Statistical Analysis of Trends and the Relationship between Greenhouse Gases and Ozone

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Abstract
Important entities to the depletion of ozone are a group of manufactured chemicals containing chlorine and bromine. The present study uses in situ readings of 13 greenhouse gases and ozone from Mauna Loa, Hawaii. First, using Non-response analysis to determine the constant nature of each greenhouse gas and ozone; followed by trend analysis of atmospheric gases: both greenhouse gases and ozone show that while some greenhouse gases are on the rise, these compounds do not significantly affect ozone which is naturally rather variant and seasonal. Using trend analysis coupled with Fourier series and identifies those gases on the rise. Then using standard regression analysis to establish a relationship between these gases and ozone; and rank the contributing terms.

Key Words: Statistical Analysis, Trend Analysis, Regression, Greenhouse Gases, Ozone

1. Introduction

Global warming and the increase in greenhouse gases has become a major scientific and political issue during the past couple of decades. Based on data obtained from NASA [5] for yearly averages as determined through ice-core sampling, between 1850 and 2010 carbon dioxide (CO_2) level has increased by more than 35%; up an additional 10% from just twenty years prior [3]. Other gases such as Methane (CH_4) have increased nearly 125% in this same time frame whereas Nitrous Oxide (N_2O) has only increased approximately 17.5%. Other chlorofluorocarbon [6] such as CFC-11 has only been around since the mid-1900s; however, between 1950 and 2000, the concentrations found have increased 26,200%, from 0.001 ppb to 0.263 ppb. However, how are these greenhouse gases trending and how do these greenhouse gases such as carbon dioxide [7] affect ozone depletion [4] from industrial chemicals? Consider the following data as measured in Mauna Loa, Hawaii.

1.1 Data

There are 14 variables of interest, listed alphabetically, with 4514 monthly readings between July 8, 1999 and November 16, 2011. Data from hourly in situ samples analyzed on a gas chromatograph located at Mauna Loa (MLO), Hawaii (19.539 N, 155.578 W, elevation: 3397 m).

1. **Carbon Dioxide** (CO_2) CCGG
2. **Carbon tetrachloride** (CCl_4)
3. **Chlorofluorocarbon-11** (CCl_3F); *(trichlorofluoromethane)*
4. **Chlorofluorocarbon -113** (CCl_2CClF_2)
5. **Chlorofluorocarbon -12** (CCl_2F_2)
6. **Halon-1211** ($CBrClF_2$)
7. **Hydrochlorofluorocarbon-142b** (CH_3CClF_2)
8. **Hydrochlorofluorocarbon-22** ($CHClF_2$)

9. **Methane** (CH_4) CCGG
10. **Methyl chloride** (CH_3Cl)
11. **Methyl chloroform** ($C_2H_3Cl_3$)
12. **Nitrogen Oxide** (N_20)
13. **Sulfur hexafluoride** (SF_6)
14. **Ozone** (O_3)

Descriptively **Carbon Dioxide** readings are the highest, Fig. 1a, with a mean concentration of 378.99 ppmv; and **Methane** readings are the second highest, Fig. 1b, with a mean concentration of 1.79 ppmv (or 1751.13 ppbv) [8]. **Nitrous oxide** (N_2) ranks third with a mean concentration of 0.314 ppmv (or 314.11 ppbv) and **Ozone** ranks fourth with a mean concentration of 0.01153 ppmv (or 11.53 ppbv), Table 1. The remaining trace gases range from 0.000568 ppmv to 0.00000426833 ppmv (or 568.44 pptv down to 4.27 pptv), Fig. 1c.

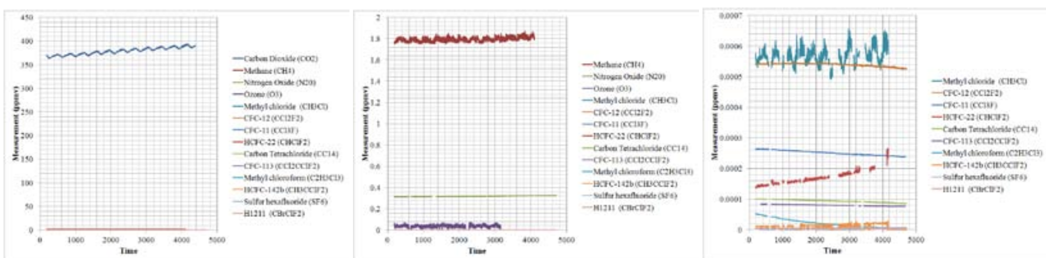

Fig. 1a **Fig. 1b** **Fig. 1c**

Figure 1: Line graph of various measurements (ppmv) over time ($t = 1$ on January 1, 1999)

Table 1: Ranking of gases by mean measurement

Rank	Gas	Min	Mean	Max	Std	Count
1	Carbon Dioxide (CO_2)	363.88	378.99	393.89	7.11	3900
2	Methane (CH_4)	1751.13	1794.21	1870.40	19.59	3917
3	Nitrogen Oxide (N_20)	314.11	320.12	325.64	2.78	3949
4	Ozone (O_3)	11.53	40.36	76.33	10.26	2749
5	Methyl chloride (CH_3Cl)	492.44	568.44	654.06	25.11	2813
6	CFC-12 (CCl_2F_2)	524.08	539.32	545.56	5.06	4042
7	CFC-11 (CCl_3F)	238.45	251.96	265.63	7.51	4044
8	HCFC-22 ($CHClF_2$)	136.28	167.92	266.54	20.50	2081
9	Carbon Tetrachloride ($CC1_4$)	86.08	94.40	101.79	4.17	3963
10	CFC-113 (CCl_2CClF_2)	76.38	80.29	85.94	2.35	3709
11	Methyl chloroform ($C_2H_3Cl_3$)	6.02	21.37	53.27	12.81	3855
12	HCFC-142b (CH_3CClF_2)	8.13	16.11	28.24	3.32	2803
13	Sulfur hexafluoride (SF_6)	4.38	5.95	7.79	0.86	3829
14	H1211 ($CBrClF_2$)	3.89	4.27	4.60	0.11	3901
				ppmv	ppbv	pptv

