

# Decay Kinetics of Toluene Phytoremediation Stimulation

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**Abstract.** *Begonia maculata*, *Ardisia crenata*, and *Ardisia japonica* plants exposed to 3.5 ppm toluene in air for 12 h displayed a pronounced stimulation (358%, 318%, and 252%, respectively) in subsequent toluene removal potential. The duration of the stimulation effect, monitored over 3 weeks, was short-lived decaying to prestimulation levels within 1 to 7 days depending on species. Elevated phytoremediation rate was dependent on the continued presence of toluene. The rapid rate of increase in phytoremediation and subsequent decay points toward a response mediated by changes in gene expression by the plant, microorganisms within the media, or both rather than an alteration in microbe population. A better understanding of the stimulation response may facilitate the use of plants for indoor air remediation in homes and offices.

Indoor plants have the ability to remove various volatile organic compounds (VOCs) (Table 1) and may be useful for remediating the air in homes and offices, reducing the potential deleterious health effects on persons exposed. The phytoremediation effect is the result of both the plant and associated microorganisms in the media (Chun et al., 2010; Orwell et al., 2004; Son et al., 2000; Wolverton, 1986; Wolverton and Wolverton, 1993; Wood et al., 2002), the latter being the primary contributor to VOC removal during the night (Kim et al., 2008). Removal efficiency is known to vary widely among plant species, the VOC in question, and other factors (Kays, 2011).

The U.S. Environmental Protection Agency (EPA) reported detection of more than 900 VOCs in the air of public buildings (EPA, 1989) and in a Finnish study (Kostiainen, 1995), over 200 VOCs were identified in each of 26 homes. Toluene is a highly toxic VOC commonly found as a component of indoor air, the presence of which can represent a serious health hazard. It is readily absorbed through the respiratory tract and to a lesser extent through the skin (EPA, 1990). Exposure to high levels is known to affect the kidneys, nervous system, liver, brain, and heart. Short-term exposure of humans to toluene (100 ppm v/v or greater) has elicited central nervous system effects such as fatigue, confusion, poor coordination, impairment of reaction time, perception, and motor control and function (NTP, 2000) in addition

to poor performance on cognitive tests and eye and upper respiratory tract irritation (ATSDR, 1989).

We recently demonstrated that the removal efficiency of plants for toluene increased rapidly and markedly with their exposure to the

gas (1.3 ppm for 18 h) (Kim et al., 2011). Of the 28 crops tested, 27 displayed an increase in toluene removal efficiency after the initial exposure with the greatest increase occurring after the first exposure. The increase in efficiency between the first and third exposure ranged from 378  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  leaf area in *Pinus densiflora* Siebold & Zacc. to -16.6 in *Salvia elegans* Vahl (mean for all crops, 156  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ) with a maximum increase of over 600%.

Increasing the efficiency of toluene removal in particular and VOCs in general from indoor air is highly advantageous and could facilitate developing a horticultural solution to a serious health problem. Because a better understanding of the mechanism(s) involved may improve use of the response for practical applications, we determined the duration of the toluene stimulation effect on phytoremediation efficiency.

## Materials and Methods

*Plant materials.* *Begonia maculata* Raddi, a herbaceous foliage plant, and *Ardisia crenata* Sims. and *Ardisia japonica* (Thumb.) Blume, woody foliage plants, were obtained from a commercial market. The plants were transplanted into pots containing a uniform growing medium comprised of Mix #4 (Sun Gro Horticulture, Bellevue, WA), bark-humus (Biocom. Co., Seoul, Korea), and sand at 5:1:1, v/v/v. Mix #4 contained Canadian sphagnum peatmoss (55% to 65% by volume),

Table 1. Volatile organic compounds that have been shown to be removed from air by plants.

