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Hydrochloric acid from chlorocarbons: a significant global source of background rain acidity

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ABSTRACT

Hydrochloric acid, measured as non-sea-salt chloride ($nssCl^-$), is a ubiquitous component of continental and marine "background" rain, with concentrations ranging between 1.5 and 3.2 μeq/l. The potential contribution of HCl to the acid–basic equilibrium ranges from ~10% to ~40%; showing that this acid plays a significant rôle in the rain chemistry of remote regions of the world. Considering that the global amount of rainfall is $\sim 5 \times 10^{17}$ liters per year, a total deposition of 1.8–5 Tg/yr of nssHCl is estimated. The most important source of gaseous HCl in the background atmosphere is the degassing of HCl from sea-salt aerosols; however, due the simultaneous scavenging of HCl and basic Cl-depleted aerosols, this HCl does not contribute to the acidity of rain. Due to the short atmospheric lifetime of HCl, other minor "local" sources (e.g., volcanoes and burning of coal, waste and biomass) do not affect remote sites of the world, in a significant and/or permanent way. Therefore, an additional, well-distributed, significant source of HCl should exist in the global background atmosphere. In one way or another, all chlorocarbons have the potential to produce HCl when they are oxidized in the atmosphere. From the amount of halocarbon (i.e., CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3CCl_3, CH_2ClCH_2Cl, $CHClCCl_2$, CCl_2CCl_2 and CHF_2Cl) that is degradated by chemical reactions, the estimated atmospheric production of HCl in the gas and liquid phase is 3.4 Tg/yr and 0.78 Tg/yr, respectively. Assuming that ~30% of the HCl produced in the gas phase is removed by dry deposition, it is obtained that ~3 Tg of HCl should be annually deposited in rainfall. This estimate agrees well with the "measured" amount of $nssCl^-$ (1.8–5 Tg/yr) deposited globally in rainfall. Therefore, this analysis suggests that a significant fraction of the HCl found in rainfall at remote sites is most likely produced in the photochemical degradation of various chlorocarbons in the troposphere. About 50% of this HCl comes from anthropogenic sources of chlorocarbons.

1. Introduction

Hydrochloric acid (HCl) is a ubiquitous compound in the atmosphere. Sources of gaseous HCl are summarized in Table 1. Degassing of sea-salt is the main global source of HCl, minor sources include fossil fuel combustion, waste incineration, volcanoes. Due to its high solubility HCl is rapidly removed from the atmosphere by wet and dry deposition, as well as by its reaction with atmospheric particles, producing a lifetime of 1–2 days. Graedel and Keene (1995) reviewed the measurements of gaseous HCl performed in the troposphere (i.e., marine, rural continental, urban). These authors conclude that in remote oceanic regions the concentration at the surface ranges between 100 and 300 pptv and that levels over remote land areas are in the same range, or perhaps lower.

The impact of sulphuric and nitric acids in rain acidity, in "clean" and polluted areas, has been extensively reviewed and analyzed (Charlson and Rodhe, 1982; Whelpdale et al., 1997).

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Table 1. *Global sources of tropospheric HCl*

	TgCl/yr	Ref.
dechlorination of sea salt aerosols	50 ± 20	Graedel and Keene (1995)
via acid displacement	7.6	Erickson et al. (1999)
coal combustion	4.6 ± 4.3	McCulloch et al. (1999)
waste burning	2 ± 1.9	McCulloch et al. (1999)
volcanoes	0.4–11	Symonds et al. (1988)
biomass burning	<6	Lobert et al. (1999)
transport from the stratosphere	0.3	Keene et al. (1999)
chlorocarbons oxidation	~ 4.2	Present paper

Furthermore, the participation of organic acids (mainly formic and acetic), specially in "clean" environments, has been the subject of various evaluations (Keene and Galloway, 1986; Sanhueza and Santana, 1994). Even though it is well recognized that hydrochloric acid is a regular constituent of rainwater, a systematic (comprehensive) evaluation of this issue has not been made. Here, a review of the pertinent literature regarding the presence of HCl (measured as $nssCl^-$) in "background" rainfall is made. It is proposed that the acid found in these rains is likely produced from the atmospheric oxidation of various halocarbons, emitted to the atmosphere by natural and anthropogenic sources.