1.2 Constant Nature of a Variable

These various gases show both trends; some increases like **Carbon Dioxide** (CO_2) and others decreasing like **CFC-11** (CCl_3F) and seasonal effect: (some regular as with CO_2 and others more sporadic such as in **Methyl chloride** (CH_3Cl). However, before we consider trends and seasonal effects in the various greenhouse gases, consider the constant nature of each variable.

Using **Non-Response Analysis** (**NRA**), for any of the measured variables x with positive measure, we have the non-response equation $\alpha x = 1$; and the observed values $\alpha x_i = 1 + \delta_i$. To minimize the sum of square errors, $W = \sum(\alpha x - 1)^2$, we have

$$\hat{\alpha} = \frac{\sum x}{\sum x^2}.$$

This approach minimizes the sum of squares in terms of percent change leading to a self-weighting mean and when treated as standard regression with unit response (non-response) gives a **coefficient of determination** of

$$R^2 = \frac{(\sum x_i)^2}{n \sum x_i^2},$$

with $R^2 = 1$ being a constant and $R^2 \to 0$ meaning highly variant.

That is the percent of variance in the system explained by the variable x. This measure is also an indication of the **constant nature of the variable** itself. Consider the sums of square error for the variable x, using the definition of variance, we have

$$\sum x^2 = \sum (x - \bar{x})^2 + n\bar{x}^2.$$

Hence, internal to the variable, the coefficient of determination is the percent of total sums of squares explained by the mean. Note: this measure is unit free; that is, it is independent of scale of the measure: ppmv, ppbv, and pptv.

The least variant gas is **Nitrogen Oxide** with $R^2 = 0.99992$ and the most variant gas is **Hydrochloroflurocarbon** with $R^2 = 0.73578$, Table 2. **Ozone** is also rather variant with $R^2 = 0.93936$.

Table 2: Ranking of greenhouse gases constant nature

Gas	$\hat{\mu}_x$	$\bar{x}$	n	R^2
Nitrogen Oxide (N_20)	320.15	320.12	3949	0.99992
CFC-12 (CCl_2F_2)	539.36	539.32	4042	0.99991
Methane (CH_4)	1794.42	1794.21	3917	0.99988
Carbon Dioxide (CO_2)	379.13	378.99	3900	0.99965
H1211 ($CBrClF_2$)	4.27	4.27	3901	0.99928
CFC113	80.36	80.29	3709	0.99914
CFC-11 (CCl_3F)	252.19	251.96	4044	0.99911
Carbon Tetrachloride ($CC1_4$)	94.59	94.40	3963	0.99806
Methyl chloroform ($C_2H_3Cl_3$)	569.55	568.44	2813	0.99805
HCFC-22 ($CHClF_2$)	170.42	167.92	2081	0.98533
Sulfur hexafluoride (SF_6)	6.07	5.95	3829	0.97957
HCFC-142b (CH_3CClF_2)	16.79	16.11	2803	0.95921
Ozone (O_3)	42.97	40.36	2749	0.93936
Methyl chloride (CH_3Cl)	29.05	21.37	3855	0.73578
			ppbv	pptv

1.3 Global-warming Potential

The **global-warming potentials** is an index based upon radiate properties that can be used to estimate the potential future impacts of emissions of different gases upon the climate system. GWP is based on a number of factors including the infrared-absorbing ability of each gas relative to that of carbon dioxide and the decay rate of each gas (the amount removed from the atmosphere over a given number of years) relative to that of carbon dioxide. For each greenhouse gas, A, with an atmospheric lifetime τ_A, [3], it's global warming potential (GWP) relative to that of CO_2over a period of t_f is given by

$$GWP = \frac{a_A \tau_A \left(1 - e^{-\frac{t_f}{\tau_A}}\right)}{a_{CO_2} \tau_{CO_2} \left(1 - e^{-\frac{t_f}{\tau_{CO_2}}}\right)},$$

where a_A and a_{CO_2} are the radiate efficiency due to a unit increase in atmospheric abundance of the substance, and τ_{CO_2} is the atmospheric lifetime of carbon dioxide, CO_2, Table 3.

Table 3: Global-warming potentials

Gas	**Lifetime**	$\boldsymbol{GWP}$ **(**$t_f = 100$**)**
Sulfur hexafluoride (SF_6)	3200	22,200-23,900
CFC-12 (CCl_2F_2)	45-116	8,100-10,900
CFC-113 (CCl_2CClF_2)	90-110	4,800-6,130
Halon1211 ($CBrClF_2$)	16	4,750
CFC-11 (CCl_2F)	55	3,800-4,750
HCFC-142b (CH_3CClF_2)	11.4	1,800-2,310
HCFC-22 ($CHClF_2$)	15.8	1,500-1,810
Carbon Tetrachloride ($CC1_4$)	47	1,400
Nitrogen Oxide (N_20)	114-132.0	296-310
Methyl chloroform ($C_2H_3Cl_3$)		45
Methane (CH_4)	10.5-12	21-25
Methyl chloride (CH_3Cl)	5-6.1	25
Carbon Dioxide (CO_2)	200-450	1

2. Trend Analysis

Intra-annual model (seasonal) variability is of a periodic nature, using Fourier series, [1]; the amount of concentrate of the various atmospheric gases is given by

$$X(t) = b_0 + b_1 t + b_2 t + \sum_{i=1}^{\infty} \left[b_{2i+1} \cos(2i\pi t) + b_{2(i+1)} \sin(2i\pi t) \right]$$

where t is measured in years ($t = 1$ corresponding to January 1, 1999).

