

Influence of Chlorine Emissions on Ozone Levels in the Troposphere

Golam Sarwar¹, Ravi Joseph², Rohit Mathur¹

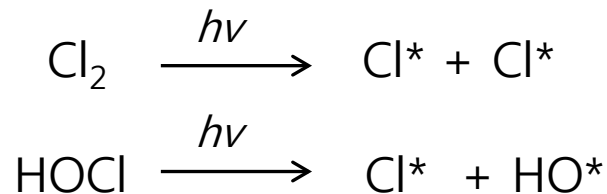
¹United States Environmental Protection Agency, ²Austin Energy, Texas

D.G.Steyn and S.T. Rao (eds). Air pollution Modelling and Its Application XX, 237pp
DOI 10,1007/978-90-481-3812-8, © Springer Science + Business Media B.V.2010

Emission gas from cooling tower

1st: only a fraction of chlorine that is added to cooling tower can be emitted into the atmosphere

2nd: chlorine emissions from cooling towers are primarily emitted as HOCl, not as Cl₂



Both Cl₂ and hypochlorous acid (HOCl) can undergo photolysis to produce chlorine radical which can enhance chemical production of O₃

☞ Photolysis rate of Cl₂ is about 8 times faster than that of HOCl (9.0 hr⁻¹ for Cl₂ vs. 1.1 hr⁻¹ for HOCl at typical summer noon)

Chlorine Gas Inhalation

Human Clinical Evidence of Toxicity and Experience in Animal Models

Carl W. White¹ and James G. Martin²

National Jewish Health and University of Colorado at Denver Health Sciences Center, Denver, Colorado; and ²McGill University, Montreal, Quebec, Canada

Thus, the forms of chlorine involved in respiratory toxicity are not limited to chlorine gas (Figure 1), but also can include **hypochlorous acid, chlorine dioxide, and chloramine**. In fact, since chlorine gas is moderately water soluble, it can form hypochlorous acid and hydrochloric acid as it dissolves into airway surface liquid when contacting mucosal surfaces and airways (Figure 2).

Workplace exposure limits for chlorine include a short-term exposure limit for up to 15-minute exposures not to exceed 1 ppm (2.9 mg/m³). That for a long-term exposure limit is for up to 6-hour exposures not to exceed 0.5 ppm (1.5 mg/m³). Levels of 0.3 ppm are associated with odor perception, levels of 1–2 ppm are “burdensome” and “irritating,” and those at 2–3 ppm are “annoying” (13). The workplace exposure limits are of interest, since the WHO Task Group proposed that ambient levels of chlorine be about **0.034 ppm (0.1 mg/m³)** to “protect the general population from sensory irritation,” and “significant reduction in ventilatory capacity”

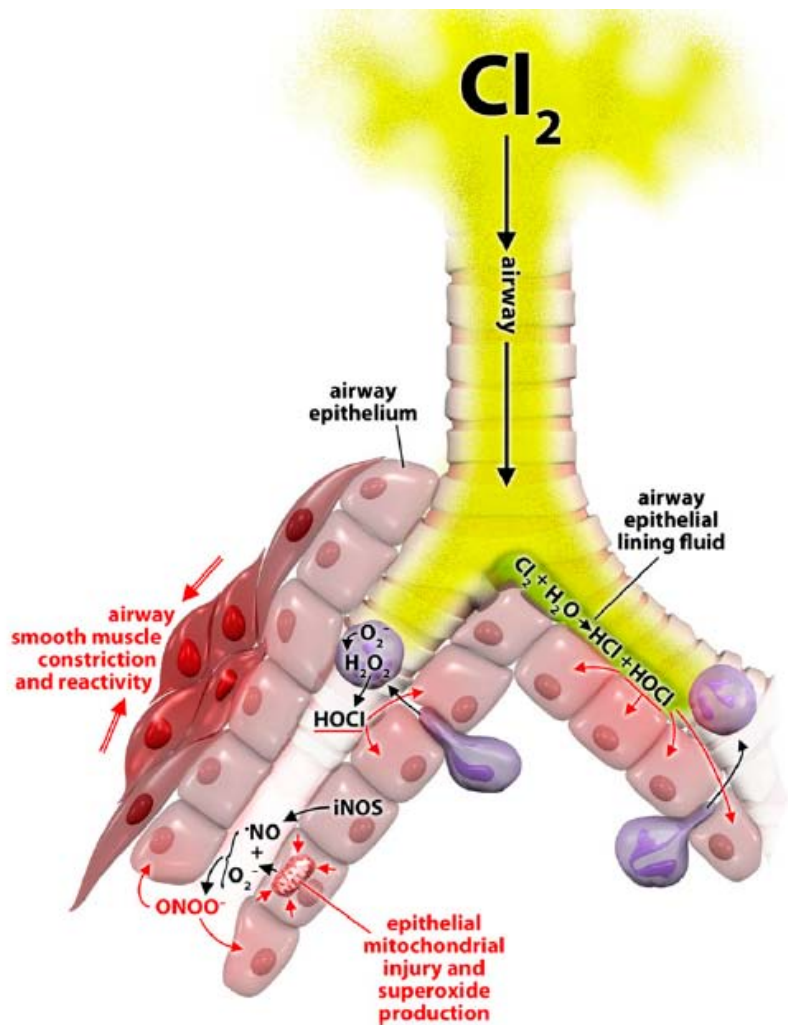


Figure 1. Postulated mechanisms for airways injury due to chlorine inhalation. Hydration of chlorine gas (Cl_2) leads to formation of HCl and HOCl (hypochlorous acid). As indicated, both Cl_2 and HOCl can react with airway lining constituents. Reactive oxygen species (ROS)

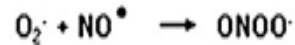
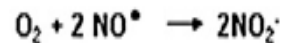
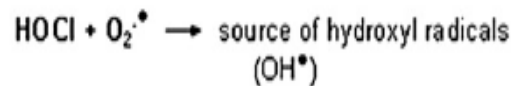
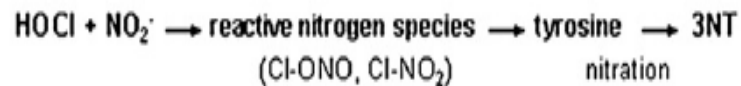


Figure 2. Scheme of some of the reactions potentially causing formation of reactive oxygen and nitrogen species in the setting of acute chlorine inhalation.

