

# Indoor Pollutant Gas Concentration and the Effect on Image Stability

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## Abstract

Image stability of unprotected prints is affected by pollutant gases in the atmosphere indoors. It is important to know the standard concentration of indoor pollutant gases, especially for the estimation of life expectancy of displayed images. Based on our measurements of indoor gas concentrations using passive samplers at various places for two years, we obtained proper data enabling us to determine the concentrations which have to be taken into account. At the same time, we displayed several kinds of unprotected prints and measured the concentration of pollutant gases at their sites. Then we analyzed the effects of these real pollutant gases on the stability of the displayed images. In this way, we were able to get a good correlation between the actual image deterioration of inkjet prints and their exposure to ozone or other gas at various indoor places.

## Introduction

Gases such as  $O_3$ ,  $NO_2$  and  $SO_2$  are indoor pollutant gases that are thought to have an effect on stability of image, yet little information is available from public institutions on their respective concentrations.<sup>1~8</sup> Furthermore, because of the diverse factors that affect concentration, it has been very difficult to clarify the actual situation.

In order to forecast the lifespan of images, it is important to know the standard concentration of these various indoor pollutant gases. In response to this need, a number of print material manufacturers have produced estimates of the average concentration of indoor ozone by comparing inkjet image fading caused by induced fading and fading within the actual environment.<sup>9~12</sup>

Against this background, we estimated the indoor concentrations of  $O_3$ ,  $NO_2$  and  $SO_2$  that must be taken into account based on year-long indoor concentration measurements of these gases in various types of rooms. We further analyzed the correlation between image deterioration and the actual concentration of gases at the display site by displaying images that were unprotected and shielded from light in rooms where gas concentration measurements were taken.

## Experiment

### 1. Measurement of Indoor Gas Concentration

#### *Measuring Device*

We used filter badges (passive samplers)<sup>13</sup> to measure the concentrations of  $O_3$ ,  $NO_2$  and  $SO_2$ . These are simple gas concentration measuring devices that have the merits of being small, inexpensive, simple to use, and non-electrical, and are suitable for multiple-site measurements.

Device used for ozone measurements:

Model 3300 (Ogawa Shokai K.K. Japan)

Device used for  $NO_2$ ,  $SO_2$  measurements:

Handy SONOX (Green Blue K.K. Japan)

#### *Measurement Sites and Durations*

##### *Japan*

The concentration of  $O_3$ ,  $NO_2$  and  $SO_2$  was continuously measured at 8 indoor sites (offices (3 sites), homes (4 sites), hospital (1 site) and outdoors for a duration of two years. Office A consisted of an entirely environmentally controlled building, while Office B consisted of an air-tight environmentally controlled room. Homes B and C used kerosene fan heaters during the winter season.

Apart from the measurements described above, measurements were also taken in 20 homes (mainly in living room) during the month of September. And the concentrations of indoor gases were measured again in January and February in 9 homes within rooms where kerosene fan heaters were used.

##### *Overseas*

Measurements were taken in February and August in New York and Los Angeles (referred collectively below as "the U.S.") and in Düsseldorf (Germany). Measurements were taken in November in Seoul (Korea) and São Paulo (Brazil). In each area, indoor gas concentrations (homes) and outdoor concentrations were measured simultaneously.

### 2. Correlation with Image Deterioration

At each measurement site in Japan, two kinds of inkjet prints, each printed with representative commercial inks,



were displayed unprotected and shielded from light. These images consisted of the single colors of cyan, magenta, and yellow, as well as gray patches ranging from white ground to the highest density level. An analysis was made of the correlation between the total exposure of each gas and the fading of single colors of cyan, magenta and yellow from an initial density of 1.0, and the rise of yellow staining. Furthermore, along with gas concentration, temperature and relative humidity were measured at each site.

Sample A: Dye based Inkjet Print produced with inks and genuine paper manufactured by Company A

Sample B: Dye based Inkjet Print produced with inks and genuine paper manufactured by Company B

## Results and Discussion

### 1. Indoor Pollutant Gas Concentration

#### Indoor Ozone Concentration

##### Annual Change of O<sub>3</sub> Concentration

Indoor O<sub>3</sub> concentrations were measured continuously at various sites to estimate real O<sub>3</sub> concentration. Figure 1 shows a portion of the indoor and outdoor measurement data gathered continuously in Japan over two-year period.