2. Hydrochloric acid in "background" rainfall

A review of the literature was made (Table 2). The concentrations of HCl, calculated as non-sea-salt chloride ($nssCl^-$), found at sites not affected by local or significant regional air pollution are summarized in Table 3. The selected "background" sites in Tables 2, 3, have NO_3^- and $nssSO_4^=$ (non-sea-salt sulphate) concentrations lower than 10 μeq l^{-1} of each anion. The $nssCl^-$ and $nssSO_4^=$ were calculated using Cl^-/Na^+ and SO_4^{2-}/Na^+ sea-salt ratios (μeq) of 1.16 and 0.12, respectively. Due to the very large concentrations of Cl^- and Na^+ in marine rainfall, it is very uncertain to estimate the $nssCl^-$ concentrations (usually a small amount) in these samples (Ayers and Ivey, 1988). With the exception of Amsterdam Island, which has 8 years data and a more reliable estimate of $nssCl^-$, sites with Na^+ and Cl^- over 100 μeq l^{-1} were excluded from the this evaluation.

The use of sea-salt correction to continental rain may produce biased results. Since continental mineral aerosols supplied more leacheable Na^+ than Cl^- (Junge and Werby, 1958; Talbot et al., 1986) the HCl in continental rain, calculated as $nssCl^-$ (given in Table 3), are likely underestimated. The Cl^-/Na^+ ratios found in atmospheric particles in the Venezuelan savannah (Sanhueza and Rondón, 1988) and the Amazon forest (Andreae et al., 1990) are lower than the Cl^-/Na^+ ratio in marine aerosols. However, considering that the ocean is a much stronger source of Cl^- (1785 Tg/yr) than crustal dust (15 Tg/yr), and that marine aerosols make a significant contribution to the chemical composition of continental atmospheres (Wagner and Steele, 1989; Willison et al., 1989; Andreae et al., 1990; Galloway et al., 1996; Williams et al., 1997), it is likely that the bias is small. In any case, the important point (discussed later) is that HCl coming from a source different than the marine aerosol and/or anthropogenic activities is found in remote rain.

Tropical, temperate, and polar sites are included in the analysis (Tables 2, 3), indicating that the presence of HCl in "background" rainfall is a global issue. The concentrations given for the South Pole and Greenland, correspond to the deposition in snow. With only few exceptions nssHCl (Table 3) concentrations range between 1.5 and 3.2 μeq l^{-1}. Considering that the deposition of $nssCl^-$ must occur everywhere (continental and marine regions) and that the global amount of rainfall is $\sim 5 \times 10^{17}$ liters per year (Graedel and Crutzen, 1993), a total deposition of 1.8–5 Tg/yr of HCl is estimated.

The contribution of HCl to the free acidity of continental precipitation has been emphasized by several authors (Legrand and Delmas, 1988; Gillett et al., 1990; Sanhueza et al., 1992; Galloway

Table 2. *Na^+ and Cl^- concentrations and pH values in remote rainfall*

Site	Location	Rainfall (mm/yr)	pH	Na^+ (μeq/l)	Cl^- (μeq/l)	Ref.
Tropics						
Lake Calado (Brazil)	3° 15′ S, 60° 34′ W	2754	4.9 4.8	2.5 2.4	4.7 4.6	Lesack and Melack (1991) Williams et al. (1997)
Katherine (Australia)	14° 28′ S, 132°18′E	1044	na	4.3	7.7	Likens et al. (1987)
Jabiru (Australia)	12° 40′ S, 132° 53′ E	1180	4.9	3.8	7.5	Gillett et al. (1990)
Turrialba (Costa Rica)	9° 53′ N, 83° 40′ W	2110	5.45	10.9	14.1	Hendry et al. (1984)
El Verde (Pto. Rico)	18° 19′ N, 65° 48′ W	3407	5.1	66	82	McDowell et al. (1990)
Venezuelan savannah[a)]	7–9° N, 63–66° W	920–1600	4.6–5.4	1.3–8.1	3.4–11.8	Sanhueza et al. (1992)
Auyantepuy (Venezuela)	5° 46′ N, 62° 32′ W	2496	5.3	$\leqslant 0.22$	2.64	Sanhueza et al. (1999)
Canaima (Venezuela)	6° 15′ N, 62° 52′ W	2559	4.8	$\leqslant 0.21$	2.43	Sanhueza et al. (1999)
Temperate						
Torres del Paine (Chile)	51° 10′ S, 71° 58′ E	750	5.0	13.2	17.0	Galloway et al. (1996)
Amsterdam Island	37° 47′ S, 77° 31′ E	1120	5.1	269	318	Moody et al. (1991)
Barrington (Australia)	na	na	5.8	19	24	Post et al. (1991)
Dorrigo (Australia)	na	na	5.5	54	65	Post et al. (1991)
Wagga Wagga (Australia)	na	570	5.6	10.5	17.7	Ayers and Manton (1991)
Polar						
Poker Flat Alaska	65° 08′ N, 147° 28′ W	285	5.0	1.3	2.7	Dayan et al. (1985)
Greenland (snow)	72° 12′ N, 37° 48′ W	209		0.21	0.48	Whitlow et al. (1992)
South Pole (snow)		na 71.2	5.5 na	0.63 0.48	1.25 0.96	Legrand and Delmas (1984) Whitlow et al. (1992)

