Airborne trace elements near a petrochemical industrial complex in Thailand assessed by the lichen *Parmotrema tinctorum* (Despr. ex Nyl.) Hale

Chaiwat Boonpeng[1] · **Wetchasart Polyiam**[1] · **Chutima Sriviboon**[2] · **Duangkamon Sangiamdee**[2] · **Santi Watthana**[3] · **Pier Luigi Nimis**[4] · **Kansri Boonpragob**[1]

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Abstract Several trace elements discharged by the petrochemical industry are toxic to humans and the ecosystem. In this study, we assessed airborne trace elements in the vicinity of the Map Ta Phut petrochemical industrial complex in Thailand by transplanting the lichen *Parmotrema tinctorum* to eight industrial, two rural, and one clean air sites between October 2013 and June 2014. After 242 days, the concentrations of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Ti, V, and Zn in lichens at most industrial sites were higher than those at the rural and the control sites; in particular, As, Cu, Mo, Sb, V, and Zn were significantly higher than at the control site ($p < 0.05$). Contamination factors (CFs) indicated that Cd, Cu, Mo, and Sb, which have severe health impacts, heavily contaminated at most industrial sites. Principal component analysis (PCA) showed that most elements were associated with industry, with lesser contributions from traffic and agriculture. Based on the pollution load indexes (PLIs), two industrial sites were highly polluted, five were moderately polluted, and one had a low pollution level, whereas the pollution load at the rural sites was comparable to background levels. This study reinforces the utility of lichens as cost-effective biomonitors of airborne elements, suitable for use in developing countries, where adequate numbers of air monitoring instruments are unavailable due to financial, technical, and policy constraints.

Keywords Biomonitor · Contamination factor · Map Ta Phut · Pollution load index

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✉ Chaiwat Boonpeng
chaiwat_u@hotmail.com

[1] Lichen Research Unit, Department of Biology, Faculty of Science, Ramkhamhaeng University, Hua Mark, Bangkok 10240, Thailand

[2] Department of Chemistry, Faculty of Science, Ramkhamhaeng University, Hua Mark, Bangkok 10240, Thailand

[3] School of Biology, Institute of Science, Suranaree University of Technology, Mueang District, Nakhon Ratchasima 30000, Thailand

[4] Department of Life Sciences, University of Trieste, Via Giorgieri 10, 34127 Trieste, Italy

Introduction

Trace elements emitted by the petrochemical industry can accumulate in human internal organs via inhalation; some of them are carcinogens and/or toxic to the nervous, respiratory, and cardiovascular systems (Kampa and Castanas 2008). The Map Ta Phut industrial park, established in 1989, is the largest petrochemical industrial area in Thailand, with an increasing hazardous health impact on the local population (Jadsri et al. 2006; Kongtip et al. 2013; Singkaew et al. 2013). Previous studies focused on the effects of volatile organic compounds (VOCs) and conventional air pollutants, i.e., CO, NO_2, O_3, PM_{10}, and SO_2 (Jadsri et al. 2006; Kongtip et al. 2013; Singkaew et al. 2013; Tanyanont and Vichit-Vadakan 2012). The spatial and temporal dispersion of benzene, toluene, and xylene were documented by Pimpisut et al. (2005). The accumulation of As, Cd, and Mn in shellfish and their potential toxic effects on human cells were recently reported by Rangkadilok et al. (2015). However, research on airborne trace elements has been largely neglected.

Lichens are widely accepted as a reliable tool in environmental forensics (Purvis et al. 2013). The element content of lichens is directly related to that in the air (Bari et al. 2001) and bulk (wet and dry) atmospheric deposition (Loppi and Paoli 2015; Sloof 1995). The use of lichens has the following advantages over recording instruments: (i) it has a relatively low cost and ease of handling; (ii) it concerns a wide range of air

pollutants; (iii) it allows a large number of monitoring points; and (iv) it reflects the harmful effects of air pollution on living organisms (Garty and Garty-Spitz 2015; Leonardo et al. 2011). In areas where domestic lichens are absent, transplanted lichens can be used (Nannoni et al. 2015; Paoli et al. 2015). Since the 1960s, biomonitoring with lichens has been established in more than 40 countries on every continent, including Greenland and Antarctica (Bajpai et al. 2014; Ferreira et al. 2012; Lucadamo et al. 2016; Kularatne and de Freitas 2013; Odiwe et al. 2014; Søndergaard 2013; Will-Wolf et al. 2015; Zvěřina et al. 2014).