2.1 Trend Analysis of Nitrous Oxide

Starting with the most consistent greenhouse gas, **nitrous oxide** is emitted by bacteria in soils and oceans; rising into Earth's atmosphere, nitrous oxide reacts with ozone in the stratosphere and is considered a major greenhouse gas. Where each molecule of carbon dioxide (CO_2) has the warming potential of 1, nitrous oxide (N_2O) has a warming potential of 310 [2].

In perspective, Fig. 2a, there appears to be a slight trend; however, when viewed in the scatter plot (not coordinated at the origin), this trend appears stronger, Fig. 2b.

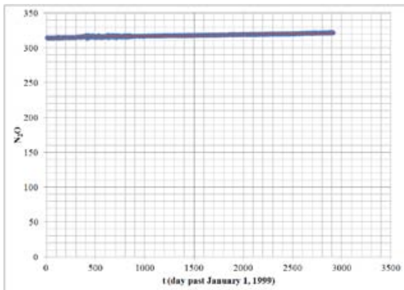

Fig. 2a

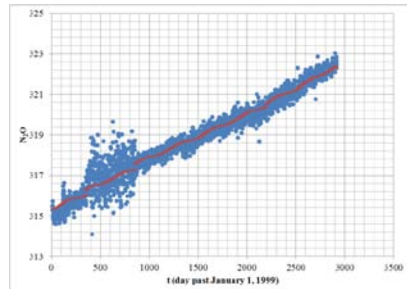

Fig. 2b

Figure 2: Scatter plots of N_2O over time

For N_2O as measured in ppbv, the fitted model is

$$\hat{X}(t) = 315.056 + 0.641117t + 0.01028t^2 + 0.067232\cos(2\pi t) + 0.001685\sin(2\pi t)$$

With an $R^2 = 0.981573$, this model explains nearly all the variance observed in the nitrous oxide (N_2O), Fig. 2b; however, in perspective, this is only a fraction of the initial measure of 315.51 ppbv in July 1999 (estimated at 315.3233 ppbv in January 1999), Fig. 2a.

At this rate, we can expect the amount of **nitrous oxide** to reach 333.137 ppbv in January 2020, a 5.649% increase in 21 years and is accelerating slightly. However, when nitrous oxide reacts with sunlight and N_2O is then photolysis the sunlight to form **nitric oxide** (NO) and **oxygen** (O), the oxygen atoms then in turn goes on to form **ozone**. Furthermore, **nitrous oxide** represents approximately 0.000325% of the dry atmosphere as measured in parts per million by volume.

2.2 Trend Analysis of Chlorofluorocarbon

Chlorofluorocarbon (CFC) is an organic compound that contains carbon, chlorine, and fluorine, produced as a volatile derivative of methane and ethane. A family of chemical compounds developed back in the 1930's as safe, non-toxic, non-flammable alternative to dangerous substances like ammonia for purposes of refrigeration (Freon) and spray can propellants; however with a GWP of 8,100, production of new stocks ceased in most countries as of 1994. The decline in **CFC-12** is clearly seen in Fig. 3b.

For **CFC-12** (CCl_2F_2), the fitted model is

$$\hat{X}(t) = 540.3863 + 1.704584t - 0.21539t^2 + 0.269512\cos(2\pi t) - 0.22108\sin(2\pi t) + 0.030673\cos(4\pi t) - 0.14027\sin(4\pi t) - 0.08223\cos(6\pi t) + 0.079499\sin(6\pi t)$$

With an $R^2 = 0.974406$ this model explains nearly all the variance observed in the **chloroflurocarbon-12** (CFC12), Figure 3; however, in perspective, this is only a fraction of the initial measure of 540.71 in July 1999. At this rate, we can expect the amount of **CFC-12** to drop as low as 481.2664 in January 2020, a 10.99% decrease in 21 years.

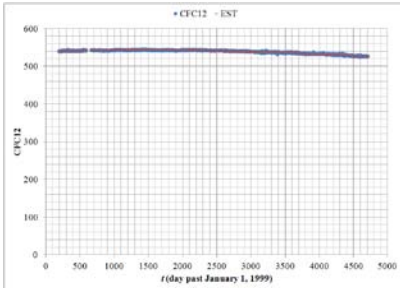

Fig. 3a

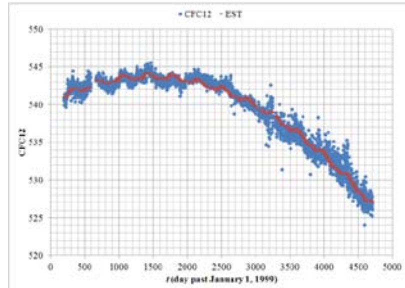

Fig. 3b

Figure 3: Scatter plots of CFC12 over time

2.3 Trend Analysis of Methane

Methane is simple alkane, the main component in natural gas and the most abundant organic compound measured.