[a)] Range of concentrations measured at 4 sites, La Paragua, J. del Tigre, Chaguarama and Guri.

et al., 1996). In order to have a first approach to the potential contribution of HCl to the acid–basic equilibrium, and considering that NH_3 is the major neutralizing compound in continental air (Dentener and Crutzen, 1994; Whelpdale et al., 1997), the $nssCl^-/(H^+ + NH_4^+)$ ratio was used. It is important to keep in mind that the buffer capacity of carboxilic acid may, in same cases, significantly affect H^+ concentrations; also, $nssCl^-/(H^+ + NH_4^+)$ ratios provide and upper limit for the potential contribution of HCl to free acidity because base cations and carbonates are not considered. The $nssCl^-/(H^+ + NH_4^+)$ ratio ranges from $\sim$10% to 40% (Table 3), suggesting that HCl plays a significant role in the rain chemistry of "clean" regions of the world. Also, the scarce data suggest a strong latitudinal variation. Using the ion concentrations and the annual amount of rain, deposition rates of $nssCl^-$ ($\mu eq/m^2/yr$) were calculated and given in Table 3. At tropical latitudes, quite similar deposition rates are produced at very different (ecosystems) and distant sites (i.e., the Amazon forest, the Venezuelan and Australian savannahs), ranging from 3000–5000 ($\mu eq/m^2/yr$). Depositions at NH and SH polar regions are quite similar (30–50 $\mu eq/m^2/yr$) between them, but about 10 times lower than the rates produced at tropical latitudes. Deposition rates at Torres del Paine (51° 10′ S) and Poker Flat (65° 08′ N) have

Table 3. *Non-sea-salt Cl^- and SO_4^{2-}, NO_3^- and NH_4^+ concentrations (μeq/l) in remote rain; also, $nssCl^-/(H^+ + NH_4^+)$ ratios and annual depositions of $nssCl^-$ are given*

Site	$nssCl^-$	NO_3^-	$nssSO_4^{2-}$	NH_4^+	$nssCl^-/(H^+ + NH_4^+)$	$nssCl^-$ dep. (μeq/m²/yr)
Tropics						
Lake Calado (Brazil)	1.8	3.5	4.2	3.0	0.09	4957
	1.8	4.2	1.7	6.6	0.09	
Katherine (Australia)	2.71	4.0	3.4	2.9	0.14	2829
Jabiru (Australia)	3.1	3.2	4.7	1.7	0.21	3658
Turrialba (Costa Rica)	1.5	1.3	3.7	3.6	0.21	3080
El Verde (Pto. Rico)	4.8	4.3	8.5	2.9	[0.44]	[16353]
Venezuelan savannah[a)]	1.9–3.2	2.7–4.6	2.1–4.4	1.9–13.4	0.07–0.30	2200–5100
Auyantepuy (Venezuela)	2.38	2.4	⩽0.44	0.31	0.44	5950
Canaima (Venezuela)	1.44	0.55	0.65	⩽0.37	0.10	3686
Temperate						
Torres del Paine (Chile)	1.6	0.5	1.2	0.6	0.14	1200
Amsterdam Island	4.3	1.6	4.8	2.4	0.4	[5400]
Barrington (Australia)	1.9	7.3	6.5	7.1	0.22	
Dorrigo (Australia)	2.0	9.7	8.5	3.3	0.31	
Wagga Wagga (Australia)	5.5	9.8	12.3	13.0	0.35	3135
Polar						
Poker Flat Alaska	1.2	1.9	7.0	1.3	0.11	410
Greenland (snow)	0.23	2.0	2.4	0.5		48
South Pole (snow)	0.52	1.4	1.4	0.16	0.15	
	0.4	1.6	1.4	0.07		29

[a)] Range of concentrations measured at 4 sites, La Paragua, J. del Tigre, Chaguarama and Guri.

intermediates values, 1200 μeq/m²/yr and 410 μeq/m²/yr, respectively.