Chlorine source

VOC source

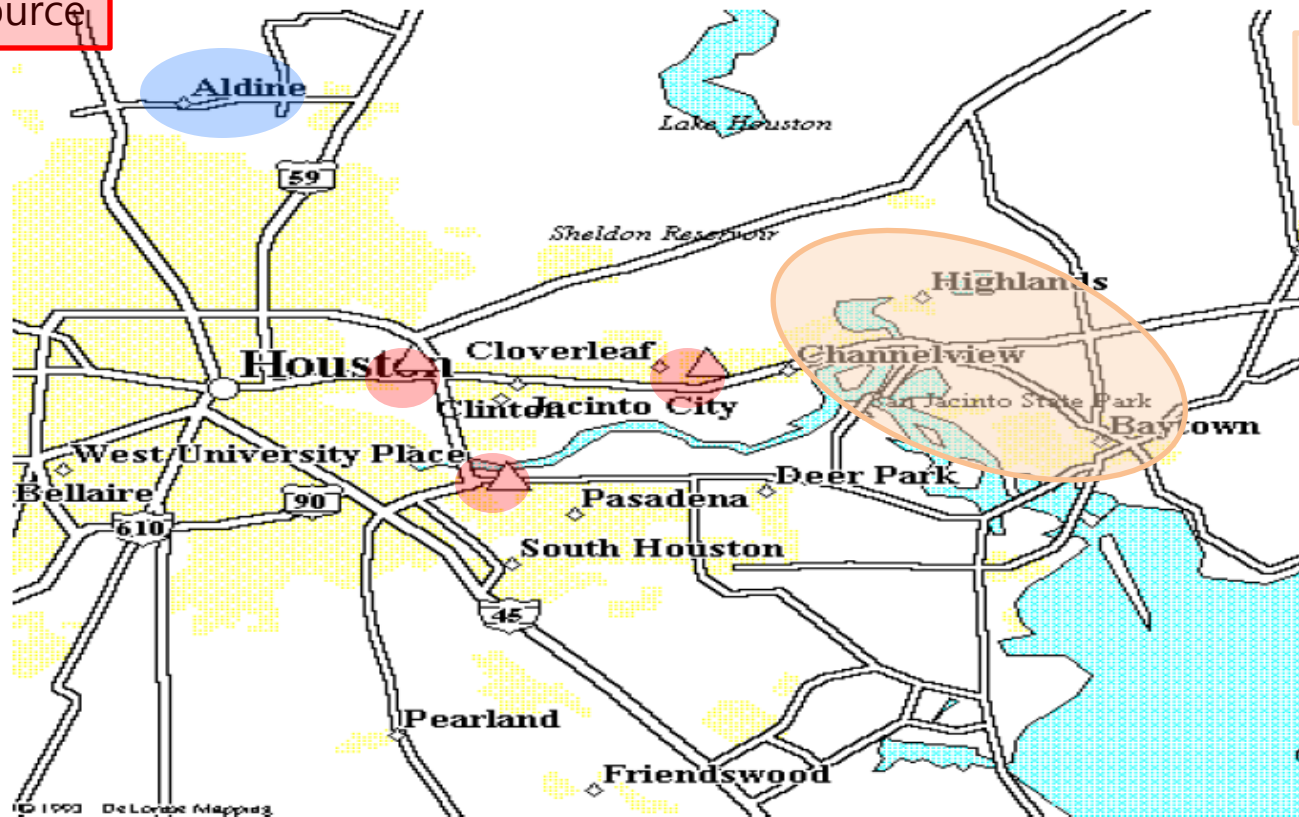


Figure 4.7 Locations of the Chlorine Sources in Relation to Monitoring Sites

On August 19, 1993 there was an unexplained ozone spike at the Aldine monitoring site. Surrounding monitoring sites like Clinton, which normally record maximum ozone concentrations similar to those observed at Aldine, all observed maximum afternoon ozone concentrations of approximately 160 ppbv. The Aldine site, however, had a maximum ozone concentration of 244 ppbv. Figure 4.8 below displays the observed ozone concentrations for