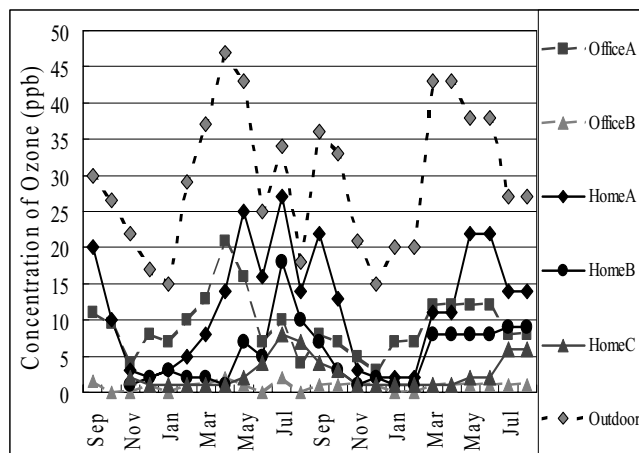


Figure 1. Concentration of ozone at various indoor and outdoor sites over two years

The concentration of atmospheric ozone fluctuates with the seasons and the concentration of indoor ozone fluctuates along with it. There is a tendency for the ratio of indoor ozone concentration to atmospheric ozone to rise during seasons in which the concentration of atmospheric ozone and air circulation rate rises (spring to autumn), and for the ratio to fall in the season (winter) in which there is a drop in the concentration of atmospheric ozone and the circulation rate.

#### Estimation of Annual Mean Concentration

Table 1 shows the annual mean concentration of ozone at various measurement locations.

**Table 1. Annual Mean Concentration of Ozone Which Were Measured Continuously by Passive Samplers in Japan**

Mean annual value	Offices			Homes				Hospital	Outdoors
	A	B	C	A	B	C	D	A	
O <sub>3</sub> concentration (ppb)	9	1	12	12	5	3	12	4	30

The annual mean indoor concentration of ozone at the eight sites was 7.3 ppb, with an average margin of about 12 ppb (average +  $\sigma$ ), while the annual mean outdoor concentration was 30 ppb. As a comparison, Table 2 shows the mean concentration for the month of September at the 8 sites, as well as the 20 homes where measurements were taken.

**Table 2. Mean Ozone Concentration in September at 20 Homes and the 8 Sites (Home & Office).**

Mean average in Sept.	8 Sites	20 Homes	Outdoors
O <sub>3</sub> concentration (ppb)	10	13	36

Taking into account the slightly high average concentration of ozone within the homes, the estimated annual mean concentration was calculated as  $7.3 \times (13/10) = 9.5$  ppb. From this, the necessary assumption for the annual mean concentration of indoor ozone would be about 10 ppb (Equivalent to one-year total exposure as 88 ppm-hr).<sup>14</sup> Moreover, it was shown that the annual mean concentration of indoor ozone is about 1/3 that of atmospheric ozone.

#### O<sub>3</sub> Concentration Overseas

Indoor O<sub>3</sub> concentrations were also measured at different countries. Table 3 shows the mean ozone concentration (average measurement for February and August) at the measurement sites in Europe and the U.S.

**Table 3. Mean Ozone Concentrations in Feb. and Aug. in U.S. and German Cities.**

O <sub>3</sub> concentration (ppb)	U.S.		Germany
	NY	LA	DUS
Indoors	7	9	5
Outdoors	28	29	28

The atmospheric and indoor ozone concentration figures for Europe and the U.S were not largely different from those for Japan.



### Indoor NO<sub>2</sub> Concentration

#### Annual Change of NO<sub>2</sub> Concentration

Indoor NO<sub>2</sub> concentrations were measured continuously at various sites as well as O<sub>3</sub>. Figure 2 shows a portion of the indoor and outdoor measurement data gathered continuously in Japan over two-year period.