3. Photochemical production of HCl from chlorocarbons

In one way or another, all chlorocarbons have the potential to produce HCl. Here we will only evaluate the compounds that seem to be the more relevant ones CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_3CH_3, CH_2ClCH_2Cl, C_2Cl_3H, C_2Cl_4 and CHF_2Cl. Therefore, the estimated production of HCl from chlorocarbons would likely represent a lower limit.

3.1. Methyl chloride (CH_3Cl)

Methyl chloride is the most abundant gaseous chlorine compound in the atmosphere, with a total burden of 4–5 Tg. Quite similar concentrations are observed in both hemispheres with an average concentration ranging from 550–600 pptv (Khalil and Rasmussen, 1999a; Kurylo and Rodriguez, 1999). Higher levels are observed in the tropics (615–620 pptv) compare with polar latitudes (573–580 pptv) (Khalil and Rasmussen, 1999a). Since the reaction with the OH radical is the dominant removal process, seasonal variation at various latitudes have been observed (Khalil and Rasmussen, 1999a). Lifetime with respect to OH reaction is ∼1.5 years. The global consumption by OH radicals is estimated to be ∼3.4 Tg/yr (Keene et al., 1999).

The evaluated sources, reviewed recently by Kurylo and Rodriguez (1999) and Keene et al. (1999), include emissions from the ocean (∼0.2–0.7 Tg/yr), biomass burning (1.0 ± 0.3 Tg/yr), wood-rotting fungi (0.1–0.16 Tg/yr), and industries (0.2–0.4 Tg/yr). Khalil and Rasmussen (1999a) using a photochemical model estimated that a global source of 3.7 Tg/yr is needed to explain the observed concentrations. Therefore, it is likely that known sources are underestimated, or that there is a major unidentified source. Furthermore, uncertainties in the reaction rate constant for the reaction between CH_3Cl and OH

may contribute to explain this discrepancy (Keene et al., 1999).

For CH_3Cl the following atmospheric oxidation mechanism has been postulated:

$$CH_3Cl + OH \rightarrow CH_2Cl + H_2O,$$
$$CH_2Cl + O_2 \rightarrow CH_2ClO_2,$$
$$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2,$$
$$CH_2ClO_2 + HO_2 \rightarrow CH_2ClO_2H + O_2,$$
$$\rightarrow CHClO + H_2O + O_2,$$
$$CH_2ClO + O_2 \rightarrow CHClO + HO_2,$$
$$CH_2ClO_2H + OH \rightarrow CH_2ClO_2 + H_2O,$$
$$CH_2ClO_2H + h\nu \rightarrow CH_2ClO + OH.$$

The atmospheric fate of formylhalide, CHClO, is not well stablished. Its photolysis and OH reaction lifetimes are 3 years and >36 days, respectively (Cox et al., 1995). There is no information about its removal by heterogeneous processes (e.g., hydrolysis in cloud water). Laboratory experiments indicate a rapid thermal decomposition (Sanhueza et al., 1976), suggesting that in the troposphere this compound decomposes to produce CO and HCl:

$$CHClO \rightarrow HCl + CO.$$

According to this mechanism, one molecule of HCl is produced in the oxidation of each molecule of $CHCl_3$. Therefore, considering that annually 3.4 Tg of CH_3Cl are consumed by OH radicals, we estimated a potential production of HCl of $\sim$2.4 Tg/yr.

3.2. *Methylene chloride (CH_2Cl_2)*

Anthropogenic industrial activities, mainly in the NH (e.g., food processing, paint stripping), are the major sources of CH_2Cl_2 (0.5–0.6 Tg/yr), with minor contributions from the ocean ($\sim$0.2 Tg/yr) and biomass burning ($\sim$0.06 Tg/yr) (Kurylo and Rodriguez, 1999; Keene et al., 1999). Levels of 40–50 pptv were found in the NH, and 15–20 pptv in the SH (Koppmann et al., 1993; Atlas et al., 1993). The photochemical lifetime is 5–6 months. The OH sink is estimated to be $\sim$0.59 Tg/yr (Keene et al., 1999).

