



Dry Deposition Velocities of Trace Metals in Saraburi, Thailand

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Abstract

Dry deposition is defined as the deposition to land or water of particulate matter. Atmospheric deposition is a major process that removes pollutants from the atmosphere and an important source of nutrients and contaminants for ecosystems. Daily dry deposition flux and Total Suspended Particulates (TSPs) in the atmosphere were measured seasonally at 4 locations in Saraburi, Thailand in 2018. The TSPs were collected using traditional Hi-Volume Air Sampler. Deposition fluxes were collected using dry deposition plates as introduced by Air Quality Laboratory, Illinois Institute of Technology, IL, U.S.A. Particulate deposited on the deposition plates and the filters from the Hi-Volume Air Sampler were analyzed for 16 trace metals using Digestion, Inductively Coupled Plasma Method. Dry deposition velocities (deposition flux/atmospheric concentration) for trace metals including Pb, Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Ni, Sb, Se, Sn, Tl, V and Ti were calculated. The results based on 2018 observations found that dry deposition plays a significant role in trace metals deposition in Saraburi, Thailand. The dry deposition velocities of 16 trace metals are 0.038, 0.042, 0.0022, 0.0018, 0.0089, 0.0097, 0.0021, 0.000136, 0.0278, 0.008, 0.0005, 0.000085, 0.000044, 0.763, 0.00153 and 0.0434 respectively

Keywords : Dry Deposition Velocity; Deposition Flux; Trace Metals

Introduction

Trace metals are found typically compositions in the ambient aerosol. They are also an important contributor to dry deposition. Dry deposition has been recognized as a source of contaminants to water bodies [1, 2]. Direct measurements of dry deposition are not commonly done due to high cost and technical difficulties, so, indirect estimation for dry deposition is commonly used [3]. The dry deposition flux of these trace metals can be calculated indirectly by measuring the trace metals concentrations in the atmosphere and multiply with dry deposition velocity of each trace metal [4-6]. The concentrations of the trace metals at any locations may be estimated by using air quality modelling. If the location specific dry deposition velocities of these trace metals are provided, the dry deposition fluxes of the trace metals may be estimated. The impacts of the removing process of these trace metals from the atmosphere to the ground may be evaluated.

Several studies have been conducted to measure dry deposition directly [7-9]. There were several studies to assess the deposition of atmospheric pollutants to monuments, statues and buildings [10]. Atmospheric deposition for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [11] and metals [9, 12] were studied.

Methodology

Dry Deposition Velocity Model

Aerosol particles will deposit on a surface due to the action of the turbulent air motion of the carrying stream. The turbulent deposition velocity can be significantly greater than the deposition velocity due to effects of

gravity, Brownian diffusion, electrical charge, diffusiophoresis and thermophoresis.

The Sehmel-Hodgson model [13] which is used to predict the deposition velocity is a three-box mass transfer model that uses mass transfer resistances to describe deposition velocity. The INT is a resistance integral involving dimensionless eddy and Brownian diffusivity between the concentration reference height and the deposition surface.

$$V_d = \frac{V_t}{1 - \exp\left(-\frac{V_t}{u^*} \text{INT}\right)} \quad (1)$$

Where V_d is the dry deposition velocity, V_t is the particle terminal settling velocity, u^* is the friction velocity, and INT the resistance integral involving dimensionless eddy and Brownian diffusivity between the concentration reference height and the deposition surface. The integral, INT, can be subdivided into component as follows:

$$\begin{aligned} \text{INT} &= \int_{z^+ \text{ at } C_z}^{z^+} \frac{dz^+}{\frac{\epsilon}{v} + \frac{D}{v}} = \text{INT1} + \text{INT2} + \text{INT3} \\ &= \int_{z^+ \text{ at } C_z}^{z^+ (1-2)} \frac{dz^+}{\frac{\epsilon}{v} + \frac{D}{v}} + \int_{z^+ (1-2)}^{z^+ (2-3)} \frac{dz^+}{\frac{\epsilon}{v} + \frac{D}{v}} \end{aligned} \quad (2)$$

