the latter to enter the food chain as highly poisonous methylmercury (Steffen et al., 2008; Saiz-Lopez and Von Glasow, 2012; Saiz-Lopez, Plane, et al., 2012), and likely leading to enhanced condensation of organics into the aerosol phase through the former. Further, through formation of IOPs, iodine oxides may lead to the production of ultrafine aerosol particles (UFAPs) (L. Carpenter, 2015). Volatile species may condense on UFAPs that can grow up to the point of becoming cloud condensation nuclei (CNN) (Saiz-Lopez, Plane, et al., 2012). Recent evidence shows that nucleation via iodine oxoacids to produce IOPs is highly efficient and sometimes competitive with sulfuric acid-ammonium driven nucleation (He et al., 2021). Moreover, heterogeneous iodine chemistry on pre-existing frozen or liquid salt particles may lead to sudden increases in gas phase iodine species (Saiz-Lopez and Von Glasow, 2012). Importantly, the reaction of bromide (Br^-) with ozone on frozen salt solutions occurs in the brine pertaining to the bulk ice phase, rather than *within* the bulk ice phase (Oldridge et al., 2011): such brines are formed when freezing solutions exclude solutes — the heterogeneous reaction of ozone with iodide on frozen aerosol is here assumed to behave similarly. In other words, the heterogeneous reaction of ozone with aerosol surfaces is assumed to be similar for frozen and liquid aerosol particles. Other heterogeneous effects may lead to substantial iodine emissions through the reaction of ozone with dissolved iodide in ocean and aerosols (Palmer et al., 2005; Liu et al., 2001; Sakamoto et al., 2009; Hayase et al., 2010). In the upper troposphere and lower stratosphere, heterogeneous recycling of iodine species is highly important: Model calculations by Saiz-Lopez, Baidar, et al. (2015) show that from the lower troposphere, convection may transport inorganic- and organic iodine species to the lower stratosphere, causing a total inorganic iodine (I_y) injection of 0.25…0.7 pptv (Saiz-Lopez, Baidar, et al., 2015). Measurements by Koenig, Baidar, et al. (2020) are in agreement with this, indicating an injection of 0.77 ± 0.10 pptv of I_y into the lower stratosphere. Associated therewith is a mixing ratio of $\chi_{IO^{\bullet}(g)} = 0.06 \pm 0.03$ pptv even for aged stratospheric air. Koenig, Baidar, et al. (2020) also observed that increases in altitude across the troposphere are associated with (1) an increase in particulate iodine and a decrease in gas phase iodine; and (2) a shift of iodide-iodate speciation in the condensed phase towards iodate. Simulations could reproduce observed $\chi_{IO^{\bullet}(g)}$ only when a recycling scheme for iodine on ice particles was applied, and when the proper partioning between condensed- and gas phase was applied. This indicates that, as for the troposphere, a recycling mechanism producing gas phase iodine monoxide radicals must exist. There is also evidence that iodate should be reduced to iodide: Pillar-Little et al. (2013) have established a pathway through which iodide and ozone cause volatilization of $I_2(g)$ and HOI(g) from watery microdroplets. However, it is still unclear *how* the necessary iodide is formed, given that most iodine should be present as iodate. Consequently, an important question to answer is: how is IO_3^- reduced to species — most likely I^- — that may, directly of after reacting, volatilise to the gas phase?

1.3 Reduction of Iodate

Saunders et al. (2012) have shown that iodate may be reduced when solutions of iodate and humic acid (HA) are irradiated with UV-A and visible (VIS) light between $\lambda \geq 310$ nm and $\lambda \approx 780$ nm. The light source was filtered to exclude infra red (IR) light and lamp output below $\lambda = 310$ nm to simulate the UV-A-VIS solar spectrum in the lower troposphere. They found that the major product of this photochemically induced process was SOI and that the proportion of iodide in the reactant solution

remained constant at approximately 20 %. Since HA is a chromophore, the suggested mechanism involves photogeneration of solvated electrons $e^-(aq)$ that, in dependence of pH, yield hypoiodous acid: $IO_3^-(aq) + 4\,e^-(aq) + 5\,H^+(aq) \longrightarrow HOI(aq) + 2\,H_2O(aq)$. From there, SOI may be created through the nucleophilic attack of hypoiodous acid on diphenolic functional groups (Saunders et al., 2012). Alternatively, molecular iodine may be produced through reaction 1.3.1, as described by Pillar-Little et al. (2013):