In this study, we tested the hypothesis that an area close to the main Map Ta Phut petrochemical industrial area shows higher trace element concentrations than an area further away from the industry, by using transplants of the lichen *Parmotrema tinctorum* (Despr. ex Nyl.) Hale as biomonitoring tools for airborne trace elements.

Materials and methods

Study area and monitoring sites

Three areas (remote, rural and industrial) were included in the study, encompassing a total of 11 monitoring sites, exposed to different types of anthropogenic activity (Fig. 1).

The Khao Yai National Park (KYNP) is a remote area with relatively clean air. It has a complex terrain, consisting of hills and mountains at elevations ranging from 50 to 1351 m, covered by a dense canopy of tropical vegetation. The park, one of the most popular tourist attractions in Thailand, experiences dense traffic during the high tourist season (ca. November to February) but normally low traffic during the rest of the year. One monitoring site was selected as the control (C) (Table 1), where weather data for the study period were available (Table 2).

The area near Wang Chan District, Rayong Province (Fig. 1), is an agricultural zone, hosting a large Para rubber (*Hevea brasiliensis*) plantation interspersed among small villages. Two monitoring sites, rural-1 (R-1) and rural-2 (R-2), located approximately 55 and 35 km northeast of the Map Ta Phut petrochemical industry, were selected (Table 1). These rural sites were located downwind of the industrial area and were used for assessing the extent of air pollution dispersion from the industry. The amount of rainfall during the study period is shown in Table 2.

The industrial area at Map Ta Phut is ca. 193 km south of the control site. The town of Map Ta Phut, in Rayong Province on the east coast of Thailand (Fig. 1), covers an area of 166 km^2 with 62,289 inhabitants (August 2015). Prior to 1989, the town was primarily inhabited by farming and fishing communities. Thereafter, four petrochemical industrial parks, Map Ta Phut Industrial Estate (MTPIE), Map Ta Phut Industrial Port (MTPIP), Hemaraj Eastern Industrial Estate (HEIE), and RIL Industrial Estate (RILIE), were established to utilize petroleum from the Gulf of Thailand and to promote economic development (Jadsri et al. 2006; Langkulsen et al. 2011; Pimpisut et al. 2005). This area currently houses over 120 factories operating in six industrial estates, including petrochemical and chemical plants (>60%), oil refineries, steel