Volatile	Source
Acetone	Oyabu et al., 2003; Tani and Hewitt, 2009
Benzaldehyde	Tani and Hewitt, 2009
Benzene	Cornejo et al., 1999; Liu et al., 2007; Orwell et al., 2004; Tarran et al., 2007; Wolverton, 1986; Yang et al., 2009; Yoo et al., 2006
<i>iso</i> -Butyraldehyde	Tani and Hewitt, 2009
<i>n</i> -Butyraldehyde	Tani and Hewitt, 2009
Crotonaldehyde	Tani and Hewitt, 2009
Diethyl ketone	Tani and Hewitt, 2009
Formaldehyde	Aydongan and Montoya, 2011; Chen et al., 2010; Kim et al., 2008, 2010; Oyabu et al., 2003; Sawada and Oyabu, 2008; Son et al., 2000; Wolverton, 1986; Wolverton and Wolverton, 1984; Xu et al., 2011
Methacrolein	Tani and Hewitt, 2009
Methyl ethyl ketone	Tani and Hewitt, 2009
Methyl isobutyl ketone	Tani and Hewitt, 2009
Methyl <i>iso</i> -propyl ketone	Tani and Hewitt, 2009
Methyl <i>n</i> -propyl ketone	Tani and Hewitt, 2009
Octane	Yang et al., 2009
Pentane	Cornejo et al., 1999
$\alpha$ -Pinene	Yang et al., 2009
Propionaldehyde	Tani and Hewitt, 2009
Toluene	Cornejo et al., 1999; Kim et al., 2011; Orwell et al., 2006; Sawada and Oyabu, 2008; Yang et al., 2009; Yoo et al., 2006
Trichloroethylene	Wolverton, 1986; Yang et al., 2009
Xylene	Cornejo et al., 1999; Orwell et al., 2004; Sawada and Oyabu, 2008; Wolverton and Wolverton, 1993

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perlite, dolomitic lime, gypsum, and a wetting agent. The plants were grown in a greenhouse for greater than 1 month after transplanting.

The plants were watered every 3 d with the excess water allowed to drain. All plants were watered the day before the gas treatments. Five pots (19-cm diameter with media volume of 2.2 L), each containing one or more plants (subsequently referred to as a plant), were placed in a chamber with a light intensity of  $60 \pm 2 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  using fluorescent lights and a 12-h photoperiod.

Three replicates (chambers) of each species were tested. Chambers without plants were used to determine toluene losses not resulting from the plants (e.g., leakage, adsorption, chemical reactions). Plant height was measured and leaf area determined using a LI-3100 leaf area meter (LI-COR Inc., Lincoln, NE) at the end of the experiment.

**Treatment system.** The treatment system consisted of controlled-environment rooms containing the test chambers and a gas generator. The rooms controlled the temperature, light intensity, and relative humidity. The test chambers, as described by Kim et al. (2011), were  $1.0 \text{ m}^3$  (90 cm wide  $\times$  90 cm long  $\times$  123 cm high) and impervious to VOCs. Interior air was circulated ( $6 \text{ L}\cdot\text{min}^{-1}$ ) and tested for toluene concentration at three locations, 12, 70, and 98 cm above the bottom of the chamber.

**Gas exposure and measurement.** Toluene gas (1.2 L) was introduced into each test chamber with the plants present, as previously described (Kim et al., 2011), and allowed to equilibrate within the chamber for 15 min. The internal concentration was determined and corrected to 3.5 ppm ( $13,181 \mu\text{g}\cdot\text{m}^{-3}$ ) for the stimulation treatment. The plants remained in the stimulation treatment for 12 h and then were moved to fresh air for 12 h. After the stimulation treatment, the subsequent toluene removal rate by the plants was determined at 0, 1, 2, and 3 weeks after stimulation. Each test date included three replications of five individual plants for a total of 75 plants plus controls (i.e., plants that were not exposed to the toluene stimulation treatment) for each species. Time 0 was after 12 h in fresh air after the toluene stimulation treatment ended. The plants were exposed a 1.3 ppm ( $4896 \mu\text{g}\cdot\text{m}^{-3}$ ) and the rate of toluene removal measured within the chambers after 6 and 12 h as previously described (Kim et al., 2011). Changes in toluene concentration within the chambers were expressed as cumulative removal ( $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{m}^{-2}$  leaf area) and as removal rate ( $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  leaf area). *B. maculata* and *A. japonica* were also tested at 0, 1, 3, 5, and 7 d after exposure. Chambers devoid of plants were treated similarly to determine gas losses resulting from chamber effects.