In which, ϵ is Eddy diffusivity, D is Brownian diffusivity, ν is the kinematic viscosity of air, $z^+ = zu^*/\nu$ is the dimensionless distance above the surface. The integration limits are (1) particle concentration, C_z , at reference height, z , and (2) particle concentration zero at the dimensionless particle radius, r^+ , from the deposition surface. Surface integral resistance, INT, was evaluated with the least square techniques of Sehmel-Hodgson as follow:

$$\begin{aligned} \text{INT3} &= -\exp \left\{ 378.051 + 16.498 \ln(Sc) + \right. \\ &\quad \left[\ln(\tau^+) + 0.3226 \ln\left(\frac{d}{z_0}\right) - 0.3385 \ln\left(\frac{\nu}{z_0}\right) \right] - \\ &\quad \left. 12.804 \ln(d) \right\} \end{aligned} \quad (3)$$

Where Sc is Schmidt number, τ^+ is dimensionless relaxation time, d is particle diameter, and z_0 is surface roughness height.

In order to calculate the flux of atmospheric particles, the following equation is applied [14]:

$$F = V_d C \quad (4)$$

Where

F = Flux, $\mu\text{g}/\text{m}^2/\text{s}$

C = Atmospheric concentration, $\mu\text{g}/\text{m}^3$

V_d = dry deposition velocity, m/s

Experiments

To evaluate the dry deposition velocities of various chemical species in the study area, Hi-Volume air samplers were used to collect for the Total Suspended Particulates (TSPs) at 4 sampling locations in the study area. At the same location and time duration, deposition fluxes were collected using dry deposition plates as introduced by Air Quality Laboratory, Illinois Institute of Technology, IL, U.S.A. Amount of 16 trace metals including Pb, Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Ni, Sb, Se, Sn, Tl, V and Ti were analyzed both in the TSPs and also in the corresponded deposition fluxes on the dry deposition plates. Sehmel and Hodgson (1978) model was applied to calculate for the deposition velocity of each trace metal [13].

Study area

The study area was in Tambol Tubkwang, Amphur Kangkhoy which is located in the north-eastern part of Saraburi Province, central Thailand. In the study area, there are located of many kinds of industry, such as, cement plants, waste-heat power plants and refuse-derived fuel (RDF) power plants. The 4 sampling sites in the study area were: 1) Bhan Kao Mai Kwaen 2) Bhan Sub Bon 3) Wad Hin Lub 4) Bhan Sub Bon School. The study area and the 4 sampling locations are as shown in Figure 1.

Sampling Instruments

1. High Volume Air Sampler.

High volume air sampler is the reference method to measure TSP in the atmosphere according to Pollution Control Department, Ministry of Natural Resources and Environment, Thailand. The method is also the U.S. EPA's Federal Reference Method for sampling total suspended particulates (TSP) in ambient air as indicated in 40 CFR Part 50, Appendix B - Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). High volume air sampler collects suspended particulates on 8 x 10-inch (20.3 x 25.4cm) filter. The sampling flow rate is 0.57 to 1.71 cubic meters per minute (CMM). According to rather high flow rate, large amount of particle ranging from 0.1 to 1 gram are collected on the filter over a typical 24-hour sampling period. This amount of particle is enough to facilitate gravimetric and chemical analysis for the chemical composition in the sample.

2. Dry Deposition Plate.

The atmospheric dry deposition fluxes were collected on the top of smooth plates which can be used to directly assess deposited material. The dry deposition plate used in this study (Noll et al, 1988) is similar to those used in wind tunnel studies (Mc Cready, 1986). The main plate was made of poly vinyl chloride (PVC) which is 16 cm long, 7.6 cm wide and thickness was 5.5 cm with thick a sharp leading edge (less than 10 degrees angle). The leading edge of the main plate is always faced to the wind direction according to a wind vane made of Poly-acrylic Plastic or plexiglass (Figure 2). Mylar strips with dimensions of 7.6 cm long and 2.5 cm wide were used as collection surfaces on the top of the deposition plate. Each strip is coated with approximately 8 mg of grease on the exposed area to collect deposit particles.