In this case, the haloalkoxy radical formed, due to reactions initiated by the OH radical, is $CHCl_2O$, which may further react:

$$CHCl_2O \rightarrow CHClO + Cl,$$
$$CHCl_2O + O_2 \rightarrow CCl_2O + HO_2.$$

According to Sanhueza and Heicklen (1975), the main reaction pathway of $CHCl_2O$ is to produce CHClO and Cl-atoms. As indicated, CHClO would thermally decomposes to produce HCl and CO. Chlorine-atoms would react with reactive hydrocarbons to produce an additional molecule of HCl. Sidebottom and Franklin (1996) have confirmed that the only final chlorinated product, in the atmospheric degradation of CH_2Cl_2, is HCl. Therefore, a global production of $\sim$0.5 Tg/yr of gaseous HCl is estimated from the global atmospheric oxidation of methylene chloride.

3.3. *Chloroform ($CHCl_3$)*

Main sources of $CHCl_3$ include the ocean (0.36 Tg/yr), soils and fungi (0.2 Tg/yr), and industry (0.075 Tg/yr) (Kurylo and Rodriguez, 1999; Keene et al., 1999). The atmospheric lifetime is about 0.5 years due to the reaction with OH. The global emission is calculated to be $\sim$0.47 (0.35–0.6) Tg/yr, with about 70% emitted in the northern middle and tropical latitudes (Khalil and Rasmussen, 1999b). The global average atmospheric concentration is $\sim$18 ppbv, with a large difference between hemispheres: SH 5–15 pptv and NH 10–33 pptv (Kurylo and Rodriguez, 1999; Keene et al., 1999; Khalil and Rasmussen, 1999b).

The reaction with the OH radicals produces CCl_3 radicals, which are oxidized, through a similar mechanism to the one given above, to produce CCl_2O and HCl, with quantum yields of $\sim$1. The global tropospheric lifetime of CCl_2O due to photolysis is $\sim$16 years and gaseous CCl_2O is mainly transferred to the liquid phase, where it is hydrolyses to produce HCl and CO_2:

$$CCl_2O \leftrightarrow CCl_2O_{(aq)},$$
$$CCl_2O_{(aq)} + H_2O \leftrightarrow 2HCl_{(aq)} + CO_2.$$

The lifetime of CCl_2O due to hydrolysis has been estimated to range between few days (Helas and Wilson, 1992) and 70 days (Kindler et al., 1995).

Considering that $\sim$0.49 Tg of $CHCl_3$ are consumed by OH every year (Keene et al., 1999), we estimate that $\sim$0.14 Tg/yr of HCl are globally produced in the gas phase, and that $\sim$0.28 Tg/yr

of HCl are likely produced in the liquid phase, from the hydrolysis of CCl_2O in aqueous phase. Then, the total global production of atmospheric HCl from chloroform is $\sim$0.42 Tg/yr.

3.4. *Methyl chloroform (CH_3CCl_3)*

Practically all atmospheric CH_3CCl_3 (1,1,1-trichloroethane) is used as a cleaning solvent. This compound is regulated by the Montreal Protocol and its atmospheric concentration is now declining. In 1992 ambient level averaged $\sim$160 pptv (Sanhueza et al., 1995) and $\sim$80 ppbv in 1996 (Kurylo and Rodriguez, 1999). CH_3CCl_3 is destroyed primary through its reaction with OH in the troposphere, with a lifetime of 4.8 ± 0.3 years, which include smaller stratospheric and ocean sinks (Kurylo and Rodriguez, 1998).

The alkoxy radical formed in the atmosphere, after the reaction with OH, is CCl_3CH_2O, which reacts with molecular oxygen to produce CCl_3CHO (Sidebottom and Franklin, 1996):

$$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2.$$

The formed haloaldehyde is photolyzed to produce CCl_3 radicals:

$$CCl_3CHO + h\nu \rightarrow CCl_3 + CHO.$$

As in the case of $CHCl_3$, the oxidation of the CCl_3 radicals produces CCl_2O and HCl, with a quantum yield of one (Kindler et al., 1995). It is estimated that $\sim$0.38 Tg/yr of CCl_3CH_3 (0.30 Tg Cl/yr) are consumed by the reaction with OH (Keene et al., 1999), therefore, due to the degradation of methylchloroform, $\sim$0.1 Tg/yr of HCl is produced in the gas phase and $\sim$0.2 Tg HCl/yr in the liquid phase, after the hydrolysis of CCl_2O.

3.5. *Dichloroethano (CH_2ClCH_2Cl)*

The 1,2-dichloroethano is used as an intermediate in the vinyl chloride production and as antiknocking agent in leaded gasoline. Emissions to the atmosphere are not well established, but a mean atmospheric concentration of $\sim$12 pptv has been estimated for the NH. The estimated lifetime, from its removal by OH, is $\sim$120 days, with a total tropospheric sink of 0.27 Tg/yr (Class and Ballschmiter, 1987).