For methane (CH_4), the fitted model is

$$\hat{X}(t) = 1788.922 - 2.63773t + 0.470285t^2 + 0.481068\cos(2\pi t) - 2.833622\sin(2\pi t)$$
$$-0.00593\cos(4\pi t) + 1.183935\sin(4\pi t) - 0.49481\cos(6\pi t) + 1.019353\sin(6\pi t)$$
$$+0.284736\cos(8\pi t) - 0.72566\sin(8\pi t) - 1.20524\cos(10\pi t) + 1.632545\sin(10\pi t)$$
$$+0.266959\cos(12\pi t) - 0.67602\sin(12\pi t) - 0.29492\cos(14\pi t) + 1.332496\sin(14\pi t)$$

With an $R^2 = 0.291367$ this model explains approximately one-third of the variance observed in the **methane**, Figure 4; however, much of the variance is unexplained. **Methane** represents 1.79 ppmv (0.000179%) of the dry atmosphere in parts per million by volume.

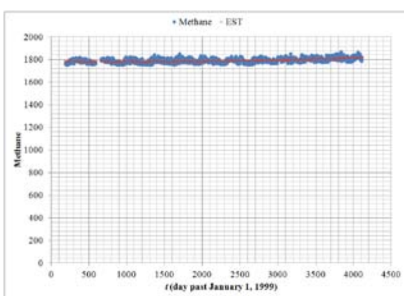

Fig. 4a

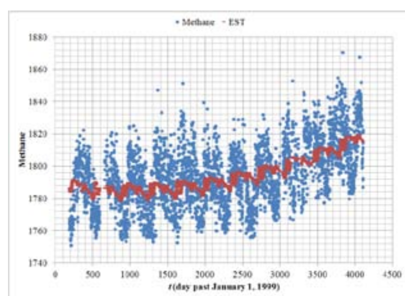

Fig. 4b

Figure 4: Scatter plots of Methane over time

2.4 Trend Analysis of Carbon Dioxide

Carbon dioxide is considered to be the primary greenhouse gas emitted through human activities such as transportation, industry, electricity, etc. This naturally occurring chemical is a colorless, odorless, incombustible gas formed during respiration, combustion, and organic decomposition and used in carbonated beverages, refrigeration, fire extinguishers, and aerosols.

For **carbon dioxide** (**CO_2**), the fitted model is

$$\hat{X}(t) = 366.4643 + 2.018753t - 1.03784\cos(2\pi t) + 2.752616\sin(2\pi t).$$

With an $R^2 = 0.98691$ this model explains nearly all of the variance observed in the carbon dioxide, Figure 5; however, in perspective, this is only a fraction of the initial measure of 370.65 in July 1999 (estimated at 365.4796 in January 1999). At this rate, we can expect the amount of carbon dioxide to increase to 408.1428 in January 2020, an 11.67% increase in 21 years. Carbon dioxide represents 394.45 ppmv (0.039445%) of the dry atmosphere in parts per million by volume. Hence, while we must vigilant to keep our land, air, and waters free of pollution, particulates, heavy metals, and pathogens; carbon dioxide (CO_2) is one pollutant that is essential to life [9].

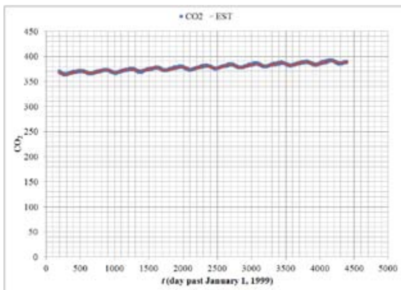

Fig. 5a

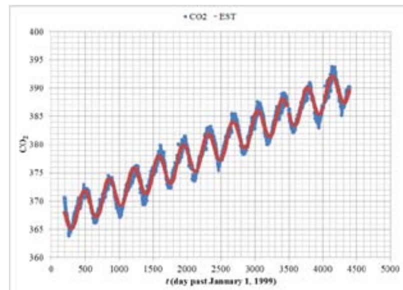

Fig. 5b

Figure 5: Scatter plots of carbon dioxide over time

2.5 Trend Analysis of Halon-1211

Bromochlorodifluoromethane or **Halon-1211** (H1211) are brominated haloalkanes, first used during World War II as fire extinguisher for aircraft and tanks and was introduced as an effective gaseous fire suppression agent around 1973. However, with a GWP of 4,750, the production of H1211 and other chlorofluorocarbons has been banned in most countries since January 1, 1994 as part of the Montreal Protocol on ozone depleting substances.

For bromochlorodifluoromethane, the fitted model is

$$\hat{X}(t) = 3.969622 + 0.125107t - 0.00941t^2 + 0.012946\cos(2\pi t) + 0.007945\sin(2\pi t) - 0.00074\cos(4\pi t) - 0.01543\sin(4\pi t) - 0.0027\cos(6\pi t) + 0.000277\sin(6\pi t)$$

In this model, there is a significant trend; over time, this was on the increase since mid-2000s has begun to decrease, Figure 6. With $R^2 = 0.899688$ this model explains nearly 90% of the variance observed in the bromochlorodifluoromethane; however, in perspective, this is only a fraction of the initial measure of 4.03 in July 1999 (estimated at 3.979 in January 1999). At this rate, we can expect the amount of bromochlorodifluoromethane to decrease to 2.44833 in January 2020, a 38.47% decrease in 21 years.