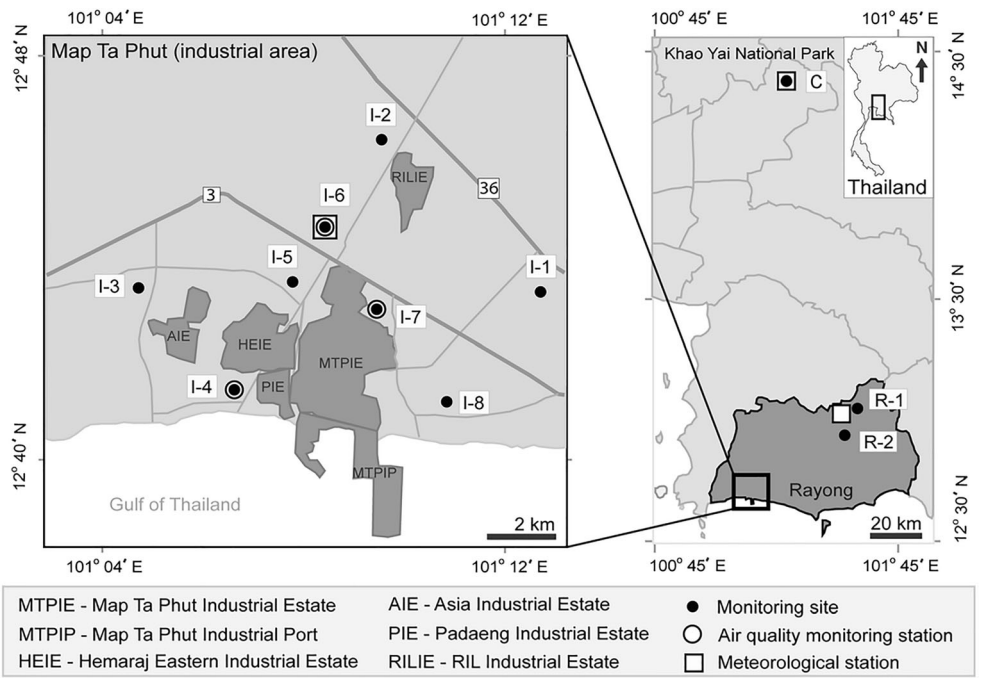

Fig. 1 The study area with 11 monitoring sites in remote (*C*), rural (*R*), and industrial (*I*) areas, including three air quality monitoring stations and three meteorological stations

Table 1 Monitoring sites

Monitoring site	Location	Latitude–Longitude	Elevation (m asl)	Distance (km)[a]
Control (C)	Khao Yai National Park	14°25′12″ N–101°22′23″ E	760	193
Rural-1 (R-1)	Prasae Reservoir Office	12°58′39″ N–101°33′23″ E	53	55
Rural-2 (R-2)	Thep Nimit Temple	12°51′23″ N–101°25′09″ E	132	35
Industrial-1 (I-1)	Khao Phai School (abandoned school)	12°43′12″ N–101°12′17″ E	24	7.7
Industrial-2 (I-2)	Princess Maha Chakri Sirindhon Herbal Garden	12°45′52″ N–101°09′46″ E	50	8.4
Industrial-3 (I-3)[b]	Prachummitbamrung Temple	12°43′19″ N–101°05′03″ E	46	7.0
Industrial-4 (I-4)	Bannongfab School	12°41′08″ N–101°06′58″ E	15	2.7
Industrial-5 (I-5)	Mapchalood Temple	12°43′21″ N–101°07′36″ E	31	3.8
Industrial-6 (I-6)	Rayong Field Crop Research Center	12°44′06″ N–101°08′08″ E	49	4.9
Industrial-7 (I-7)	Sophonwanaram Temple	12°42′32″ N–101°09′50″ E	20	3.2
Industrial-8 (I-8)	Khlongnamhu Irrigation Office	12°40′45″ N–101°10′52″ E	8	4.6

[a] Linear distance to the center of main industrial area (12°41′28″ N–101°08′25″ E)

[b] This site is not in the area of the Map Ta Phut municipality according to city planning, but it is only 7 km away from the main industrial area at Map Ta Phut; therefore, it has been included as another industrial site in this study

Table 2 Daily average climatic parameters and PM_{10} concentrations during the study period from the monitoring stations in the industrial, rural, and remote areas

Data	Collection period	Industrial[a] (Map Ta Phut)	Rural[b] (Wang Chan)	Remote[c] (KYNP)
Rainfall (mm)	October 18, 2013–December 8, 2013	150	28	185
	December 9, 2013–January 27, 2014	11	5	0
	January 28, 2014–March 24, 2014	115	5	117
	March 25, 2014–June 16, 2014	275	209	612
Relative humidity (%)	October 18, 2013–December 8, 2013	76		81
	December 9, 2013–January 27, 2014	63		71
	January 28, 2014–March 24, 2014	76		79
	March 25, 2014–June 16, 2014	76		83
Temperature (°C)	October 18, 2013–December 8, 2013	26.7		21.2
	December 9, 2013–January 27, 2014	24.4		17.7
	January 28, 2014–March 24, 2014	27.1		22.2
	March 25, 2014–June 16, 2014	29.8		24.5
Wind direction–speed[d]	October 18, 2013–December 8, 2013	NE-13		
	December 9, 2013–January 27, 2014	NE-16		
	January 28, 2014–March 24, 2014	SW-12		
	March 25, 2014–June 16, 2014	SW-8		
PM_{10} ($\mu g\ m^{-3}$)[e]	October 18, 2013–December 8, 2013	45		
	December 9, 2013–January 27, 2014	89		
	January 28, 2014–March 24, 2014	51		
	March 25, 2014–June 16, 2014	25		