It seems that no laboratory studies about the degradation mechanism of this compound have been made. The likely acyl chloride compound, produced in the oxidation of this halocarbon, is $CH_2ClC(O)Cl$. This acetylhalide may photolyze (30 days lifetime; Cox et al., 1995) to produce CO, Cl atoms, and CH_2Cl radicals:

$$CH_2ClC(O)Cl + h\nu \rightarrow CH_2Cl + CO + Cl,$$

or may also hydrolyze in the liquid phase:

$$CH_2ClC(O)Cl_{(aq)} + H_2O \rightarrow CH_2ClCOOH_{(aq)} + HCl_{(aq)}.$$

The CH_2Cl radical should react as indicated in the methylchloride section, producing HCl in the gas phase.

From this compound, the potential production of atmospheric HCl should range between 0.1 to 0.2 Tg/yr, depending on which pathway (hydrolysis or photolysis) occurs.

3.6. *Trichloroethylene ($CHClCCl_2$)*

Anthropogenic emission ($\sim$0.25 Tg/yr), from industrial usage as a degreasing agent, is the major source of atmospheric C_2HCl_3, with minor contribution from the ocean ($\sim$10%), however, calculations suggest a substantially higher contribution ($\sim$44%) from natural sources (Keene et al., 1999). Due to a fast reaction with OH the lifetime is $\sim$1 week and atmospheric concentrations are very low: NH $\sim$3 pptv and SH $\sim$0.7 pptv.

In the atmospheric oxidation of this chloroethylene, initiated by OH radicals, two ethoxy-radicals may be produced: $OCHClCCl_2OH$ and $HOCHClCCl_2O$. These radicals can decompose by C–C cleavage to produce $COCl_2$ and CHClO:

$$\text{(i)} \quad OCHClCCl_2OH \rightarrow CHClO + HOCCl_2$$
$$HOCCl_2 + O_2 \rightarrow CCl_2O + HO_2,$$
$$\text{(ii)} \quad HOCHClCCl_2O \rightarrow CCl_2O + HOCHCl$$
$$HOCHCl + O_2 \rightarrow CHClO + HO_2.$$

In smog chamber experiments, Tuazon et al. (1988) obtained a production yield of CCl_2O of 0.40 ± 0.06, however, the yield of CHClO was only 0.067 ± 0.01. To explain the low yield of CHClO in the Cl-atom sensitized oxidation of chloroethenes, Sanhueza et al. (1976) invoked reaction channel leading to an energetic CHClO molecule, which always decomposes to CO and HCl. This may also explain the low yield of CHClO observed by Tuazon et al. (1988).

On the other hand, kinetic data show that Cl atoms are generated from the reaction of OH with trichloroethylene, with a quantum yield of 1.2 ± 0.9 (Edney et al., 1986), indicating that the $OCHClCCl_2OH$ and $HOCHClCCl_2O$ radicals should also decompose by C–Cl cleavage, to produce acyl chloride compounds and Cl atoms:

$$OCHClCCl_2OH \rightarrow HOCCl_2COH + Cl,$$

$$HOCHClCCl_2O \rightarrow HOCHClCOCl + Cl.$$

The acylhalides produced in these reactions should likely photolyse or hydrolyse to produce additional molecules of HCl in the gas or liquid phase, respectively.

Therefore, we speculate that $\sim 50\%$ of the ethoxyradicals decomposes by C–C cleavage and $\sim 50\%$ by C–Cl cleavage. Since ~ 0.43 Tg/yr of C_2Cl_3H are consumed by OH (Keene et al., 1999), ~ 0.15 Tg/yr of HCl should be produced in the gas phase (0.06 Tg/yr from Cl reaction with hydrocarbons and 0.09 Tg/yr from CHClO decomposition) and 0.09 Tg/yr in the liquid phase (from CCl_2O hydrolysis). Total ~ 0.24 Tg HCl/yr, which is likely a lower limit.

3.7. *Tetrachloroethylene (CCl_2CCl_2)*

Tetrachloroethylene is mainly used as a solvent for industrial degreasing and for dry cleaning, with a mean global emission of 0.36–0.48 Tg/yr (Wiedmann et al., 1994; Keene et al., 1999). Atmospheric concentration are: NH ~ 15 pptv and SH ~ 2.5 ppbv (Rudolph et al., 1996; Wiedmann et al., 1994). The main removal process of C_2Cl_4 is reaction with OH, with a flux of ~ 0.51 Tg/yr (Keene et al., 1999), and an atmospheric lifetime of approximately 3 to 4 months (Kurylo and Rodriguez, 1999).