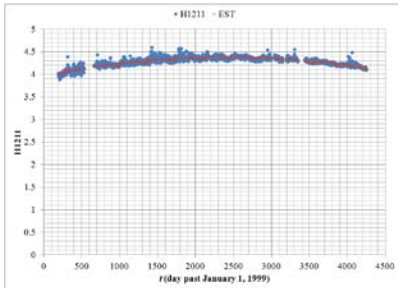

Fig. 6a

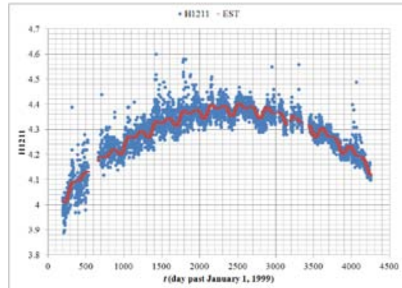

Fig. 6b

Figure 6: Scatter plots of bromochlorodifluoromethane over time

2.6 Trend Analysis of CFC-113

A common subclass is the **hydrochlorofluorocarbons** (**HCFCs**), which contain hydrogen; **CFC-113 (CCl_2CClF_2)** is a very non-reactive chlorofluorocarbon which can be broken down by ultraviolet radiation. Originally used as a coolant (Freon) in refrigerators and air conditioners. The Montreal Protocol in 1987 called for the phase out of all CFC's, including CFC-113 by 2010.

For CFC-113 (CCl_2CClF_2), the fitted model is

$$\hat{X}(t) = 84.75778 - 0.64569 - 0.00412t^2 + 0.031264\cos(2\pi t) + 0.034912\ (2\pi t)$$
$$-0.04022\cos(4\pi t) - 0.03087\sin(4\pi t)$$

A decreasing trend, explaining 98% of the variance seen in CFC-113, Figure 9; at the rate this gas will take up to 122 years for this gas to decompose and completely dissipate using the developed model:

$$\hat{X}(t) = 84.89267 - 0.70028t.$$

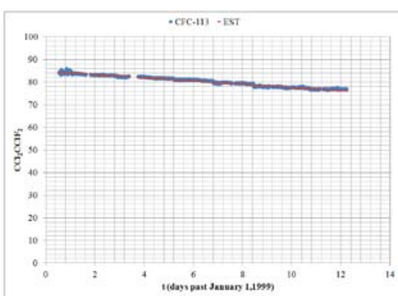

Fig. 7a

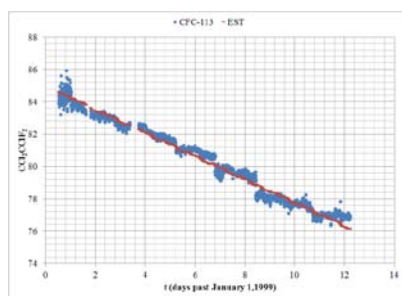

Fig. 7b

Figure 7: Scatter plots of CFC-113 over time

2.7 Trend Analysis of CFC-11

Trichlorofluoromethane or **CFC-11** (CCl_3F), also called freon-11 is a chlorofluorocarbon whose production in the US ended in January 1, 1995.

For Trichlorofluoromethan, the fitted model is

$$\hat{X}(t) = 266.791 - 2.28459t + 0.010984t^2 + 0.270462\cos(2\pi t)$$
$$- 0.00278\ \sin(2\pi t)$$
$$-0.003264\cos(4\pi t) - 0.11264\sin(4\pi t)$$

A decreasing trend, explaining 99.5% of the variance seen in CFC-11, Figure 8; at the rate this gas will take up to 125 years for this gas to decompose and completely dissipate using the developed model:

$$\hat{X}(t) = 266.4296 - 2.1379t.$$

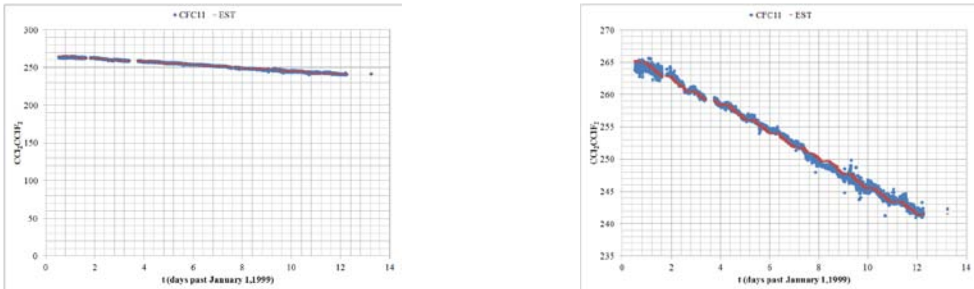

Fig. 8a **Fig. 8b**

Figure 8: Scatter plots of CFC-11 over time

2.8 Trend Analysis of Carbon Tetrachloride

Carbon Tetrachloride (**$CC1_4$**) is an organic compound used in fire extinguishers, a precursor to refrigerants and a cleaning agent. In 1992, production in the U.S., Europe and Japan was estimated at 720,000 tons; however, has steeply declined in the following decades.

For carbon tetrachloride or tetrachloromethane ($CC1_4$), the fitted model is

$$\hat{X}(t) = 101.6751 - 0.86198t - 0.0232t^2 + 0.093387\cos(2\pi t) - 0.03693\ \sin(2\pi t)$$
$$-0.0105\cos(4\pi t) - 0.12412\sin(4\pi t) - 0.01337\cos(6\pi t) + 0.082862\ \sin(6\pi t)$$
$$+0.012956\cos(8\pi t) - 0.03269\sin(8\pi t) - 0.02327\cos(10\pi t)$$
$$+\ 0015486\sin(10\pi t)$$
$$-0.01065\cos(12\pi t) - 0.00016\sin(12\pi t) + 0.032501\cos(14\pi t)$$
$$+\ 0.001226\ \sin(14\pi t)$$

A decreasing trend, explaining 99.2% of the variance seen in carbon tetrachloride, Figure 9; at the rate this gas will take up to 50 years for this gas to decompose and completely dissipate using the developed model:

$$\hat{X}(t) = 101.6618 - 0.85734t - 0.0235t^2.$$

Since this model has no seasonal effect, we can solve for time when there will be no more of this gas in the atmosphere; here we have $t = 50.01$ years. That is, all traces of this gas should be eliminated by January 1, 2049.