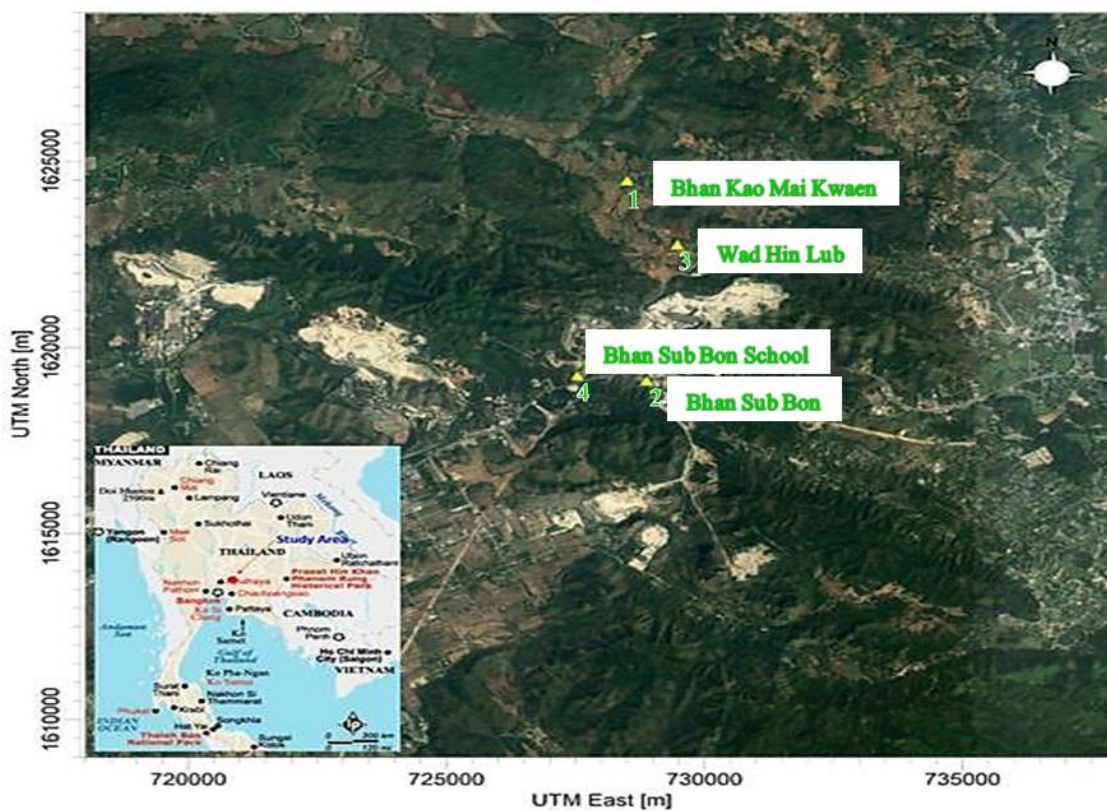


Figure 1 Study area

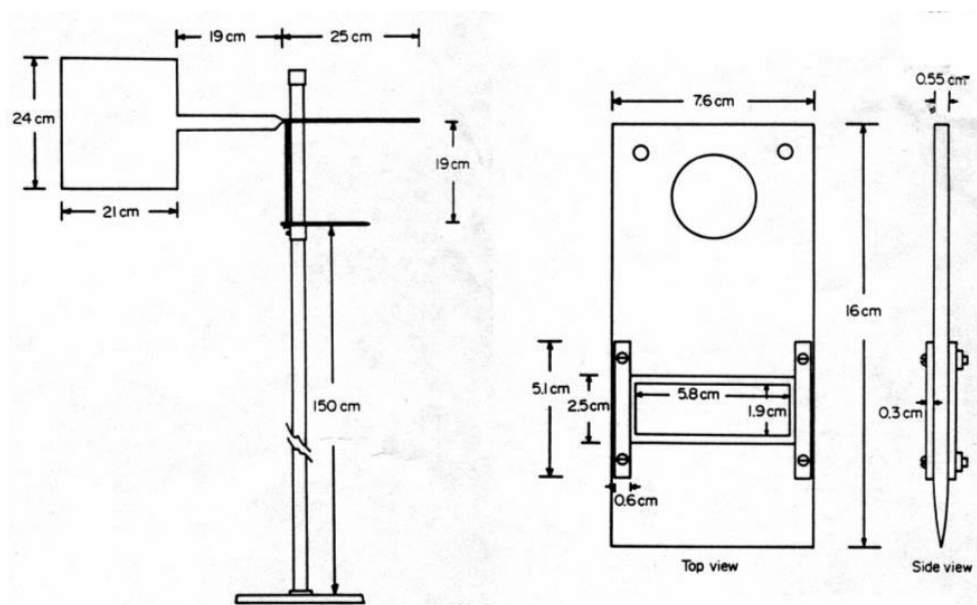


Figure 2 Dry deposition plate

The atmospheric dry deposition fluxes were calculated using the following equation:

$$F = \frac{M \times (60 \times 24)}{A \times t} \quad (5)$$

Where

F = Dry deposition flux ($\text{mg}/\text{m}^2 \cdot \text{d}$)