[a] The meteorological station at Huaypong is close to the site I-6 installed by the Thai Meteorological Department (TMD)

[b] The cumulative rainfall recorded at Wang Chan rain station is located between the sites R-1 and R-2, by TMD

[c] The cumulative rainfall measured at Khao Yai National Park (KYNP) rain station by TMD, relative humidity, and temperature were recorded using a CR1000 datalogger (Campbell Scientific Inc., USA), by Lichen Research Unit, Ramkhamhaeng University

[d] The most frequent wind direction, with NE = northeast, SW = southwest; wind speed in kilometers per hour

[e] Mean concentrations of PM_{10} in Map Ta Phut were calculated from the daily average concentrations at the three air quality monitoring stations, operated by the Air Quality and Noise Management Bureau, Pollution Control Department (PCD), Thailand and by Map Ta Phut Industrial Estate Office, Industrial Estate Authority of Thailand (IEAT)

and heavy industries, power plants, and fertilizer factories. In addition, a transport system network along Sukhumvit Road (Thailand Route 3) and Thailand Route 36 is an additional source of atmospheric pollution. Eight monitoring sites (industrial-1 (I-1) to industrial-8 (I-8) were selected in this area based on distance and direction from the main industrial area (Fig. 1, Table 1). Meteorological data and daily average particulate matter <10 μm are shown in Table 2.

Lichen samples and sampling procedures

The epiphytic foliose lichen *P. tinctorum*, a cosmopolitan species (Louwhoff and Elix 2000), was chosen. This lichen has a wide distribution in Thailand and is abundant in the remote area at KYNP, which provided a sufficient supply of material for this study. This species has been recently used as a biomonitor of atmospheric deposition (Dohi et al. 2015; Käffer et al. 2012). Since its growth rate is low (<30 mm/year, Wannalux 2014), collecting the whole thallus is not the way to support the conservation and sustainable utilization of lichen resource. Therefore, only the peripheral parts of the thalli (approximately 2–3 cm from the lobe tips) were picked from their substrate. There are totally 308 thallus fragments, and each fragment of approximately 10 cm^2 was fixed on a frame of polyethylene netting (2 × 2 mm mesh size) using nylon string to avoid element contamination from the bark (Bargagli and Mikhailova 2002).

The transplanted material was placed at the control site for approximately 4 months (June 2013–October 2013) to allow physiological adaptation and homogenization of the samples. Lichen material was randomly collected and analyzed for element contents before exposure. All of the remaining thalli were transferred to the 11 monitoring sites on October 18, 2013. The lichen material was fixed to tree branches with an inclination of approximately 30°–60° approximately 3–4 m above ground to avoid soil contamination. Twenty-eight thalli were exposed at each monitoring site, and six of them were collected on the following dates: December 8, 2013 (52 days), January 27, 2014 (102 days), March 24, 2014 (158 days), and June 16, 2014 (242 days). The lichens experienced the climatic conditions shown in Table 2.