$$HOI(aq) + I^- + H^+(aq) \longrightarrow I_2(aq) + H_2O(l) \qquad [R1.3.1]$$

Since molecular iodine is insoluble (Saiz-Lopez, Plane, et al., 2012), there will be volatilisation of molecular iodine to the gas phase. Overall, the mechanism suggested by Saunders et al. (2012) produces primarily hypoiodous acid molecular iodine — the production pathway of iodide has not been elucidated. The presence of iodide, however, appears necessary for the production of $I_2(g)$. It is hypothetised that iodide may be regenerated from SOI (Saunders et al., 2012; Baker, 2005). Finally, Saunders et al. (2012) have reported oscillations in the release of $I_2(g)$. This is likely associated with formation of hydrogen peroxide (H_2O_2) as a byproduct of HA photolysis (Saunders et al., 2012). Indeed, Cooper et al. (1988) have shown that hydrogen peroxide is a common product when irradiating aqueous solutions of chromophores. Given hydrogen peroxide, oscillations in I_2-IO_3^- are known as the Bray-Liebhafsky mechanism (BLM), first described by Bray (1921) and Bray and Liebhafsky (1931): hydrogen peroxide interacts with molecular iodine and iodate via

$$2\,IO_3^-(aq) + 2\,H^+(aq) + 5\,H_2O_2(aq) \rightleftharpoons I_2(aq) + 5\,O_2(g) + 6\,H_2O(l) \qquad [R1.3.2]$$
$$I_2(aq) + 5\,H_2O_2(aq) \rightleftharpoons 2\,IO_3^-(aq) + 2\,H^+(aq) + 4\,H_2O(l) \qquad [R1.3.3]$$

to yield a net catalytic decomposition of hydrogen peroxide via

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g) \qquad [R1.3.4]$$

The oscillation reaction has a *stable* regime — here, all species reach steady state except H_2O_2: likely, $O_2(g)$ volatilises and Le Chatelier's principle (LCP) dictates that hydrogen peroxide consequently depletes. The *unstable* regime where either reaction 1.3.2 or 1.3.3 occur preferrentially, leads to oscillations in molecular iodine and iodate. These oscillations are modulated by initial pH (Bray, 1921) and temperature. Including an organic reducing agent and a metal-ion catalyst results in the Briggs-Rauscher mechanism (BRM) after Briggs et al. (1973), elucidated by Schmitz et al. (2012): Briefly, in addition to reaction 1.3.3, the presence of some organic species $R-H_2$ will induce the following reactions:

$$H^+(aq) + IO_3^-(aq) + 2\,I_2(aq) + 5\,R{-}H_2(aq) \longrightarrow 5\,R{-}HI + 3\,H_2O \qquad [R1.3.5]$$
$$H^+(aq) + IO_3^-(aq) + 2\,I_2(aq) + 5\,R{-}HI(aq) \longrightarrow 5\,R{-}I_2 + 3\,H_2O \qquad [R1.3.6]$$
$$R{-}I_2 + R{-}H_2 \rightleftharpoons 2\,R{-}HI \qquad [R1.3.7]$$

The backward reaction likely proceeds via the metal ion catalyst, although Schmitz et al. (2012) reported the possibility of non-catalysed pathways.
A lot has been learned so far: organic substances may lead to the reduction of iodate, via chromophore activity. Furthermore, observed oscillations in gas phase I_2 may be explained through BLM-BRM mechanisms. However, the suitability of HAs to represent organic aerosol has been questioned: Graber et al. (2006) suggested that humic-like substances found in aerosol particles may differ substantially from

humic substances found in soil. More specifically, Graber et al. (2006) argue that terrestrial sources — from which the HA used by Saunders et al. (2012) likely originate — may not be the origin of the majority of humic-like substances in aerosol. Differences may be found in terms of molecular weight, aromatic moiety content, surface properties and other properties (Graber et al., 2006). Although HAs as organics have profen useful to elucidate the mechanisms of I_2 recycling, quantitatively constraining this recycling better requires more realistic organics. Another important question to answer, therefore, is: are there proxies that represent organics in aerosol more accurately, and to which the same chromophore-dependent pathway of iodine recycling applies?

1.4 Reduction of Iodate: Proxies for Secondary Organic Aerosol

A. Guenther et al. (1995) modelled global natural volatile organic compound (VOC) emissions in 1990. They found a total flux of 1150 TgC yr^{-1}, of which 44 % (503 TgC yr^{-1}) was isoprene (2-metyhl-1,3-butadiene) (CH_2=C(CH_3)−CH=CH_2) and 11 % (127 TgC yr^{-1}) were monoterpenes such as α-pinene (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene). Thereof, approximately 75 % orginated from forests. In 2006, The annual atmospheric VOC injection was further specified in 2012 when A. B. Guenther et al. (2012) reported the following emissions of VOCs for the year 2000: total emissions were 1089 TgC yr^{-1}, of which isoprene emissions were 49.1 % (535 TgC yr^{-1}) and the monoterpenes α-pinene, β-pinene (6,6-dimethyl-2-methylidenebicyclo[3.1.1]heptane) and limonene (1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene) contributed 6.7 % (66.1 TgC yr^{-1}), 1.7 % (18.9 TgC yr^{-1}) and 1.0 % (11.4 TgC yr^{-1}), respectively. isoprene and monoterpene emissions are biogenic and mostly linked to vegetation — overall they contributed approximately 65 % to global VOC emissions in 2000 (A. B. Guenther et al., 2012), rendering them a major source of atmospheric VOCs.