M = Chemical mass collected on the greased strip (mg)

A = Exposed collection surface ($1.8 \times 5.7 \text{ cm}^2$)

t = Exposure time (min)

Sampling and analysis

TSPs and dry deposition fluxes were collected for 24-hr sampling for 3 consecutive days 3 times in 2018 to represent the data in the summer (Between 26-29 April 2018), rainy season (between 16-19 September 2018), and winter (between 11-18 November 2018) at 4 locations which were 1) Bhan Kao Mai Kwaen 2) Bhan Sub Bon 3) Wad Hin Lub 4) Bhan Sub Bon School.

All Mylar strips and filters from High Volume Air Sampler were analyzed for 16 trace metals using Digestion, Inductively Coupled Plasma Method. The amounts of the 16 trace metals in TSPs were determined as the concentrations of the metals in the atmosphere in the unit of $\mu\text{g}/\text{m}^3$. The amount of the 16 trace metals in the dry deposition fluxes were determined for the deposition fluxed for the trace metal in the unit of $\mu\text{g}/\text{m}^2 \cdot \text{s}$.

Result

The concentration of each metal in the atmosphere ($\mu\text{g}/\text{m}^3$) was plotted with the dry deposition flux ($\mu\text{g}/\text{m}^2 \cdot \text{s}$) of the corresponded trace metal. Least squares best fit straight-line method was applied. The slope of the straight-line was determined for the dry deposition velocity of the trace element. The plots for the dry deposition velocities of 16 trace metals are as shown in Figure 3 to Figure 18 respectively. The dry deposition velocities of the 16 trace metals result from this study are as shown in Table 1.

In addition, when compared to the results of the study conducted by the Environmental Science Research Laboratory, N.E. Minnesota, US.EPA [15], most of the deposition velocities of trace metals found in the study area were greater (Table 1). This indicates the possibility of faster removal of trace metals from the atmosphere.