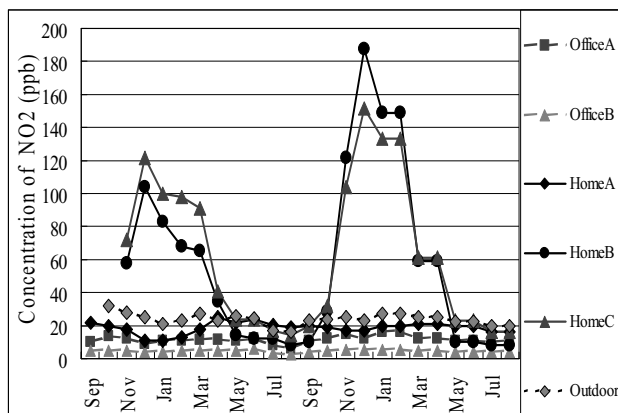


Figure 2. Concentration of Nitrogen Dioxide at various indoor and outdoor locations over two years

During the winter, kerosene fan heaters were used in Homes B and C and a sharp rise occurred in the concentration of indoor NO<sub>2</sub>. In estimate of NO<sub>2</sub> concentration, it is important to specify clearly whether there is an indoor source of NO<sub>2</sub> or not.

#### With an Indoor Source of NO<sub>2</sub> (in Japan)

It is a special characteristic of Japan that many homes use kerosene fan heaters in the winter. In the annual measurements, two homes (Homes B and C) had an annual mean indoor NO<sub>2</sub> concentration of 60 ppb, while the annual mean outdoor NO<sub>2</sub> concentration was 24 ppb. On the other hand, during the period when kerosene fan heaters were used (January and February), the indoor NO<sub>2</sub> concentration was about the same in the two homes mentioned above, as well as for nine other homes where measurements were taken (the mean value in Jan. and Feb. was about 141 ppb for the former and 135 ppb for the latter). From this, the necessary assumption for the annual mean indoor NO<sub>2</sub> concentration would be about 60 ppb in homes that use kerosene fan heaters.

#### Without an Indoor Source of NO<sub>2</sub>

When there is no indoor source of NO<sub>2</sub>, all homes had an indoor concentration that was lower than the atmospheric concentration. Table 4 shows the annual mean concentration of NO<sub>2</sub> at the remaining six sites which did not use kerosene fan heaters.

Table 4. Annual Mean Concentration of Nitrogen Dioxide Measured Continuously by Passive Samplers in Japan.

Mean annual concentration	Offices			Homes		Hospital	Outdoors
	A	B	C	A	D	A	
NO <sub>2</sub> (ppb)	11	5	12	19	23	8	24

Table 5. Mean Concentration of Nitrogen Dioxide in September at 20 Homes and the 6 Sites (Home & Office).

Mean value in Sep.	6 Sites	20 Homes	Outdoors
NO <sub>2</sub> concentration (ppb)	13	13	23

The annual mean indoor NO<sub>2</sub> concentration at 6 sites was 13 ppb, with an average margin of about 20 ppb (average +  $\sigma$ ), while the figure for outdoors was 24 ppb. As a comparison, Table 5 shows the mean concentration for the month of September at the 6 sites, as well as the 20 homes where measurements were taken.

From the fact that the mean concentration was the same for the 6 sites and 20 homes, the required assumption for the indoor NO<sub>2</sub> concentration would be about 15 ppb (Equivalent to one-year total exposure as 131 ppm-hr).

#### NO<sub>2</sub> Concentration Overseas

Indoor NO<sub>2</sub> concentrations were also measured at different countries. Table 6 shows the mean indoor NO<sub>2</sub> concentration (average measurement for February and August) at the measurement sites in Europe and the U.S.

Table 6. Mean Concentration of Nitrogen Dioxide in Feb. and Aug. in U.S. and German Cities.

NO <sub>2</sub> concentration (ppb)	U.S.		Germany
	NY	LA	DUS
Indoors	11	17	18
Outdoors	16	34	24

The mean concentrations of NO<sub>2</sub> at sites in Europe and the U.S. did not differ greatly from the corresponding figures for Japanese sites with no indoor source of NO<sub>2</sub> and so the concentration may be considered to be about the same (15ppb).

Due to variations in the regulation of atmospheric pollutant gases and the topographical features of the location (e.g., a basin, etc.) the mean concentration of atmospheric NO<sub>2</sub> in some locations reached the neighborhood of 100 ppb.<sup>15</sup> In these locations, the indoor NO<sub>2</sub> concentration was found to be about 30 ppb (Table 7).