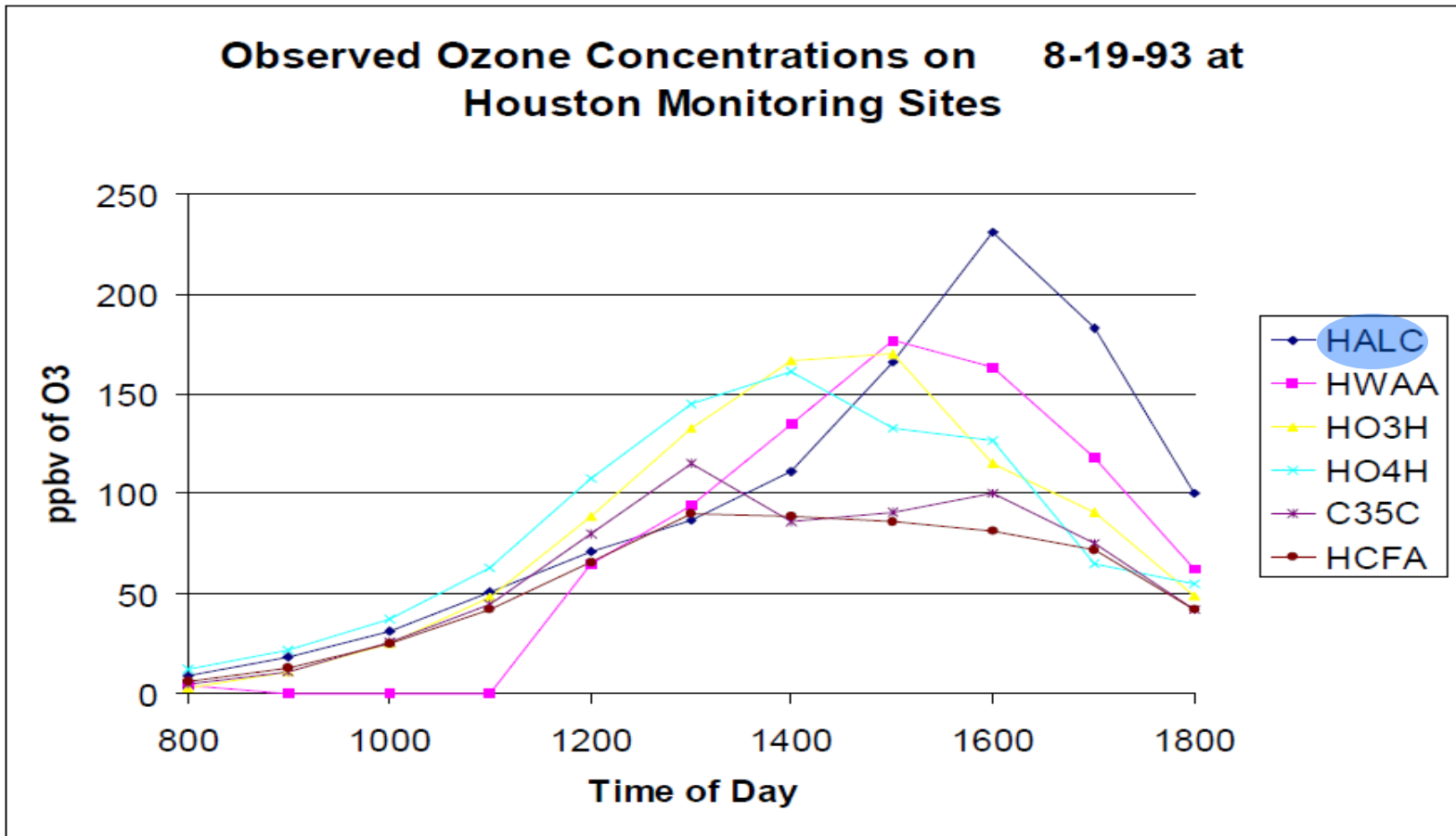


Figure 4.8 Observed O₃ Concentration in the Houston Area on 8-19-93

Measuring site
HALC: Aldine site
 C35C: Clinton site

Emission Inventory of Atomic Chlorine Precursors in southeastern Texas

Molecular chlorine emission	Kg/day	Remark
Industrial point sources	650	Data : Toxic Release Inventory
Cooling tower	6,426	①18.4 kg/day/cooling tower * 350 cooling tower ②m/u water 1.44 MGD (227 ton/hr) ③ flash-off fraction: 0.1
Swimming pools	4,540	①16,200 kg: NaOCl/day in 11 counties (2 gal/NaOCl/pool/week) ②90-900 kg: mass transfer coefficient for HOCl: 10-100 $\mu\text{gm}^{-2} \text{mim}^{-1}$ ③ 15,000 kg: 50 m ³ , 2ppm, 150,000 pools
Reactions of sea salt aerosol	1.6	
Tap water use , etc	-	
Total	~12 ton	

Results from smog chamber experiments



The results of the chamber experiments were used to assess the potential impact of chlorine chemistry for an August 19, 1993 episode. The observations for this episode were consistent with the chemistry observed in the chamber experiments, suggesting that chlorine may play a significant role in some ozone episodes.

Summary of results from smog chamber experiments

Chlorine (ppb _c)	Initial NO (ppb _v)	Initial TVOC (ppb _c)	O ₃ Maximum (ppb _v)
0	78	850	40
12	85	980	83
16.5	90	1,600	120
40	90	1,400	262

- 1) Injection of chlorine into the simulated air mass in the smog chamber resulted in a dramatic increase in ozone production
- 2) The effects of chlorine on ozone production were rapid, occurring in approximately the first 15 minutes