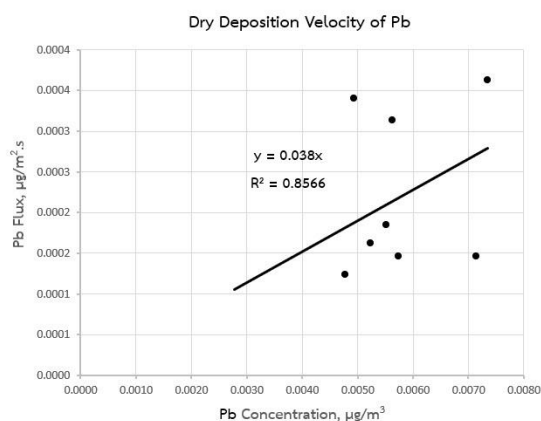


Figure 3 Plotting for Dry Deposition Velocity of Pb

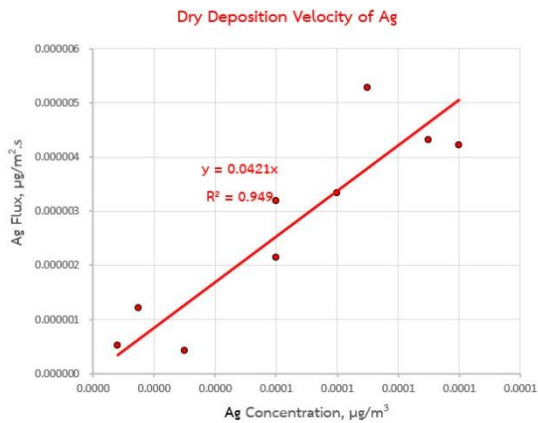


Figure 4 Plotting for Dry Deposition Velocity of Ag

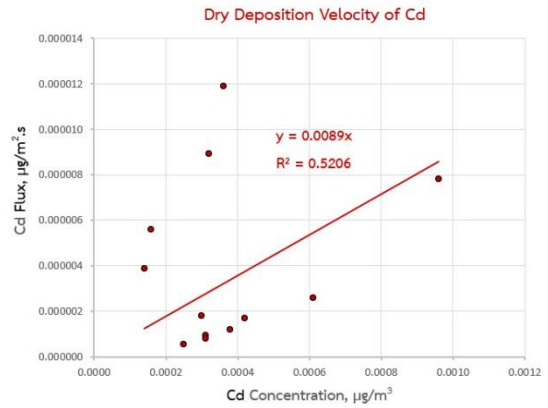


Figure 7 Plotting for Dry Deposition Velocity of Cd

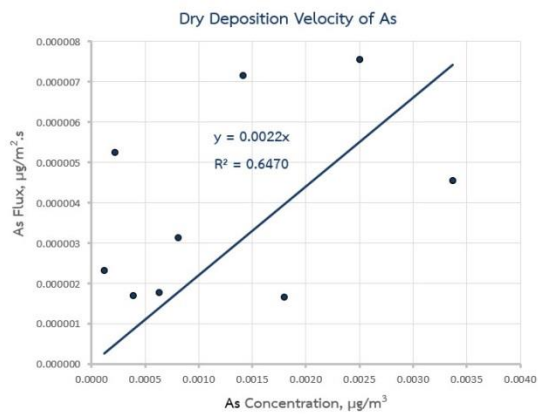


Figure 5 Plotting for Dry Deposition Velocity of As

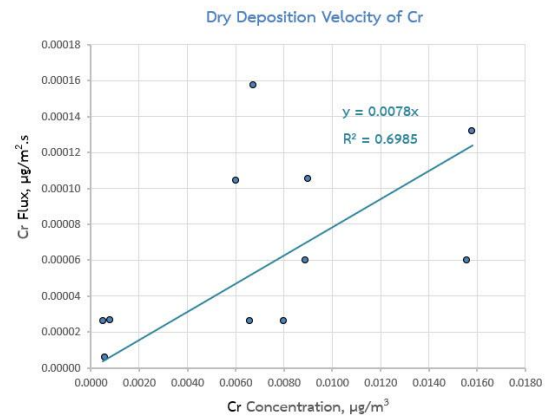


Figure 8 Plotting for Dry Deposition Velocity of Cr

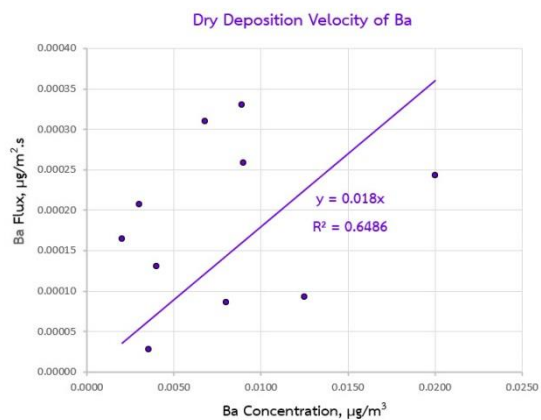


Figure 6 Plotting for Dry Deposition Velocity of Ba

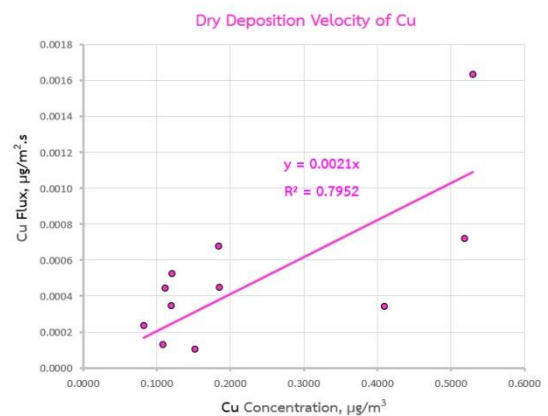


Figure 9 Plotting for Dry Deposition Velocity of Cu

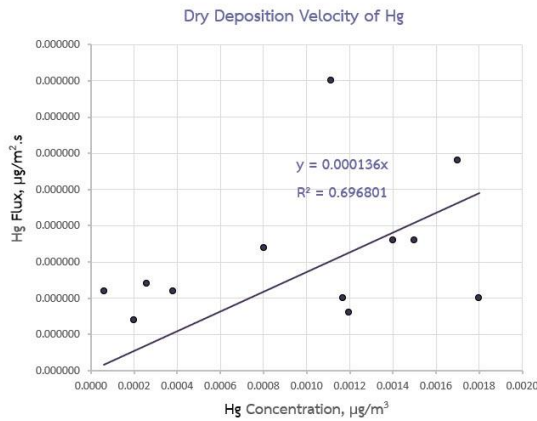


Figure 10 Plotting for Dry Deposition Velocity of Hg

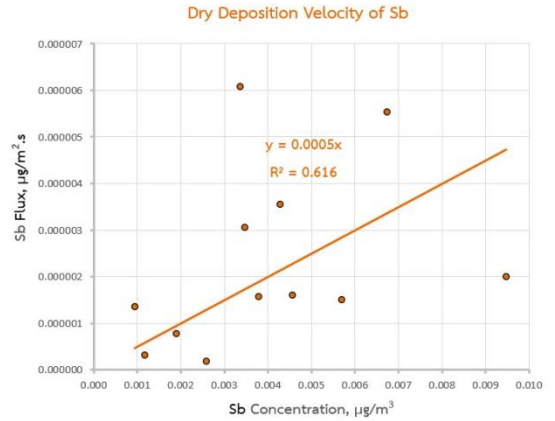


Figure 13 Plotting for Dry Deposition Velocity of Sb