Since the rate constant for addition of a chlorine atom to C_2Cl_4 is about 300 times greater than that for the addition of the OH, it has been estimated that, at a global scale, about 13% of this olefin reacts with Cl atoms to produce CCl_3CCl_2 radicals, which leads to the formation of CCl_3COCl and hence to trichloroacetic acid by hydrolysis (Sidebottom and Franklin, 1996):

$$CCl_3COCl_{(g)} \rightarrow CCl_3COCl_{(aq)} (+ H_2O)$$

$$\rightarrow CCl_3COOH_{(aq)} + HCl_{(aq)}.$$

On the other hand, the products from the oxidation initiated by the addition of OH are not well established. Tuazon et al. (1988) found CCl_2O as the only product, but with a yield of only ~ 0.45. Therefore, the production of HCl from C_2Cl_4 is estimated in ~ 0.11 Tg/yr, all in the aqueous phase. However, we should have in mind that the potential contribution is ~ 0.4 TgHCl/yr.

3.8. *HCFC-22 (CHF_2Cl)*

$CHClF_2$ is currently the most widely used HCFC, as an interim replacement for some chlorofluorocarbons restricted under the Montreal Protocol. Therefore, the concentration of HCFC-22 is increasing throughout the global troposphere, with a rate of 5.0 pptv yr^{-1} for the period 1992 to 1996. The mean concentration in mid-1995 was 117 pptv. The atmospheric lifetime is 11.5 ± 0.7 yr (Kurylo and Rodriguez, 1999). This gas has anthropogenic sources only; and it is used in air conditioning, refrigeration and foam generation.

The CF_2ClO radical formed in the oxidation process, decomposes to produce CF_2O and Cl atoms (Sanhueza, 1977), with a likely yield of ~ 1. Therefore, considering that annually ~ 0.057 Tg of CHF_2Cl is removed by OH (Keene et al., 1999), a global production of 0.03 Tg of HCl yr^{-1} is estimated in the gas phase.

4. Discussion and conclusions

Hydrochloric acid, measured as non-sea-salt chloride, is found globally in rain, indicating a well distributed global source of the acid (see Table 3). The known sources of atmospheric HCl are given in Table 1. Field measurements indicate that marine aerosols have a Cl^-/Na^+ ratio lower than that of seawater (Martens et al., 1973; Clegg and Brimblecombe, 1985; Pio and Lopes, 1998) and most evidences indicate that there is a Cl loss from marine aerosols due to the release of HCl to the gas phase. Three mechanism have been postulated to explain the Cl loss from marine aerosols: (i) reaction with strong acids (Duce, 1969), (ii) a mechanism initiated by the OH radicals (Behnke and Zetzsch, 1989; Keene et al., 1999), and (iii) the reaction with ozone (Cauer, 1951; Behnke and Zetzsch, 1989). It seems that the global production of HCl from the reaction of marine aerosols

with OH radicals or O_3, has not been estimated. For the reaction due to acidification, Graedel and Keene (1995) estimated an emission of 50 ± 20 Tg/yr, however, recently, based in model calculations, Erickson et al. (1999) indicate a much lower production of HCl of 7.6 Tg/yr. This low value is in agreement with findings of Ayers et al. (1999) in clean marine air in the southern hemisphere, where Cl loss from marine aerosols appears to be relatively small

According with values in Table 1, by far, the most important source of atmospheric gaseous HCl is the degassing of the acid from sea-salt aerosols. However, due to a separation of sea-salt Cl^- and Na^+ during transport from sea to continent, a decrease in the Cl^-/Na^+ ratio in continental rain occurs (Möller, 1990), also, due to a simultaneous scavenging of HCl and basic Cl-depleted aerosols, it is very unlikely that the HCl (measured as $nssCl^-$) found in rainfall is the acid produced from the dechlorination of sea-salt aerosols, specially at continental sites; Kritz and Rancher (1980) have reported dry deposition velocities over the ocean surface of 0.4 cm/s for aerosol Na^+ and 0.8 cm/s for gaseous HCl.