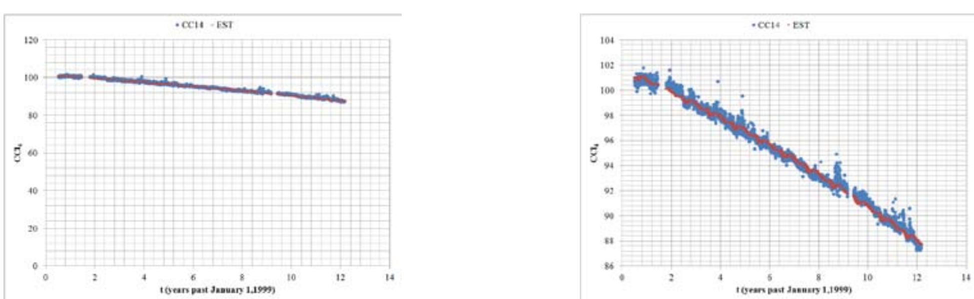

Fig. 9a **Fig. 9b**

Figure 9: Scatter plots of Carbon Tetrachloride ($CC1_4$) over time

2.9 Trend Analysis of Methyl Chloroform

Methyl chloroform ($C_2H_3Cl_3$) is used in many consumer products: household cleaners, glue and aerosol sprays; it is also used as a solvent and as a degreasing agent in industry.

For methyl chloroform ($C_2H_3Cl_3$), the fitted model can take one of the following forms:

$$\hat{X}(t) = 55.68 - 7.66745t + 0.304447t^2 + 0.179893\cos(2\pi t) - 0.215492\sin(2\pi t) \quad (1)$$

$$\hat{X}(t) = 55.68986 - 7.66595t + 0.304085t^2 \quad (2)$$

$$\hat{X}(t) = 59.15135e^{-0.17685t} \quad (3)$$

A decreasing trend, explaining 99.8% of the variance seen in methyl chloroform, Figure 10; at the rate this gas will take up only 26 years for this gas to decompose and dissipate to 1% of the amount measured in January 1999 based on the third exponentially decaying model.

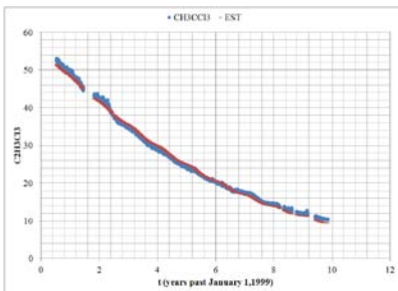

Fig. 10a

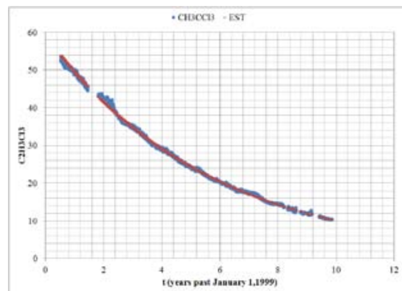

Fig. 10b

Figure 10: Scatter plots of Methyl chloroform ($C_2H_3Cl_3$) over time: model 1 and model 3

2.10 Trend Analysis of HCFC-22

Chlorodifluoromethane or **difluoromonochloromethane**, **HCFC-22** (**$CHClF_2$**), is a hydrochlorofluorocarbon (HCFC), a colorless gas commonly used as propellant and refrigerant. While being phased out in developed countries; this compound is in high demand in developing countries, mainly for air conditioning applications. In addition, companies in China and India that make the refrigerant hydrochlorofluorocarbon-22 (HCFC-22) may stop capturing and destroying a by-product gas with potent greenhouse effects, now that a profitable carbon credit trading system has ended [10]; this effect can be seen a dramatic increase over the past year, Figure 11.

For **Chlorodifluoromethane** (**$CHClF_2$**), the fitted model is

$$\hat{X}(t) = 143.8269 + 1.206312t + 0.503085t^2 - 0.33113\cos(2\pi t) + 0.238636\sin(2\pi t) - 1.38105\cos(4\pi t) - 1.36543\sin(4\pi t) + 0.754694\cos(6\pi t) + 0.341918\sin(6\pi t)$$

There has been a dramatic increase in this gas with highs reaching 266.54 in May 2010, an 93.3% increase over the reading of 137.87 in July 1999.

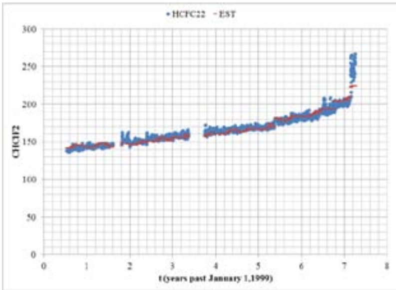

Figure 11: Scatter plots of **Chlorodifluoromethane** (CHClF2) over time.

2.11 Trend Analysis of SF_6

Sulfur hexafluoride (**SF_6**) is an inorganic, colorless, odorless, and non-flammable greenhouse gas. Sulfur hexafluoride is the most potent greenhouse gas that it has evaluated by the Intergovernmental Panel on Climate Change, with a global warming potential of 23,900 times that of Carbon Dioxide when compared over a 100-year period.

For sulfur hexafluoride (SF_6), the fitted model is

$$\hat{X}(t) = 4.41989 + 0.161906t + 0.006144t^2 + 0.006676\cos(2\pi t) + 0.00247\sin(2\pi t) - 0.00447\cos(4\pi t) - 0.0116\sin(4\pi t) - 0.00078\cos(6\pi t) + 0.004857\sin(6\pi t) + 0.006437\cos(8\pi t) + 6.76\times 10^{-5}\sin(8\pi t)$$

In this model, while some of the variance is season, there is a significant trend; over time, this compound has continued to increase at an accelerating rate, Figure 12. This model explains 99.3% of the variance in sulfur hexafluoride.