**Toluene quantification.** Air samples were collected at the appropriate time intervals using a quartz cold trap [120 mm long, 2.9 mm o.d., 1.0 mm i.d. (inlet), 2.0 mm i.d. (outlet); Markes International Ltd., Llantrisant,

U.K.] connected to each chamber with the air collected for 5 min at  $5 \text{ mL}\cdot\text{min}^{-1}$ . An automated thermal desorption system with Air Server autosampler (UNITY; Markes International Ltd.) was connected to the injection port of the gas chromatograph–mass spectrometry (TRACE DSQ; Thermo Electron Co., Waltham, MA). The desorbed sample was cryofocused at  $5 \text{ }^\circ\text{C}$  for 5 min on the first few centimeters of the column, desorbed at  $280 \text{ }^\circ\text{C}$ , and separated using a ZB-624 capillary column (30-m length  $\times$  0.25-mm i.d., 1.40- $\mu\text{m}$  film thickness of 6% cyanopropylphenyl, 94% dimethylpolysiloxane; Phenomenex, Torrance, CA). The injection port temperature was  $180 \text{ }^\circ\text{C}$  with a split

ratio of 29:1. Helium was used as the carrier gas at a flow rate of  $1.0 \text{ mL}\cdot\text{min}^{-1}$ . The column temperature was held at  $45 \text{ }^\circ\text{C}$  for 1 min and increased at a rate of  $15 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $100 \text{ }^\circ\text{C}$  and held for 1 min and then increased at a rate of  $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $135 \text{ }^\circ\text{C}$ .

**Data analysis.** Gas concentrations were expressed as  $\mu\text{g}\cdot\text{m}^{-3}$  with the data normalized to  $24 \pm 1 \text{ }^\circ\text{C}$  and 100 kPa (Hines et al., 1993). Data were expressed as the average of three replicates. The accumulated removal of toluene per unit leaf area [Eq. 1] and the removal efficiency per unit leaf area and time [Eq. 2] were calculated (Kim et al., 2008, 2011) as:

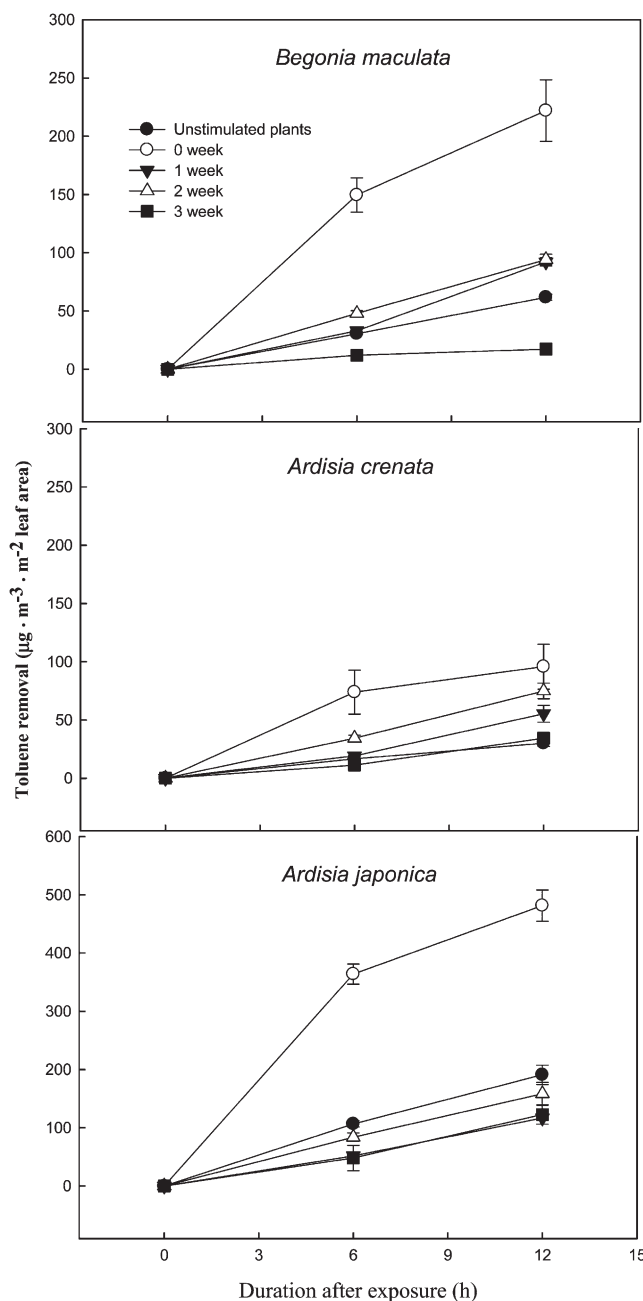


Fig. 1. Accumulated removal of toluene (1.3 ppm in air) by potted plants as affected by the length of time after the initial toluene stimulation treatment. Unstimulated plants were not exposed to the stimulation treatment; 0 time indicates assessment of toluene removal rate 12 h after the stimulation treatment.

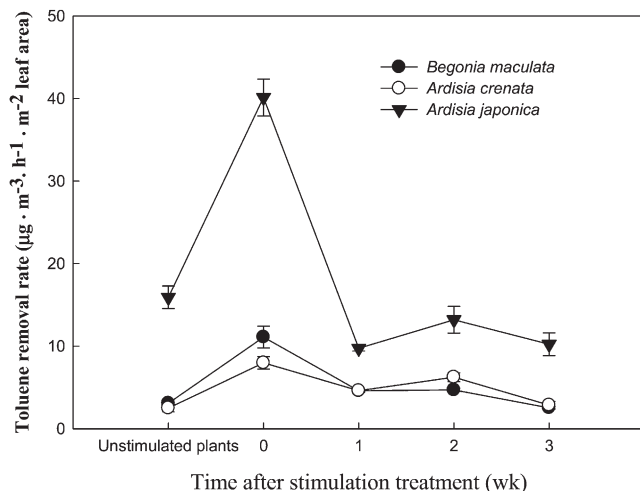


Fig. 2. Changes in the subsequent toluene (1.3 ppm in air) removal rate by potted plants as affected by the length of time (0 to 3 weeks) after the initial toluene stimulation treatment. Unstimulated plants were not exposed to the stimulation treatment; 0 time indicates assessment of toluene removal rate 12 h after the stimulation treatment.

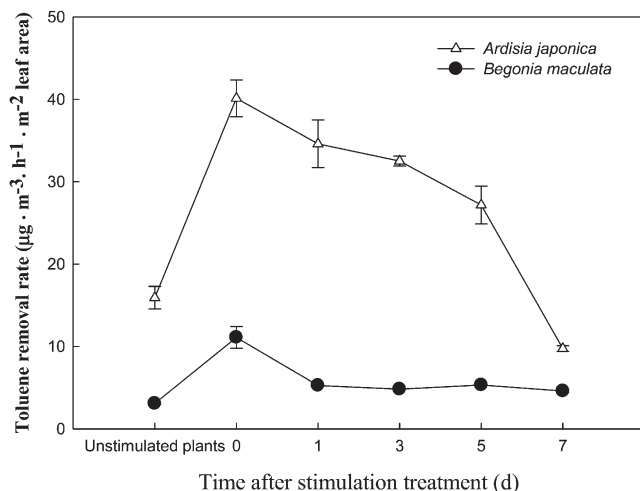


Fig. 3. Changes in toluene (1.3 ppm in air) removal rate by potted plants as affected by the length of time (0 to 7 d) after initial toluene stimulation pretreatment. Unstimulated plants were not exposed to the stimulation treatment; 0 time indicates assessment of toluene removal rate 12 h after the stimulation treatment.