As already mentioned, HCl has a short atmospheric lifetime and direct emissions from coal combustion and waste burning, which are produced at urban and industrial locations, should not contribute to the $nssCl^-$ measured at background remote sites. Volcanoes are located randomly around the world, also volcanic eruptions have highly temporal variability, therefore, this source should be "patchy" and mainly affect the areas nearby the volcanoes, specially during eruption periods; e.g., as far its is known, the Amazon forest and the Venezuela savannah regions, where a significant contribution of HCl to rain acidity is observed (Table 3), are not affected by volcanic emissions. HCl emission from tropical biomass burning would only be relevant during the dry season, when less (e.g., Amazon forest) or practically no (Venezuelan and Australian savannahs) rain occurs. Additionally, since similar Na^+/Cl^- ratios were observed in rain collected during burning and non-burning periods at various Venezuelan sites (Sanhueza et al., 1992), it seems that both Na^+ and HCl (or particulate Cl^-) are produced in biomass burning.

From the above discussion, it seems that none of the known or evaluated tropospheric sources of HCl (Table 1) could explain the $nssCl^-$ found in remote rain, therefore, an additional, well distributed, significant source of HCl should exist in the background atmosphere. As presented in Section 2 (Table 3), the rain data indicate a larger deposition rate of $nssCl^-$ at tropical latitudes, compared with mid-latitude and polar sites. Also, a significant seasonal variation of $nssCl^-$ was observed at Torres del Paine, with higher concentration during the summer (Galloway et al., 1996). These facts suggest a photochemical source of HCl in the remote atmosphere.

In Table 4 are summarized the estimated production rates of HCl from the atmospheric degradation of chlorocarbons, whose photooxidation mechanisms were presented in Section 3. By far, the major contribution is made by CH_3Cl. The total estimated tropospheric production of HCl is ~ 4.2 Tg/yr, with ~ 3.4 Tg/yr produced in the gas phase and ~ 0.78 Tg/yr in the liquid phase. This source would represent about 6% of the global budget of tropospheric HCl (Table 1). For our purposes, we must include the stratosphere–troposphere exchange of HCl, which has been estimated in ~ 0.3 Tg HCl/yr (Prather et al., 1990; Keene et al., 1999), to the production of HCl in the troposphere. The stratospheric HCl is mainly produced from the chemical degradation of man-made chlorofluorocarbons.

The percentage of global deposition due to dry deposition of $SO_4^=$ and NO_3^- given by Whelpdale et al. (1997) presents a very large spatial variation, however, for relatively "clean" regions the data suggest a value of $\sim 30\%$ (e.g., tropical America and Africa 10–30%, global oceans $< 50\%$). Therefore, assuming that $\sim 30\%$ of the gaseous tropospheric HCl is removed by dry deposition and that the rest is scavenged by rain, it is estimated that a total of ~ 3 Tg of HCl should be annually deposited in rainfall. This value agrees well with the "measured" amount of $nssCl^-$ (1.8–5 Tg/yr) deposited globally in rainfall (discussed above). About 50% of this HCl is from anthropogenic sources of chlorocarbons.

Due to regulations of the Montreal Protocol, the production of HCl from methyl chloroform should decrease relatively fast in the future, however, the increasing emissions of HCFC-22 and other chlorinated CFC substitutes (e.g., HCFC-141b, HCFC-142b, HCFC-123) should likely compensate, and even exceed, the decreasing

Table 4. *Global tropospheric production of HCl from chlorocarbon oxidation*

Chlorocarbon	Total source[a] (Tg/yr)	Global OH sink (Tg/yr)	HCl production gas phase (Tg/yr)	HCl production aqua phase (Tg/yr)
CH_3Cl	3.7 (30–50%)[b]	3.4	2.4	—
CH_2Cl_2	0.76–0.86 (~80%)	0.56	0.5	—
$CHCl_3$	0.35–0.6 (~12%)	0.49	0.14	0.28
CH_3CCl_3	0.74 (100%)	0.38	0.1	0.2
CH_2ClCH_2Cl	?	0.27	0.05–0.1	0.05–0.1
$CHClCCl_2$	0.25–0.36 (70–90%)	0.43	0.15	0.09
CCl_2CCl_2	0.36–0.48 (~95%)	0.51	?	0.11
$CHClF_2$	0.15 (100%)	0.057	0.03	—

[a] See text for references.
[b] Percentage of anthropogenic emissions.

contribution of CH_3CCl_3. Therefore, monitoring of the concentrations of this acid in rain water should be made, specially in remote pristine continental sites. Practically nothing is known about the effect of HCl over natural ecosystems.

In conclusion, the data suggest that HCl found in rainfall at remote sites, is most likely produced in the photochemical degradation of various chlorocarbons in the troposphere. This acid plays a significant role in the acid–basic equilibrium of those rains and likely future changes should be monitored.

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