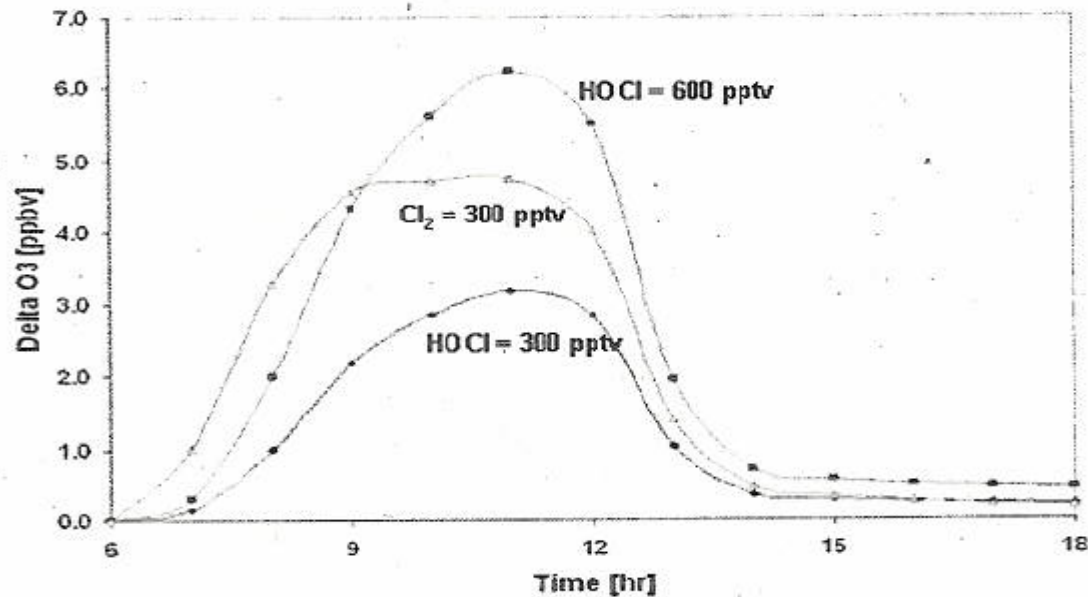


Figure 1: The relative impact of Cl₂ and HOCl on O₃ in the troposphere

	Concentration (pptv)		Δ Max Ozone (ppbv)	remark
HOCl	300		~3.2	Equal amount of Cl ₂ (mole basis)
		600	~6.2	Equal amount of Cl ₂ (mass basis)
Cl ₂	300		~4.7	

This mode run was performed with prescribed initial conditions for urban conditions

https://www.google.co.kr/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&sqi=2&ved=0CDcQFjAA&url=http%3A%2F%2Fcfpub.epa.gov%2Fsi%2Fsi_public_file_download.cfm%3Fp_download_id%3D495748&ei=fLl4UeGuHIygiQeCmoDABQ&usg=AFQjCNGVGhfrT6Bw7u97qr9pOf2jr4TdKg&sig2=OCZZcFDfR3m6JzGaEl_VLQ&bvm=bv.45645796.d.aGc&cad=rjt

Modeling the Effect of Chlorine Emissions on Ozone Levels over the Eastern United States

GOLAM SARWAR AND PRAKASH V. BHAVE*

Atmospheric Modeling Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina

(Manuscript received 15 February 2006, in final form 10 October 2006)

- 1) This paper presents model estimates of the effect of chlorine emissions on atmospheric ozone concentrations in the eastern United States.
- 2) Chlorine sources: anthropogenic molecular chlorine emissions, hypochlorous acid emissions from cooling towers and swimming pools, and chlorine released from sea-salt aerosols.
- 3) Chlorine emissions: The daily maximum 1-h ozone concentrations increased by up to 12 parts per billion by volume (ppbv) in the Houston area and 6 ppbv in the New York–New Jersey area.
- 4) Chlorine emissions and chemistry enhanced the volatile organic compound oxidation rates and, thereby, increased the ozone production rate.

울산 오존·이산화황 농도 전국 최고

울산 화산리는 환경기준 초과까지...미세먼지는 줄어

2011.10.23 (일) 20:41:17

정재환 (hani@ulsanpress.net)

국립환경과학원 측정

울산지역 대기 중 미세먼지 농도는 감소했지만 오존과 이산화황의 농도는 전국 7대 도시에서 높은 수준인 것으로 조사됐다.

23일 국립환경과학원이 미세먼지 등 7개 대기오염물질에 대해 측정 분석한 자료에 따르면 지난해 울산의 미세먼지 농도는 $48\mu\text{g}/\text{m}^3$ 로 나타났다.

이는 10년전인 2001년 $55\mu\text{g}/\text{m}^3$ 에 비해 크게 감소한 것으로, 전년도인 2009년 $49\mu\text{g}/\text{m}^3$ 에 이어 2년 연속으로 연간대기환경기준($50\mu\text{g}/\text{m}^3$)을 달성했다.

미세먼지 감소 원인으로는 황사 강도의 감소, 기상특성의 변화에 따른 지역 배출원의 영향 감소, 울산시의 미세먼지 저감 대책 추진 등이 영향을 미친 것으로 보인다.

반면 울산지역 오존의 연평균 농도는 0.023ppm으로 10년 전 0.020ppm 보다 0.003ppm이 증가했다. 오존은 도시생활을 하면서 화학반응을 일으켜 발생하는 2차 오염원으로, 자동차가 늘고 도시 빌딩이 더 많아지면서 발생량이 늘어난 것으로 추정된다.

지난해 이산화질소 연평균 농도(0.023ppm)는 10년전 0.022ppm보다 0.001ppm이 늘었다.

이산화황(0.008ppm)의 경우 10년전보다는 대폭 개선됐지만, 여전히 전국(평균 0.005ppm)에서 농도가 가장 높을 뿐 아니라 전국에서 유일하게 온산읍 화산리 측정소에서 1시간 환경기준을 초과하기도 했다.

2010년부터 환경기준($5.0\mu\text{g}/\text{m}^3$)이 적용되기 시작한 벤젠은공단지역인 울산의 1개 측정소(여천동, $5.7\mu\text{g}/\text{m}^3$)에서 환경기준을 초과한 것으로 조사됐다. 정재환기자 hani@

울산시] 울산시, 5월1일부터 오존 경보제 실시

2011년 04월 27일 (수) 09:28:50

워터저널 webmaster@waterjournal.co.kr

울산시는 대기 중 오존(O₃)의 피해를 최소화하고 오존농도 저감을 위한 시민들의 자발적인 참여를 유도하기 위해 오는 5월1일부터 9월30일까지 '오존 경보제'를 실시한다고 밝혔다.