Therefore, in the above-mentioned homes in Japan that use kerosene fan heaters or areas with a high atmospheric NO<sub>2</sub> concentration, it is necessary to assume an indoor concentration that conforms to conditions different from the standard.



**Table 7. Mean Concentration of Nitrogen Dioxide in Nov. and Aug. in Cities in Brazil and Korea**

NO <sub>2</sub> concentration (ppb) in Nov.	Brazil SAO	Korea SEL
Indoors	31	27
Outdoors	75	115

**Indoor SO<sub>2</sub> Concentration**

At sites with no indoor source of SO<sub>2</sub>, the indoor concentration was found to be lower than that of atmospheric SO<sub>2</sub>. The indoor concentration throughout the year in Japan, Europe and the U.S. was about 1 ppb, and so the required assumption for indoor SO<sub>2</sub> concentration would be about 1 ppb.

**2. Correlation with Image Deterioration****Correlation Between Image Deterioration of Inkjet Print A and Total Ozone Exposure**

We analyzed the effects of these real pollutant gases on stability of the displayed images that were unprotected and shielded from light. Figure 3 shows the correlation between changes in the residual optical density of the color dyes in Sample A at Office A and the total ozone exposure (ppm-hr) at various measurement points during an elapsed time period of five months.

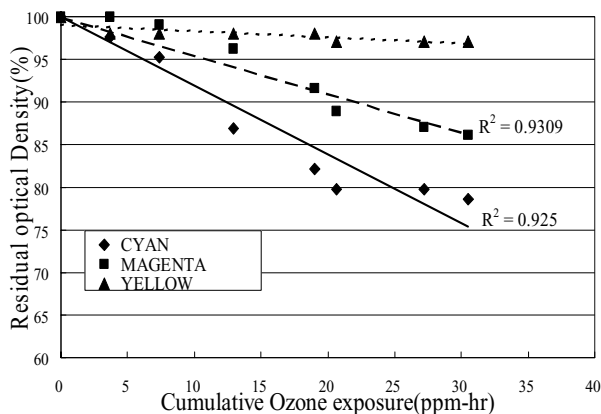


Figure 3. Correlation between residual optical density and cumulative ozone exposure at office A.

Figure 4 shows the correlation between change in the residual optical density of the color dyes in Sample A at various locations after an elapse of five months and the total ozone exposure (ppm-hr) over the five-month period at each location.

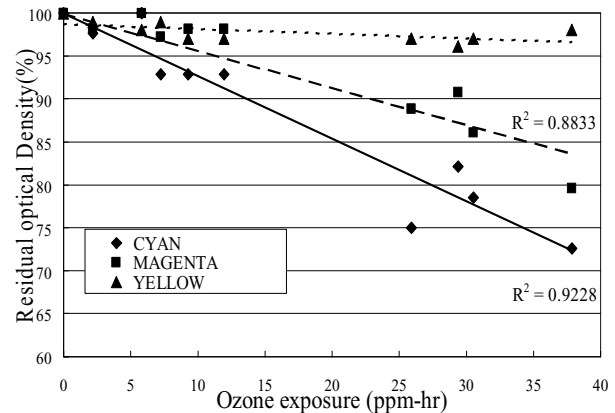


Figure 4. Correlation between residual optical density and total ozone exposure at various indoor sites

Whether the time-elapse change in the optical density occurred at one indoor location or at different indoor locations, there was a high correlation between the residual optical density of each color (especially cyan and magenta) and the respective total ozone exposure at the location ( $R^2 = \text{approx. } 0.9$ ). There was no correlation found between color fading and total NO<sub>2</sub> / SO<sub>2</sub> exposure, or temperature / relative humidity measured within the period, as was shown in Figures 3 and 4. From these facts, it is possible to deduce that ozone was the main cause of color fading in Sample A.

**Correlation Between Yellow Staining of Inkjet Print B and Total NO<sub>2</sub> Exposure**

Figure 5 shows the correlation between changes in yellow staining in the white ground (paper) in Sample B and the total NO<sub>2</sub> exposure (ppm-hr) at the various locations after an elapsed time period of 1.5 months.