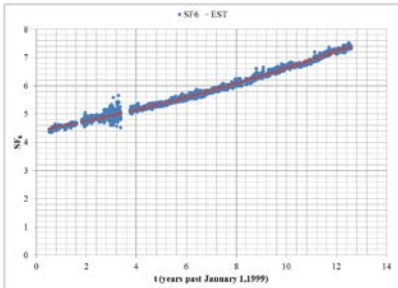

Figure 12: Scatter plots of **Sulfur hexafluoride** (**SF_6**) over time.

2.12 Trend Analysis of HCFC-142b

HCFC-142b (**CH_3CClF_2**) is a known by its trade name Freon 142b, it is an haloalkane and is primarily used as a refrigerant. For **Freon 142b** (CH_3CClF_2), the fitted model is

$$\hat{X}(t) = 11.0592 + 0.441407t + 0.042352t^2$$

In this model, there is a significant trend; over time, this compound has continued to increase at an accelerating rate, Figure 13. There is no apparent seasonal variation and only 89.8% of the variance in HCFC-142b is explained by the developed model.

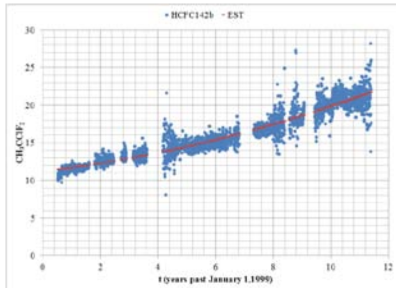

Figure 13: Scatter plots of **Dichlorofluromethane** (CH_3CClF_2) over time.

2.13 Trend Analysis of Methyl Chloride

Methyl chloride (**CH_3Cl**) occurs naturaly in the environment in low levels, produced by marine phytoplankton in oceans and by forest fires on land. Methyl chloride is also produced by cigarette smoke, polystyrene insulation and aerosol prepellants. Higher levels occur near chemical plants. The EPA has classified methyl chloride as a Group D carcinogen; that is, not a human carcinogenic. For Methyl chloride (CH_3Cl), the fitted model is

$$\hat{X}(t) = 566.9658 - 2.99958t + 0.407342t^2 + 6.262908\cos(2\pi t) + 25.0545\sin(2\pi t)$$
$$+0.191786\cos(4\pi t) - 3.75117\sin(4\pi t) - 1.83188\cos(6\pi t) - 1.32444\sin(6\pi t)$$
$$-1.34893\cos(8\pi t) + 1.144562\sin(8\pi t) - 1.4714\cos(10\pi t) - 0.4406\sin(10\pi t)$$

This model only explains 66.5% of the variance in Methyl chloride.

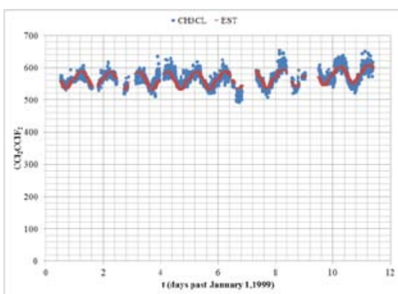

Fig. 14a

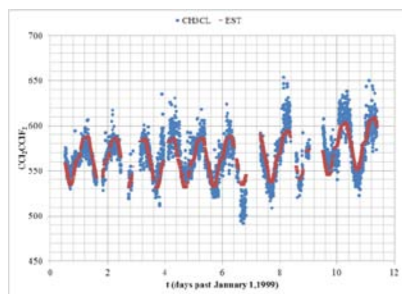

Fig. 14b

Figure 14: Scatter plots of Methyl chloride (CH_3Cl) over time.

2.14 Trend Analysis of Ozone

Ozone (**O_3**) is a gas that occurs both at ground level and in Earth's upper atmosphere. In the troposphere, near the Earth's surface, ozone is a pollutant that is a serious health risk; however, in the stratosphere, ozone forms a layer around the Earth, protecting it from harmful ultraviolet rays.

For Ozone (O_3), the fitted model is

$$\hat{X}(t) = 38.26693 + 0.840195t - 0.06647t^2 + 0.81281\cos(2\pi t) + 5.222734\sin(2\pi t)$$
$$-0.92749\cos(4\pi t) - 1.51999\sin(4\pi t) + 1.174845\cos(6\pi t) - 0.45651\sin(6\pi t)$$
$$+0.0692361\cos(8\pi t) + 0.908214\sin(8\pi t) - 0.85313\cos(10\pi t) + 0.043399\sin(10\pi t)$$
$$-0.42653\cos(12\pi t) - 0.55539\sin(12\pi t) + 0.547743\cos(14\pi t) + 0.536827\sin(14\pi t)$$

This model only explains 18% of the variance in ozone; that is, ozone is rather constant with seasonal effects, Figure 15.

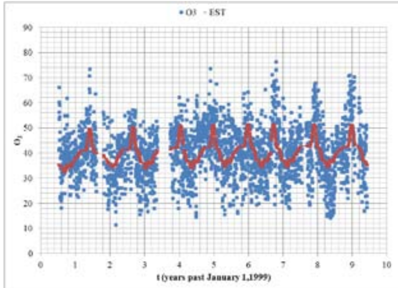

Figure 15: Scatter plots of Ozone (O_3) over time based on trend and seasonal effect.