오존경보는 주의보 0.12ppm/h 이상, 경보 0.3ppm/h 이상, 중대경보 0.5ppm/h 이상이면 각각 발령된다. 오존 환경기준은 1시간 0.1ppm 이하, 8시간 0.06 ppm 이하이다

오존경보 발령은 중구, 남구, 동구, 북구, 울주군 온산읍, 울주군 청량면 등 6개 권역으로 구분 발령된다. 울산시는 오존경보가 발령되면 정부기관, 언론기관, 구·군 권역(480개소) 등 총 517개소에 통보한다. 또한 휴대폰 문자 메시지 서비스(UMS) 가입 시민들(현재 9천662명 가입)에게도 발령 상황을 즉시 전파한다. 오존경보 발령시 단계별 조치사항을 보면 '주의보' 발령시에는 주민의 실외 활동 및 자동차 사용을 자제해야 한다.

'경보' 발령시에는 주민의 실외활동 제한 요청, 자동차 사용의 제한 명령, 사업장의 연료 사용량의 감축 권고 등이, '중대경보' 발령시에는 주민의 실외활동 금지요청, 자동차의 통행금지 및 사업장의 조업시간 단축 명령 등이 내려진다.

울산시 관계자는 "여름철 오존 저감을 위해서는 가능한 승용차 사용을 자제하고 대중교통을 이용하는 것이 바람직하다"고 강조하고 "오존 경보가 발령되면 특히 호흡기 질환자, 노약자, 유아 등은 외출을 삼가야 한다."고 밝혔다.

한편 울산지역에는 지난해 총 9회(7일) 오존 경보제가 발령됐다. 지역별로는 남구 6회, 동구 1회, 북구 1회, 울주(청량) 1회 등이다. <권다인 기자>

【표 III-4-4】

【표 III-4-4】

전국 및 7대 도시의 대기오염 농도(2009~2011)

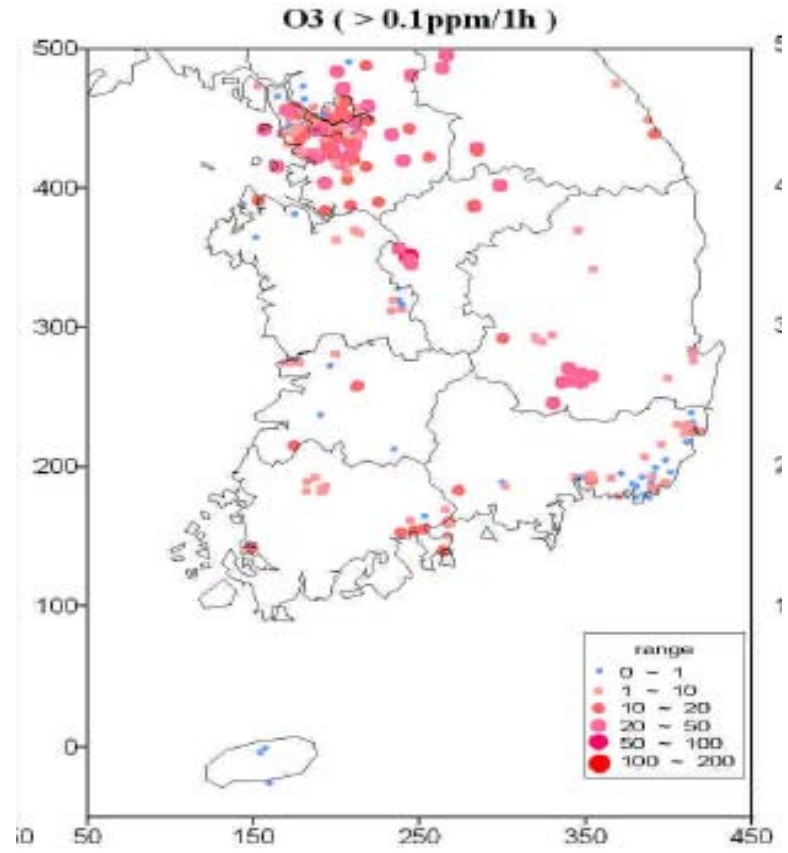
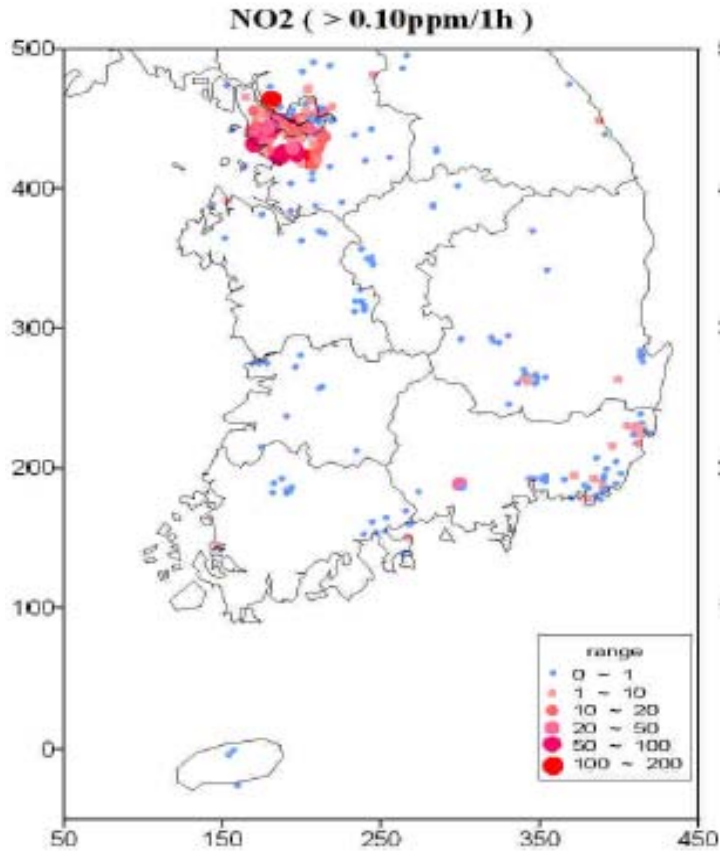
(단위 : ppm)

