

Appendix A

Ogawa ozone passive sampler range of measurements

Andrzej Bytnerowicz, Michael J. Arbaugh, Pamela E. Padgett, Antonio Davila and Diane Alexander

USDA Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive,
Riverside, CA 92507

Capsule: upper detectable range of Ogawa ozone samplers is much greater than specified by the manufacturer.

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Abstract

Test of the Ogawa ozone (O₃) passive samplers were performed in continuously stirred tank reactors (CSTR) at controlled O₃ concentrations. Concentrations determined with passive samplers and Dasibi Model 1003AH active UV absorption monitor were highly correlated (R²=0.9949). This linear relationship held up to a dose of 52,500 ppb O₃ x h, indicating that the samplers are capable of reliable O₃ monitoring for at least 477 hours at 110 ppb. This value is substantially higher than the upper detectable range specified by the manufacturer (<168 h at 110 ppb O₃) indicating that ~ 3-times longer periods of passive sampler exposure can be applied. This finding also means that by extending sampler exposure times, costs of O₃ monitoring can be significantly reduced.

Keywords: ambient air, monitoring, exposure dose, time of exposure.

Introduction

In recent years passive sampling of gaseous pollutants have received considerable attention (Krupa and Legge, 2000). Passive samplers, mostly for ozone (O₃) have been widely used for ambient monitoring in Europe (Blum et al., 1997; Bytnerowicz et al., 2002 a), North America (Brace and Peterson, 1998; Cox and Malcolm, 1999; Ray, 2001; Bytnerowicz et al., 2002 b; Frączek et al., 2003) and at a global scale (Carmichael et al., 2003). Among various types of O₃ passive samplers, the Ogawa & Company USA, Inc. sampler (Koutrakis et al., 1993) has been probably the most commonly used in the United States. Due to a growing interest in passive sampler use by scientists and federal land managers (Bytnerowicz et al., 2001), information on their performance and proper use is of a high practical value.

Methodology

In the beginning of the exposures, 20 Ogawa Ozone (O_3) passive samplers (Koutrakis et al., 1993) were placed in the continuously stirred tank reactors (CSTR) with controlled concentrations of O_3 (24 average between 99 and 146 ppb). Concentrations of O_3 were monitored with the UV absorption instrument (Dasibi Model 1003 AH) which was calibrated against the California Air Resources Board transfer standard instrument. After 1, 2, 3, 5, 7, 9, 11, 13, 15 and 17 days of exposure a single sampler was removed from the chamber. Two replicate pre-covered with nitrite (NO_2^-) cellulose collection pads (Ogawa PS-114) were removed from each sampler immediately after the exposures and placed in 10 mL Nalgene vials stored at $-18^\circ C$. Two replicate pads from each exposed sampler and four blank, unexposed pads were analyzed. Five mL deionized/distilled H_2O were added to each vial. Vials were placed on a wrist shaker for 15 min for extraction. One mL of the extract was taken from each vial and diluted with 4 mL deionized/distilled H_2O . Concentrations of nitrate (NO_3^-), a product of NO_2^- oxidation by O_3 , were measured with Dionex 4000I ion exchange chromatograph. Amount of NO_3^- formed on each pad was calculated and expressed as $\mu g NO_3^-/filter$. Ozone exposures were presented as an accumulative dose (concentration in ppb multiplied by time of exposure in hours).

Results and Discussion

Throughout the experiment O_3 concentrations determined with passive samplers and the UV absorption monitor were highly correlated ($R^2=0.9949$) (Figure 1). This linear relationship held up to a dose of 52,500 ppb $O_3 \times h$, indicating that the Ogawa passive samplers can reliably monitor O_3 for at least 477 hours at 110 ppb. This value is substantially higher than the upper detectable range specified by the manufacturer (<168 h at 110 ppb) (<http://www.ogawausa.com/faq.htm>). That means that at least ~ 3-times longer periods of passive sampler exposure could be applied. Further tests are needed to determine what is the upper limit for what O_3 measurement, i.e. at what dose a linear relationship between the O_3 dose and amount of NO_3^- formed on sampler pads ceases.

The samplers showed very high precision of measurements - on the average the relative standard deviation (standard deviation/mean value) was 4.8%, with a range of 1.2-22.0%. Our findings show that much longer exposure periods can be applied for monitoring ambient concentrations of the pollutant with the Ogawa passive samplers. In our studies, typically 2-week long exposure periods have been used even in highly polluted areas of Southern California mountains (Alonso et al., 2002; Bytnerowicz et al., 2002, a, b). In less polluted areas, even longer periods of exposures could be used assuming that average 2-week long averages rarely exceed 90 ppb (Frączek et al., 2003). Extending sampler exposure times could reduce the costs of O_3 monitoring over long time periods.

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Ogawa O₃ sampler calibration

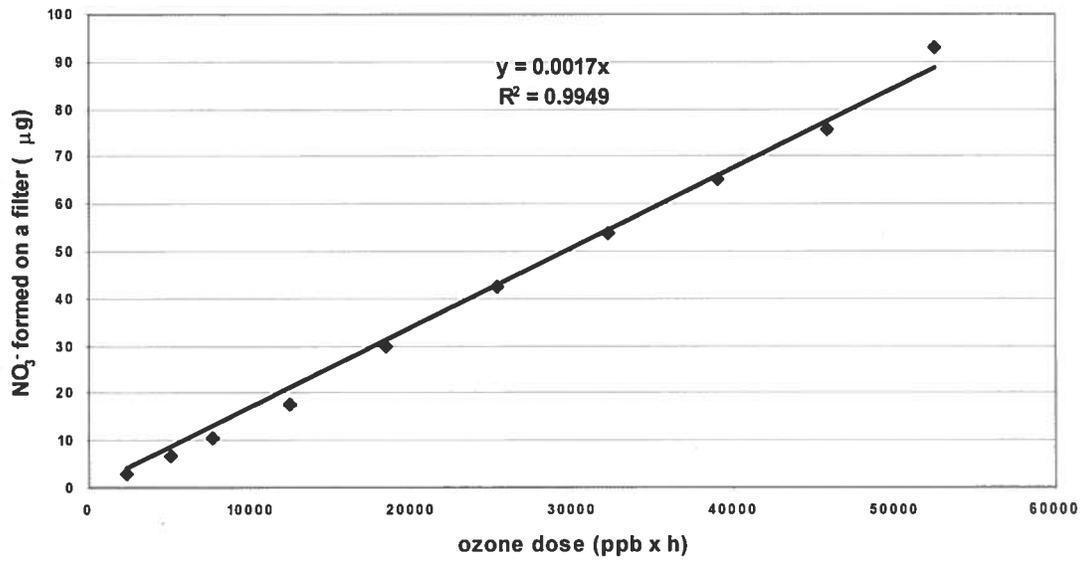


Figure 1. Relationship between dose of ozone measured with UV absorption active monitor and amount of nitrate formed on the Ogawa passive sampler collection pad.