3. Regression Analysis

Consider the relationship between these various gases and ozone using standard regression analysis:

$$Y = X\beta,$$

where X is the data matrix containing all the atmospheric gases, X_{ij} for $i = 1, \ldots, 13$, the thirteen greenhouse gases including second order terms and interaction for $j = 1, \ldots, n$, β is the parameter matrix (column array) and Y is the subject response, ozone.

3.1 Linear Regression

In terms of linear modeling, we have the following model:

$$Y = \beta_0 + \beta_t t + \sum_{i=1}^{13} \beta_i X_i$$

which when fitted (below) only explains 47.6% of the variance in ozone as shown in Fig. 16a.

$$\hat{Y} = -467.4909106 - 0.057276687t - 1.883586491N_20 + 8.527862402SF6$$
$$+0.043279585Methane + 0.541882845CO2 - 1.385001307CC14$$
$$+0.931294753CH3CCI3 - 8.971940941CFC11 + 5.491139638CFC113$$
$$+4.505146784CFC12 + 0.249565061CH3CL + 15.84530924H1211$$
$$+0.249121882HCFC142b + 1.104266504HCFC22$$

With thirteen contributing variables and time, only 47.6% of the variation in ozone is explained by the above linear regression model.

3.2 Regression with Interaction

Consider ozone as it depends on time, the thirteen greenhouse gases and their interaction with each other. The model becomes

$$Y = \beta_0 + \beta_t t + \beta_{t^2} t^2 + \sum_{i=1}^{13} \beta_i X_i + \sum_{i \le k} \beta_{ik} X_i X_k + \sum_{i=1}^{13} \beta_{it} X_i t$$

with a total of 120 terms of which 74 terms are found to be significantly contributing at the 1% level of significance including t^2 and all $X_i t$ terms. Other significantly contributing terms include interactions mainly with N_2O, Methane, and CO_2.

The 32 terms in Table 4 are significant with *p-values* less than 10^{-302} and the developed model explains 66% of the variance in ozone, Figure 16b.

Table 4: Significantly contributing terms

Term	Beta	SE	Term	Beta	SE
Time×Time	-9.70E-05	4.44E-09	Methane×CC14	0.167512	0.001279
Time×N_20	0.009356	4.99E-05	Methane×CH_3CCI_3	-0.03722	6.84E-05
Time×Methane	-0.00125	4.64E-08	Methane×CFC-11	-0.25272	0.000757
Time×CO_2	0.005028	5.15E-06	Methane×CFC-113	0.085266	0.001198
Time×$CC1_4$	-0.03701	0.000293	Methane×CFC-12	0.029202	0.00019
Time×CH_3CCI_3	-0.02043	1.72E-05	Methane×CH_3CL	0.001321	2.53E-07
Time×CFC-11	0.077109	0.00016	Methane×HCFC142b	-0.03094	8.35E-05
Time×CFC-113	-0.07123	0.000496	CO_2×CO_2	-0.10409	0.001468
Time×CFC-12	-0.00413	5.34E-05	CO_2×CH_3CL	0.048061	3.16E-05
Time×CH_3CL	7.26E-05	6.03E-08	CO_2×HCFC142b	-0.52926	0.008161
Time×HCFC142b	-0.00811	1.97E-05	CH3CCI3×CH_3CCI_3	-1.18935	0.018247
Time×HCFC22	0.007263	3.20E-06	CH3CCI3×CH_3CL	-0.0264	0.000112
N_20×Methane	0.029992	0.000251	CFC12×CH_3CL	0.033282	0.000286
N_20×CH_3CL	0.045339	0.000419	CH_3CL×CH_3CL	-0.00073	1.66E-07
Methane×Methane	0.000166	1.01E-07	CH3CL×HCFC22	0.003702	1.89E-05
Methane×CO_2	0.002272	1.62E-05	HCFC22×HCFC22	-0.06974	0.000355

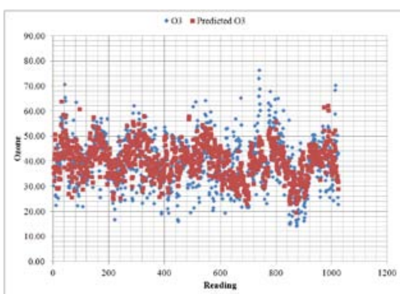

Fig. 16a

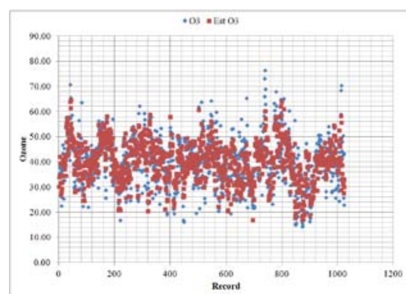

Fig. 16b

Figure 16: Scatter plots of Ozone (O_3) over time with estimates based (a) on trend and linear regression and (b) on trend and second order regression with interactions.

4. Conclusion

The main greenhouse gases that are trending downward include **CFC-12**, **Halon-1211**, **CFC-113**, **CFC-11**, **Carbon Tetrachloride**, and **Methyl Chloroform**; however, **Nitrous Oxide**, **Methane**, **Carbon Dioxide**, **HCFC-22**, **Sulfur hexafluoride**, **HCFC-142b**, and to a lesser degree, **Methyl Chloride** show an increasing trend. On the other hand, **Ozone** over Mauna Loa appears rather variant second only to **Methyl Chloride** and the variance in the measured amount of **Ozone** is only partially explained by these greenhouse gases and their interaction. With only 66% of the variance in **Ozone** explained by resulting regression model and 18% explained by time and season effects, further analysis is need to better understand ozone depletion.

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