오염물질 연도 지역	SO ₂ (0.02)			NO ₂ (0.03)			O ₃ (-)			CO (-)			PM-10 ¹⁾ (50)		
	'09년	'10년	'11년	'09년	'10년	'11년	'09년	'10년	'11년	'09년	'10년	'11년	'09년	'10년	'11년
전국	0.006	0.005	0.005	0.025	0.025	0.024	0.024	0.023	0.024	0.5	0.5	0.5	53	51	50
서울	0.005	0.005	0.005	0.035	0.034	0.033	0.021	0.019	0.019	0.6	0.5	0.6	54	49	47
부산	0.005	0.006	0.006	0.021	0.021	0.020	0.027	0.026	0.027	0.4	0.4	0.4	49	49	47
대구	0.005	0.005	0.005	0.024	0.025	0.024	0.023	0.022	0.025	0.5	0.5	0.5	48	51	47
인천	0.007	0.007	0.007	0.030	0.030	0.030	0.024	0.021	0.022	0.6	0.6	0.5	60	55	55
광주	0.004	0.004	0.003	0.021	0.020	0.019	0.026	0.024	0.026	0.5	0.5	0.5	46	45	43
대전	0.005	0.004	0.004	0.022	0.023	0.021	0.023	0.021	0.022	0.5	0.5	0.5	43	44	44
울산	0.008	0.008	0.008	0.022	0.023	0.023	0.024	0.023	0.025	0.5	0.5	0.5	49	48	49
경기	0.006	0.005	0.005	0.030	0.030	0.030	0.022	0.020	0.021	0.6	0.6	0.6	60	58	56

()는 연평균 환경기준

1) PM-10 단위는 ug/m³

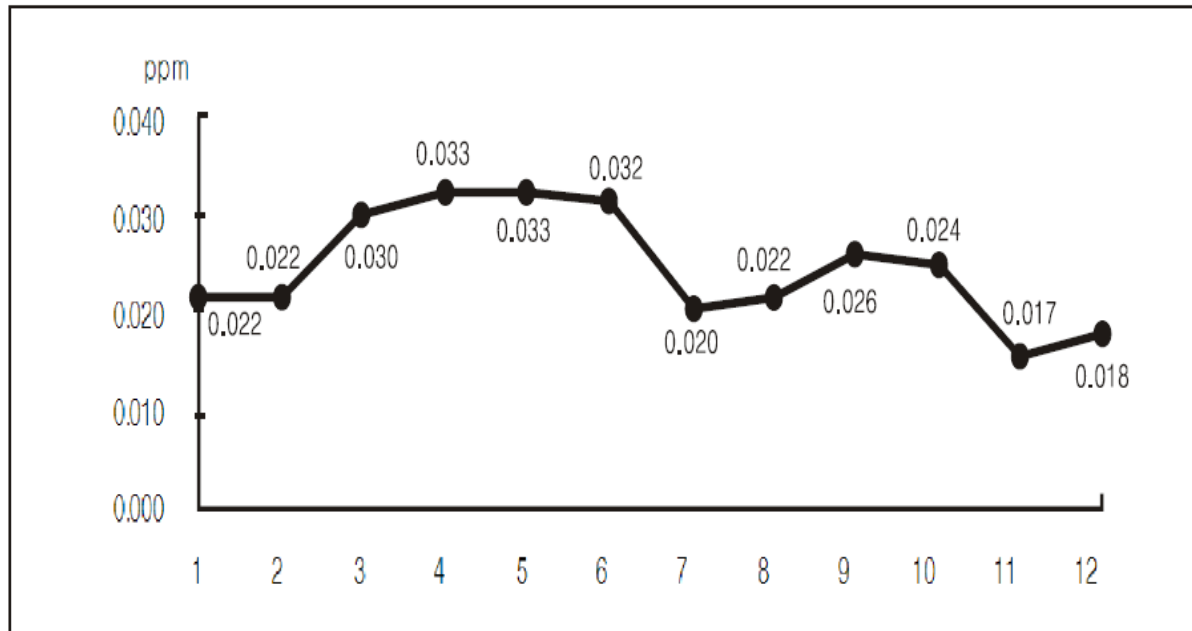
2011년 측정소별 환경기준농도 초과횟수



오존경보 발령기준(1시간 오존오염도 기준)

구 분	발 령 기 준	해 제 기 준
주 의 보	오존농도가 0.12ppm이상일 때	오존농도가 0.12ppm미만일 때
경 보	오존농도가 0.3 ppm이상일 때	오존농도가 0.3 ppm미만일 때
중대경보	오존농도가 0.5 ppm이상일 때	오존농도가 0.5 ppm미만일 때

2011년 월별 오존 오염도



※ 자료 : 환경통계연감

울산시의 경우도 1999년도에 오존경보제를 도입하였으며 오존주의보는 2005년 3회, 2006년 4회, 2007년 8회, 2008년 9회, 2009년 12회, 2010년 9회, 2011년 1회 발령되었다.