Analysis of element contents

In the laboratory, lichen samples were air-dried in a closed room and then carefully cleaned to remove dirt and debris. Because washing could remove some elements from the lichen surface, unwashed samples were used for elemental analysis. The analytical method followed the procedure by Sangiamdee (2014). Briefly, the lichen material was immersed in liquid nitrogen and subsequently pulverized and homogenized with a ceramic mortar and pestle. It was then separated through a 500-μm sieve plate. Approximately 200 mg of lichen powder were mineralized with 2 ml of conc. HNO_3, in a block digestion system (AIM 600, Aim Lab, Australia), at 150 °C for 150 min. The concentrations of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Ti, V, and Zn were determined using inductively coupled plasma mass spectrometry (ICP–MS, NexION 300Q, PerkinElmer, USA). The results were expressed on a dry weight basis (μg/g dw), and the analytical quality was assessed with the certified reference material BCR-482 (lichen, *Pseudevernia furfuracea*). The recoveries (n = 7) ranged between 95.3% (As) and 99.5% (Cr). Moreover, some samples were spiked by adding known amounts of Co, Mo, Sb, Ti, and V to assess the analytical accuracy because certified reference material was not available (Rusu 2002). Recoveries (n = 7) ranged from 92.3% (Sb) to 100.9% (Mo). The analytical precision, expressed as percent relative standard deviation (%RSD), was less than 6% (n = 7) for all of the analyzed elements. The method detection limits (MDL) were 0.005 μg/g for As, 0.013 μg/g for Cd, 0.01 μg/g for Co, 0.963 μg/g for Cr, 0.345 μg/g for Cu, 0.001 μg/g for Hg, 0.005 μg/g for Mo, 0.129 μg/g for Ni, 0.07 μg/g for Pb, 0.003 μg/g for Sb, 0.059 μg/g for Ti, 0.005 μg/g for V, and 4.545 μg/g for Zn. All elemental analyses were carried out in the laboratory at the Department of Chemistry, Faculty of Science, Ramkhamhaeng University.

Contamination factor and pollution load index

The level of atmospheric contamination of each element at each monitoring site was estimated using a contamination factor (CF) as follows: CF = Cs/Cc, where Cs is the grand average concentration of each element in the transplanted lichens at a monitoring site and Cc is the grand average concentration of the same element in the transplanted lichens at the control site. The CF values used in this study differ slightly from the EC (exposed-to-control) ratio described by Frati et al. (2005), who used the concentrations of elements in pre-exposed lichens as control values. We chose the CF due to the fact that lichens collected in the same unpolluted areas at different times have been reported to show variations in the concentrations of several elements (Corapi et al. 2014; Malaspina et al. 2014). The CF value was categorized into the following four classes: CF < 1.2 = no contamination, 1.2 ≤ CF < 2 = light contamination, 2 ≤ CF < 3 = medium contamination, and CF ≥ 3 = heavy contamination (Boamponsem et al. 2010).

The pollution load index (PLI) originally proposed by Tomlinson et al. (1980) was also used to evaluate the overall air pollution load, as follows: $PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \ldots \times CF_n)^{1/n}$, where CF is a contamination factor and n is number of studied elements. A PLI value less than 0.9 indicates an unpolluted area, a PLI approaching 1 (1 ± 0.1) an air pollution load close to the background level (Salo et al. 2012), and a value higher than 1 indicates low pollution

(1.1 < PLI < 1.5), moderate pollution (1.5 ≤ PLI < 2.0), high pollution (2.0 ≤ PLI < 2.5), or very high pollution (PLI ≥ 2.5).

Multivariate analysis

Differences between concentrations of trace elements at the control and the monitoring sites were analyzed by a one-way ANOVA and Duncan's multiple range test at $p < 0.05$. A principal component analysis (PCA) using Varimax rotation was used to identify the possible sources of the elements. A cluster analysis carried out with Ward's method of linkage with the squared Euclidean distance as a measure of similarity was employed to segregate the monitoring sites based on the element contamination level. All statistical analyses were performed using SPSS software (Version 22, IBM Corp, Armonk, NY, USA).

Results

Element contents

Element concentrations fluctuated during the exposure period, showing unclear trends; therefore, arithmetic means for each element from all collection times at each monitoring site were calculated to arrive at grand averages (Table 3). The highest concentrations of most elements were observed from the sites near the main industrial area. Remarkably high concentrations of Mo, Sb, and Ti were observed at I-4, while Co, Cr, and Hg were elevated at I-5; these sites were approximately 2.7 and 3.8 km away from the main industrial area, respectively. Likewise, As, Cd, and Zn were noticeably higher at I-6, while Ni and V were elevated at I-7. Only Cu and Pb were notably high at I-3, which was only 7 km northwest of the main industrial area.

Altogether, the concentrations of every element at all industrial sites were higher than those at the control site, except for Co, Hg, and Ni at I-1 and Co at I-2. Six of the 13 elements at the industrial sites had significantly higher concentrations than those at the control site ($p < 0.05$). These included As at I-5 and I-6, Cu at I-3, Mo at I-4 and I-5, Sb at I-4, V at I-7, and Zn at I-2, I-3, I-4, I-5, I-6, and I-7. Conversely, element concentrations from both rural sites were comparable to those at the control site, except for As, Cr, Pb, and Ti at R-1, which were slightly higher (but not significantly different).