(a) Accumulated removal =

$$\frac{[(P_i - (C_i - C)) - P]}{(F \times CV)/L} \quad [1]$$

(b) Removal efficiency =

$$\frac{[(P_i - (C_i - C)) - P]}{(L \times T)} \quad [2]$$

where P is the gas concentration measured in a chamber with plants ( $\mu\text{L}\cdot\text{L}^{-1}$ );  $P_i$  the initial gas concentration measured in a chamber with plants ( $\mu\text{L}\cdot\text{L}^{-1}$ ); C the gas concentration measured in a chamber without plants ( $\mu\text{L}\cdot\text{L}^{-1}$ );  $C_i$  the initial gas concentration measured in a chamber without plants ( $\mu\text{L}\cdot\text{L}^{-1}$ ); F the toluene conversion factor for volume ( $\mu\text{L}\cdot\text{L}^{-1}$ ) to mass ( $\text{mg}\cdot\text{m}^{-3}$ ); CV the volume of the chamber ( $\text{m}^3$ ); L the total leaf area per chamber ( $\text{m}^2$ ); and T the gas exposure time (h).

The loss of toluene ( $C_i - C$ ) not resulting from the plant and media was determined using empty chambers.

### Results and Discussion

The actual toluene removal rate of *B. maculata*, *A. crenata*, and *A. japonica* increased 358%, 318%, and 252%, respectively, after the initial exposure to toluene. When expressed as accumulated removal on a mass per unit leaf area ( $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{m}^{-2}$ ) basis, *B. maculata* and *A. japonica* displayed substantially higher increases in phytoremediation as a result of the initial toluene exposure (stimulation treatment) than *A. crenata*, which had a modest although statistically significant effect (Fig. 1). Each species progressively removed subsequent toluene over the 12-h test period. With the exception of plants that were re-exposed immediately after the initial stimulation exposure (0 time),

there were only small differences by 1, 2, or 3 weeks, indicating that the stimulation of toluene removal declines fairly rapidly, essentially reaching pre-exposure phytoremediation rates by 1 week. Assessing changes in the stimulation of toluene removal efficiency, expressed as  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$  leaf area, the decline in the initial increase in efficiency was striking, essentially reverting back to base levels (unstimulated control plants) within the first week (Fig. 2). The decline was most pronounced in *A. japonica*, which had the highest overall removal rate of the three species.

In subsequent tests in which the decline in the initial increase in toluene removal efficiency was assessed over a 7-d period, the timing of the decline was more precisely illustrated (Fig. 3). The decay in the stimulation response varied depending on the plant species tested. *B. maculata* declined essentially back to the initial prestimulation rate in a single day, whereas *A. japonica* declined progressively over the entire week. The cause of the difference in the rate of loss of the stimulation response between species is not clear. Based on the rapidity of the response, it is highly probable that the stimulation in phytoremediation efficiency with the initial exposure to toluene was the result of changes in gene expression, although whether it was the result of changes in the plant, microorganisms in the media, or both is not known.

From a practical standpoint, the stimulation in phytoremediation requires continual exposure to toluene so preconditioning the plants before sale would at this time appear to be of no apparent value. It is significant, however, that the plants can very rapidly alter their metabolism in response to the chemistry of the surrounding air, greatly increasing their phytoremediation effectiveness. In addition to toluene, a stimulation in phytoremediation efficiency has been shown for benzene (Orwell et al., 2004) and formaldehyde (Kil et al., 2008), the latter being structurally very dissimilar from benzene and toluene.

It is evident that in closed systems, certain plant species can effectively remove a cross-section of VOCs; however, how effectively this translates to real-world situations in which there is a continual flux of VOCs being released into and escaping from the air in homes and offices remains to be seen. Maximizing the VOC removal efficiency of plants will help to expand the range of situations in which plants can be effectively used.

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