발령일자	발령지역	발령		해제	
		시간	농도(ppm)	시간	농도(ppm)
2009. 8. 14	남구 전역	13:00	0.125	14:00	0.08
			0.124		0.08
2009. 8. 18	북구 전역	15:00	0.122	16:00	0.085
2009. 8. 22	동구 전역	12:00	0.123	13:00	0.112
	동구 전역	16:00	0.121	17:00	0.107
	북구 전역	17:00	0.12	18:00	0.093
2010. 6. 5	북구 전역	14:00	0.122	17:00	0.108
	남구 전역	14:00	0.120	18:00	0.093
	청량면 전역	15:00	0.124	16:00	0.118
2010. 6. 16	남구 전역	16:00	0.120	17:00	0.087
2010. 6. 29	남구 전역	14:00	0.126	15:00	0.062
2010. 7. 7	남구 전역	12:00	0.125	13:00	0.096
2010. 8. 21	남구 전역	13:00	0.152	15:00	0.112
2010. 8. 22	남구 전역	12:00	0.121	13:00	0.087
2010. 9. 18	동구 전역	15:00	0.164	16:00	0.052
2011. 6. 21	남구 전역	14:00	0.120	18:00	0.103

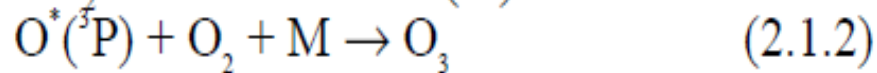
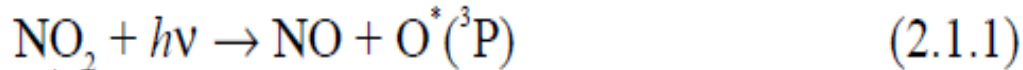
※ 자료 : 환경관리과

울산지역 냉각탑에서 배출되는 HOCl (차염소산) 예상 총량

RR (순환수량)	flash-off	amount of emission		Remark
ton/hr		kg/day	ton/year	
2,000,000	10%	576	210	
2,000,000	15%	864	315	
2,000,000	20%	1,152	420	
3,000,000	10%	864	315	
3,000,000	15%	1,296	473	
3,000,000	20%	1,728	631	
NaOCl	12%	as Cl ₂	1	ppm/RR

Atmosphere Chemistry of the Troposphere (I)

In the absence of VOCs yield a steady state ozone concentration



Reaction 2.1.3 acts as an ozone sink

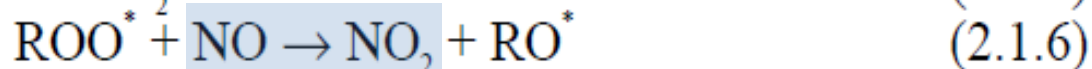
M: any third body like N_2

- ☞ The amount of ozone produced is strongly dependent on the ultraviolet sunlight intensity, the concentration of VOCs and NO_x in the lower atmosphere, temperature, humidity, and cloud cover.

Atmospheric Chemistry of the Troposphere (II)

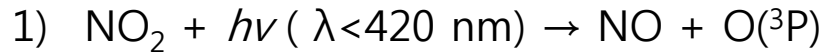
In the presence of VOCs higher ozone concentration results

because of both an increase in O₃ source (NO₂) & a reduction in the O₃ sink (NO)



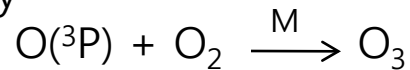
- 1) The formation (2.1.5) and reduction (2.1.6) reaction of the peroxyradical ROO*
- 2) These steps allow ozone to accumulate by reducing the ozone sink (NO) and increasing ozone sources (NO₂)

Sources & function of Ozone (O₃)



: O₃ adsorbs light in the region from 290 to 320 nm

followed by



M: any third molecule that stabilizes the excited intermediate before dissociates back into reactants *eg* N₂

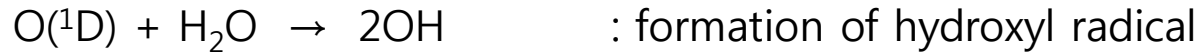
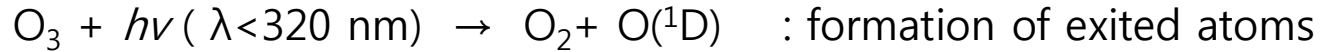
2) Ozone is a source of the hydroxyl radical (OH)

: reacts rapidly with most air pollutants and trace species found in the atmosphere

☞ Although some NO₂ is emitted directly into the atmosphere by combustion process, most is formed by oxidation of NO (the major nitrogenous byproduct of combustion) after dilution in air

Sources of OH (1)

1) Photolysis of O₃: major source



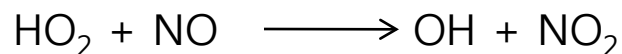
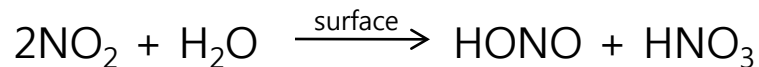
2) Photolysis of nitrous acid: significant source in polluted atmosphere



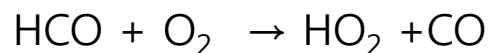
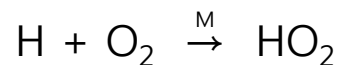
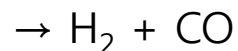
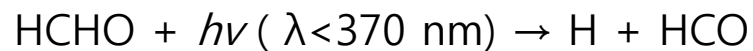
☞ Source & ambient concentration of HONO are not well known

Sources of OH (2)