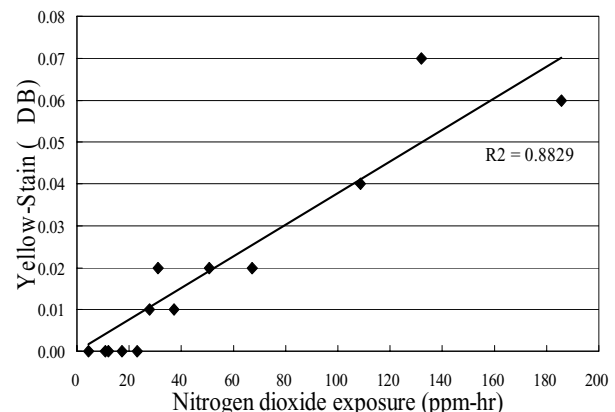


Figure 5. Correlation between yellow staining (delta BD) and total Nitrogen dioxide exposure at various indoor sites.



In light of the high correlation between staining at each location and the total NO<sub>2</sub> exposure at each place ( $R^2$ =approx. 0.9), as well as the lack of any correlation between staining and total ozone or SO<sub>2</sub> exposure, it is possible to deduce that NO<sub>2</sub> was the main cause of yellow staining in sample B.

We found that staining mainly occurred at locations that used kerosene fan heaters, and that in some instances image deterioration increased as the NO<sub>2</sub> concentration increased.

### Conclusion

By using passive samplers, we have directly measured indoor pollutant gas concentrations at various sites for two years. As a result, we have estimated standard concentration that should be assumed for indoor pollutant gases, which were 10 ppb for ozone, 15 ppb for NO<sub>2</sub> in places with no indoor source, 60 ppb for NO<sub>2</sub> in places where kerosene fan heaters are used in Japan, and 1ppb for SO<sub>2</sub>.

Image deterioration (fading and staining) in inkjet prints A and B, both are made with representative commercial inks were found to have a high correlation with real total ozone or NO<sub>2</sub> exposure at each location.

This study analyzed the correlation between image deterioration and gas concentrations; however, in addition to gases, temperature and humidity, light also has an effect on displayed images. For this reason, we are planning to carry out a comprehensive analysis in the future that will take into account image deterioration caused by light.

### References

1. Stock, T. H., Kotchmar, D. J. et. al., Journal of the Air Pollution Control Association,35, pg1266 (1985)
2. Liu, L. J. S., Koutrakis, P. et. al., Journal of the Air & Waste Management Association,45, pg223 (1995)
3. Reiss, R., Ryan, P. B. et. al., Journal of the Air & Waste Management Association, 45, pg811 (1995)
4. Romieu, I., Lugo, M. C. et. al., Journal of the Air & Waste Management Association,48, pg327 (1998)
5. Avol, E. L., Navidi, W. C. et.al., Environmental Science & Technology,32, pg 463 (1998)
6. Bernard, N. L., Gerber, M. J. et. al., Environmental Science & Technology,33, pg217 (1999)
7. Lee, K., Xue, X. P., Geyh, A. S. et. al., Environmental Health Perspectives,110. pg145 (2002)
8. Chao, C. Y. H., Building and Environment,36, pg999 (2001)
9. Matthew Thornberry and Steven Looman, IS&T's NIP19, pg426 (2003)
10. K. Kitamura, Y. Oki, H. Kanada and H. Hayashi, IS&T's NIP19, pg 415 (2003)
11. Michelle Oakland, Douglas Bugner, Rick Levesque, and Richard Vanhanehem, IS&T's NIP17, pg 175 (2001)
12. Barbara Vogt and Franziska Frey, IS&T's NIP17, pg 218 (2001)
13. Petros Koutrakis, Jack M. Wolfson, Koichiro Hirano et. al., Analytical Chemistry, Vol.65,No.3,pg 209 (1993)
14. Y. Shibahara, H. Ishizuka, N. Muro, Y. Kanazawa and Y. Seoka, IS&T's NIP18, pg 330 (2002)
15. Organization for Economic Co-operation and Development, OECD Environmental Data Compendium (1999)

### Biography

**Yukihiko Kanazawa** received his master's degree in engineering from Osaka University in Japan in 1984. Since then, he has worked in the Ashigara Research Laboratory at Fuji Photo Film Co.,Ltd in Japan. His work has primarily focused on the development and evaluation of imaging materials and in related areas.