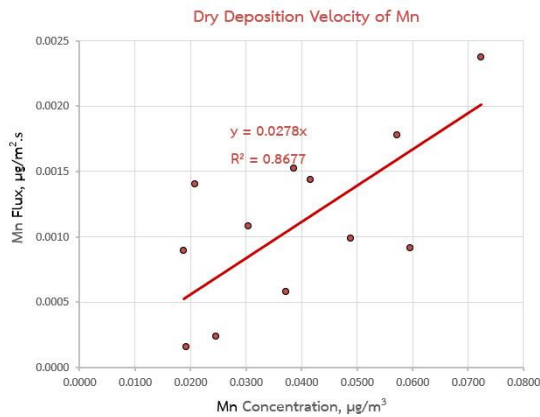


Figure 11 Plotting for Dry Deposition Velocity of Mn

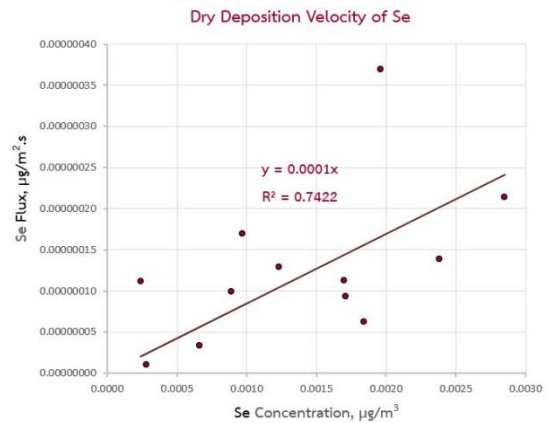


Figure 14 Plotting for Dry Deposition Velocity of Se

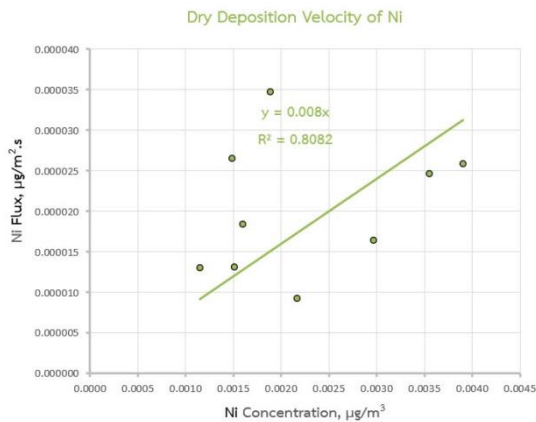


Figure 12 Plotting for Dry Deposition Velocity of Ni

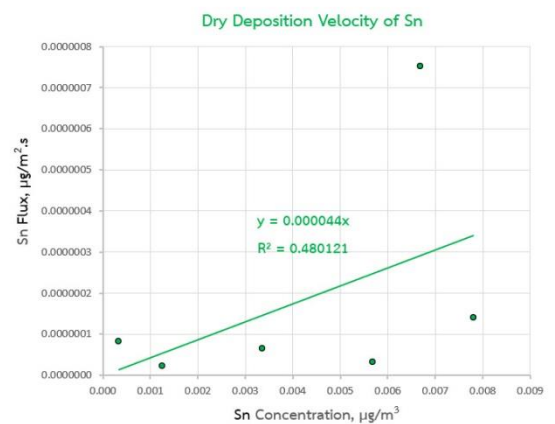


Figure 15 Plotting for Dry Deposition Velocity of Sn

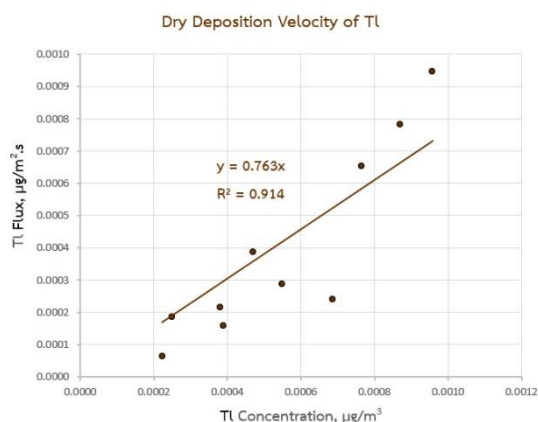


Figure 16 Plotting for Dry Deposition Velocity of TL

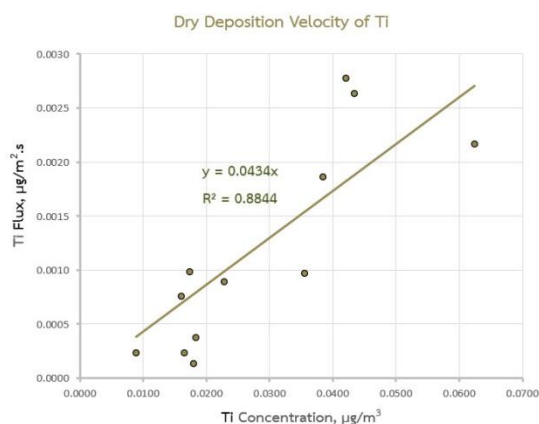


Figure 18 Plotting for Dry Deposition Velocity of TI

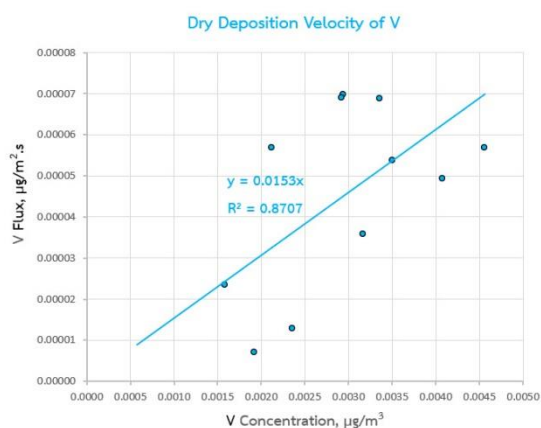


Figure 17 Plotting for Dry Deposition Velocity of V

Table 1 Dry deposition velocities of the 16 trace metals

Trace Metals	Dry Deposition Velocity, cm/s (from this study)	Dry Deposition Velocity, cm/s (N.E. Minnesota, Environmental Science Research Laboratory, US.EPA) [15]
1. Lead (Pb)	0.038	0.017
2. Silver (Ag)	0.042	-
3. Arsenic (As)	0.0022	0.0018
4. Barium (Ba)	0.0018	-
5. Cadmium (Cd)	0.0089	0.0025
6. Chromium (Cr)	0.0097	0.008
7. Copper (Cu)	0.0021	0.009
8. Mercury (Hg)	0.000136	0.000029

Table 1 Dry deposition velocities of the 16 trace metals (cont.)

Trace Metals	Dry Deposition Velocity, cm/s (from this study)	Dry Deposition Velocity, cm/s (N.E. Minnesota, Environmental Science Research Laboratory, US.EPA) [15]
9. Manganese (Mn)	0.0278	0.23
10. Nickel (Ni)	0.008	0.0065
11. Antimony (Sb)	0.0005	0.0004
12. Selenium (Se)	0.000085	0.000075
13. Tin (Sn)	0.000044	-
14. Thallium (Tl)	0.763	0.800
15. Vanadium (V)	0.00153	0.0009
16. Titanium (Ti)	0.0434	-

Conclusions

1. Dry deposition velocities of trace metals can be determined from the relation between dry deposition flux and the concentrations of those metals.