3) Heterogeneous sources of HONO

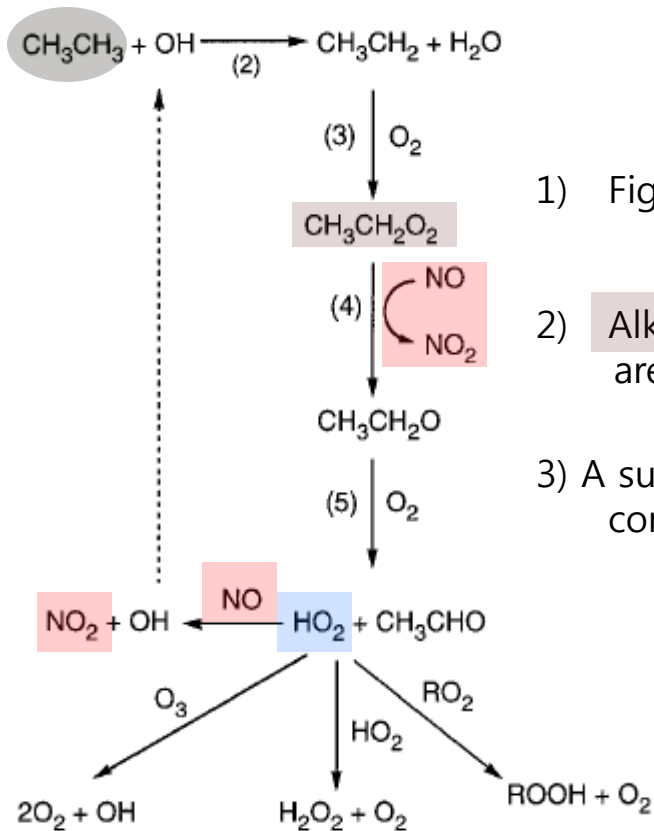


4) Photolysis of organic compounds like formaldehyde



👉 The O₃-alkene reaction is also source of OH

Conversion of NO to NO₂



1) Fig. 2 illustrates chemistry, using ethane as the simplest example

2) Alkyl peroxy (RO₂) and hydroperoxy (HO₂) free radicals are generated (step 3 and 5) which oxidize NO to NO₂

3) A substantial fraction of the time, the OH is regenerated to continue the reaction

Fig. 2. Example of the role of organic compounds in the conversion of NO to NO₂.

☞ Parts of the oxidation of organic compounds, initiated by reactive species such as the OH radical

Potential reaction of NO₂

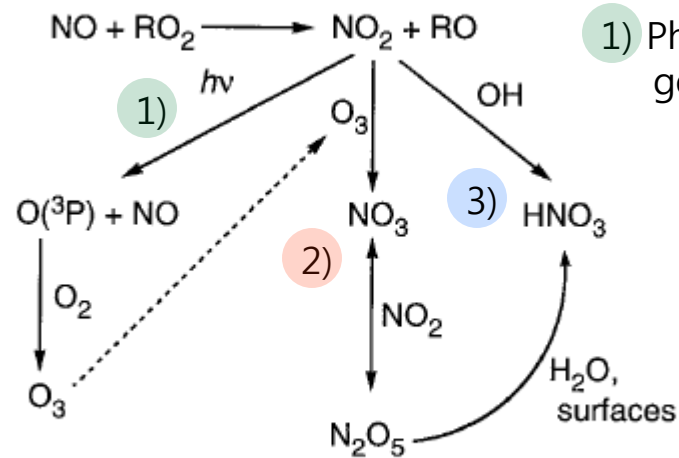


Fig. 3. Summary of the major reaction paths for NO_x in air.

1) Photolysis to form ground-state oxygen atoms O(³P) which generate O³, as well as reaction with OH to form nitric acid

2) When there are sufficient concentrations of both NO₂ & O₃, the nitrate radical (NO₃) and dinitrogen pentoxide (N₂O₅) are formed

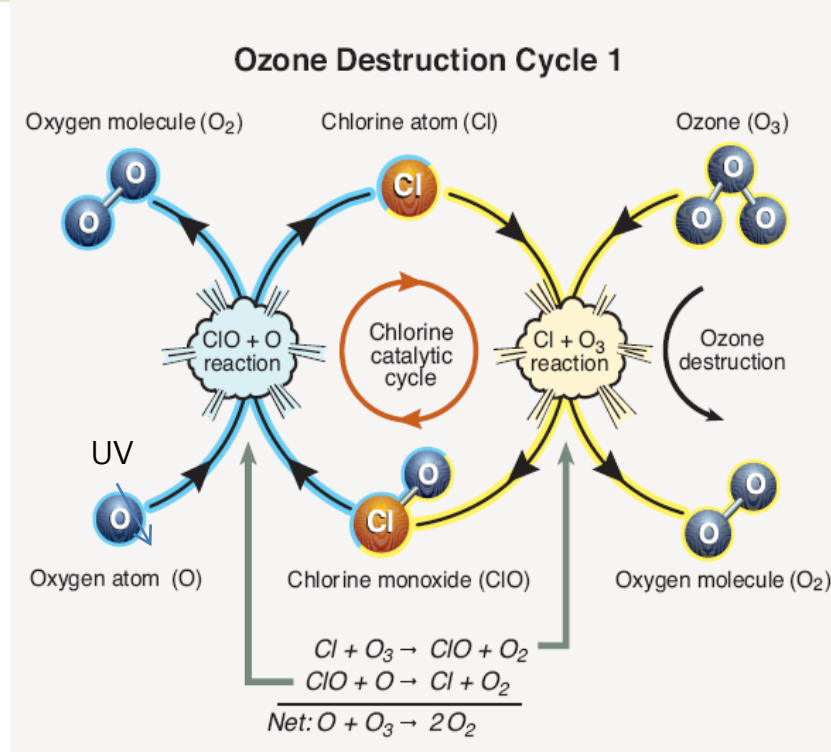
3) Like OH, NO₃ reacts with organics to initiate their oxidation.

👉 NO₃ chemistry is important only at night because it photolyzes rapidly during the day

Section II: THE OZONE DEPLETION PROCESS

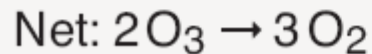
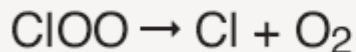
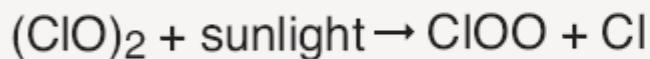
What are the chlorine and bromine reactions that destroy stratospheric ozone?

Reactive gases containing chlorine and bromine destroy stratospheric ozone in "catalytic" cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many thousands of ozone molecules before it leaves the stratosphere. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer.



Ozone Destruction Cycles in Polar Regions

Cycle 2



Cycle 3