Organic matter in aerosol is present either as primary organic aerosol (POA) or secondary organic aerosol (SOA). POA and SOA comprise the largest share of *fine* particles with diameters $d \leq 2.5\,\mu$m. On the other hand, large particles with diameters $d > 2.5\,\mu$m are mostly comprised of particles formed mechanically, including soil and mineral dust, sea salt particles and plant particles (J. Ziemann et al., 2012). POA requires no chemical reactions to condense to the aerosol phase. Conversely, SOA is created when volatile precursor species are chemically altered to lower volatilities, and consequently condense to the aerosol phase. Likely, SOA constitues a large fraction of organic aerosol Bianchi et al., 2019; Hallquist et al., 2009. As a general rule of thumb, higher oxygen content of a molecule indicates *lower* volatility. Therefore, oxidation reactions are highly important in SOA formation because oxidation effectively *decreases* volatility. Recent work summarised by Bianchi et al. (2019) suggests that there exists class of of low-volatile species referred to as highly oxidised organic molecules (HOMs) with low volatility. Such HOMs are formed through *autooxidation* reactions involving peroxy radicals: this process is detailed by Bianchi et al. (2019), and the subtle but important difference between HOMs and molecules with high oxygen content is laid out. Briefly, HOMs are species of very low vapour pressure so that condensation onto existing particles is very probable and almost irreversible (Bianchi et al., 2019). High yields of HOMs have been observed for isoprene and the monoterpenes α-pinene and especially limonene (Bianchi et al., 2019), with total yields of 4 % (isoprene), (7.0 ± 3.5)...(3.4 ± 1.0) % (α-pinene) and 17.0 ± 8.5 % (limonene), respectively (Bianchi et al., 2019; Jokinen et al., 2015; Ng et al., 2008; Ehn et al., 2014; Kirkby et al., 2016). It may therefore be assumed that derivatives — or more precisely oxidation products — of monoterpenes or isoprene are common in SOA. Building on the work of Saunders et al. (2012), chosing an oxidation product of isoprene or monoterpenes as the investigated organics may constitute a more realistc proxy for aerosol organics.

Recently, Reza et al. (2024) have performed similar experiments as Saunders et al. (2012), but using organic species better representing VOC oxidation. Recent observations have shown elevated concentrations of $IO^{\bullet}$ (g) in dust layers above the Atacama and Sechura deserts: Koenig, Volkamer, et al. (2021) measured a ten-fold enhancement of iodine monoxide radical concentrations compared to the regional

background signal of 0.10…0.25 pptv. Because iron is hypothetised to catalyse photochemistry in dust particles, and since it is the most abundant transition metal in dust minerals (A. Al-Abadleh et al., 2023), iron may serve as a proxy for dust when investigating the reduction of iodate. In a series of coated wall flow tube reactor (CWFTR) experiments, Reza et al. (2024) used a cavity-enhanced differential optical absorbtion spectroscopy (CE-DOAS) to detect I_2(g) and a ?? to detect oxygenated volatile organic compounds (OVOCs) associated with iodate reduction in thin aqueous films. The films were inserted into the CWFTR and consisted of an organic or inorganic matrix and iodate. The organic matrices included iron(III)-citrate, citric acid (CA) and 1,2,3,4 butanetetracarboxylic acid (BTCA). CA was found in aerosol (Lienhard et al., 2012) and is a proxy for oxygenated organic species. Fe-Cit, as a known photoactive compound, is considered a suitable proxy for Fe(III) carboxylate complexes found in the atmosphere (Reza et al., 2024). Importantly, CA has well-characterised hygroscopic properties (Reza et al., 2024) so that this matrix can be used to control against matrix effects of organics that are due to iron when using Fe-Cit. These matrices were mixed with a solution of sodium iodate ($NaIO_3$) to introduce iodate at a concentration of $\approx$ 30 mM. The results show that irradiation with VIS for films containing Fe-Cit led to the reduction of $\approx$ 40 % of the initially present iodate. Likely, Fe-Cit undergoes a ligand-to-metal charge transfer (LMCT) induced through irradiance with a photon at $\lambda < 500$ nm to yield citrate (Cit) radicals and solvated electrons e^-(aq), as described by Saunders et al. (2012). Likely, reduction of iodate is driven through these solvated electrons. Furthermore, Reza et al. (2024) report that the speciation of the chromophores may include iodine-containing compounds.