2. From this study, the dry deposition velocities of 16 trace metals, Pb, Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Ni, Sb, Se, Sn, Tl, V and Ti were determined and found in range of 0.000044 - 0.0763 cm/s.

3. Among 16 trace metals, the dry deposition velocity of Thallium (Tl) was found the highest value of 0.763 cm/s.

4. From this study, Tin (Sn) had the smallest dry deposition velocity with the value of 0.000044 cm/s.

5. Comparing with the deposition velocities of trace metal studied by Environmental Science Research Laboratory, N.E. Minnesota, US.EPA (Reference 14), the values found in this study were generally higher than the values indicated in the document, except Copper (Cu) and Thallium (Tl).

6. Considering the deposition velocities of trace metal in Saraburi, Thailand, found by this study, the process of removing of these trace metals from atmosphere to land of the study area may faster than the process occurs in USA.

Acknowledgement

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References

- [1] Davis A.P., Shokouhian M. and Ni S. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44(5): 997-1009.
- [2] Van Metre P.C. and Mahler B.J. 2003. The contribution of particles washed from rooftops to contaminant loading to urban streams. *Chemosphere*, 52(10): 1727-1741.

- [3] Zhang L., Fang G.C., Liu C.K., Huang Y.L., Huang J.H. and Huang C.S. 2012. Dry deposition fluxes and deposition velocities of seven trace metal species at five sites in Central Taiwan—a summary of surrogate surface measurements and a comparison with model estimation. *Atmos. Chem. Phys.*, 12, 3405-3417.
- [4] Holsen T.M. and Noll K.E. 1992. Dry deposition of atmospheric particles: application of current models to ambient data. *Environ. Sci. Technol.*, 26(9): 1807-1814.
- [5] Caffery P.F., Ondov J.M., Zufall M.J. and Davidson, C.I. 1998. Determination of size dependant dry particle deposition velocities with multiple intrinsic tracers. *Environ. Sci. Technol.*, 32(11): 1615-1622.
- [6] Stolzenbach K.D., Lu R., Xiong C., Friedlander S., Turco R., Schiff K. and Tiefenthaler L. 2001. "Measuring and Modeling of Atmospheric Deposition on Santa Monica Bay and the Santa Monica Bay Watershed." Report to the Santa Monica Bay Restoration Project.
- [7] Paode R.D. and Holsen T.M. 1996. Standard operating procedure for preparation, handling and extraction of dry deposition plates: dry deposition of atmospheric particles. Revision 2.
- [8] Tai H.S., Lin J.J. and Noll K.E. 1999. Characterization of atmospheric dry deposited particles at urban and non-urban locations. *Journal of Aerosol Science*, 30(8): 1057-1068.
- [9] Shahin U.M., Yi S.M., Paode R.D. and Holsen T.M. 2000. Long-term elemental dry deposition fluxes measured around lake Michigan with an automated dry deposition sampler. *Environmental Science and Technology*, 34, 1887-1892.
- [10] Dloske D.A. 1995. Deposition of atmospheric pollutants to monuments, statues and buildings. *Science of the Total Environment*, 167, 15-31.
- [11] Simcik M.F., Franz T.P., Zhang H. and Eisenreich S.J. 1998. Gas-particle partitioning of PCBs and PAHs in the Chicago urban and adjacent coastal atmosphere: state of equilibrium. *Environmental Science and Technology*, 32, 251-257.
- [12] Zufall M.J., Davidson C.I., Caffrey P.F. and Ondov J.M. 1998. Airborne concentrations and dry deposition fluxes of particulate species to surrogate surfaces deployed in Southern Lake Michigan. *Environmental Science and Technology*, 32, 1623-1628.
- [13] Sehmel G.A. and Hodgson W.H. 1978. A model for predicting dry deposition of particles and gases to environmental surface, DOE report PNLSA-6721. Pacific Northwest Laboratory, Richland, WA.
- [14] Chamberlain A.C. 1953. Aspects of travel and deposition of aerosol and vapour clouds. Atomic Energy Research Establishment, Report AERE-HP/R-1261.
- [15] Environmental Engineering Program. Precipitation Chemistry and Atmospheric Deposition of Trace Elements in Northeastern Minnesota. Department of Civil and Mineral Engineering, University of Minnesota, Minneapolis, Minnesota.