Contamination factors and pollution load indexes

The contamination factor (CF) values for each element at the rural and industrial sites ranged from 0.7 (Co at R-2) to 9.7 (Mo at I-4), indicating variable atmospheric pollution.

Among the 104 CFs at all industrial sites, 63 (61%) indicated light contamination, 20 (19%) medium contamination, 13 (12%) heavy contamination, and only 8 (8%) indicated a lack of contamination. Among the 26 CF values at the two rural sites, 18 (69%) were categorized as uncontaminated and 8 (31%) indicated light contamination (Table 4).

The pollution load index (PLI) values ranged from 1.0 to 2.1, the sites adjacent to the primary industrial area having the highest values, indicating a higher pollution load than at the sites further away. The pollution levels at the sites assumed the following order: I-4, I-5 > I-6, I-7 > I-3 > I-8 > I-2 > I-1 > R-1 > R-2, C (Table 4).

Multivariate analysis

The matrix with the concentrations of 13 elements from 4 collection periods at 11 monitoring sites (13 variables × 128 samples) was submitted to PCA. Two principal components (PCs) showed eigenvalues greater than 1, which explained 68.4% of the total variance in the data set (Table 5). PC1 explained 47.5% of the total variance and was positively correlated with Hg, V, Sb, Ti, As, Ni, Mo, Cr, and Co. PC2 explained 20.9% of the total variance and was positively correlated with Pb, Zn, and Cu. Cd had a positive association with both components.

The hierarchical cluster analysis of the CF values categorized the sites into three major groups, at (Dlink/Dmax) × 25 < 5, as shown in Fig. 2. Group 1 included the control and the two rural sites. Group 2 comprised the following two sub-groups: sub-group 2A, which consisted of I-1, I-2, and I-3 and sub-group 2B, which consisted of I-6, I-7, and I-8. Lastly, Group 3 consisted of I-4 and I-5, two sites situated adjacent to the main industrial area.

Discussion

At all sites the concentrations of the trace elements accumulated in the lichen *P. tinctorum* varied without clear trends during the 8 months after transplantation. Similar findings have been reported from the lichen *Pseudevernia furfuracea*, transplanted to an industrial area in Southern Italy for a year (Corapi et al. 2014). In addition, Mikhailova and Sharunova (2008) observed that metal accumulation in the transplanted lichen *Hypogymnia physodes* was non-linear, depending on the dynamics of pollutant input and leaching. Rainwater is the most important factor that affects such variations (Branquinho et al. 2008; Brown and Brown 1991). Boonpragob and Nash (1990) reported that the concentrations of Cd, Cu, Pb, Ti, and Zn, in the lichen *Ramalina menziesii* were significantly higher in the dry season than in the wet season. In contrast, Adamo et al. (2003) reported that the accumulation of As, Cr, Cu, Mo, Ni, Pb, Ti, and V in the

Table 3 Arithmetic means ± SD (n = 3) and grand averages ± SD (n = 4) of 13 elements from the lichen *Parmotrema tinctorum* before and after transplantation in the control, rural, and petrochemical industrial sites exposed to different climatic conditions (μg/g dry weight (dw))

Site	Days after exposure (climatic condition)	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Ti	V	Zn
All	Pre-exposure	0.24 ± 0.04	0.04 ± 0.02	0.17 ± 0.03	<MDL	1 ± 0	0.04 ± 0.00	0.09 ± 0.02	1.5 ± 0.3	1 ± 0	0.03 ± 0.01	1 ± 1	0.4 ± 0.1	11 ± 1
C	52 (H-MR)	0.33 ± 0.02	0.15 ± 0.03	0.23 ± 0.03	2.1 ± 1	5 ± 1	0.10 ± 0.01	0.09 ± 0.03	2.3 ± 0.7	7 ± 2	0.06 ± 0.01	8 ± 2	1.1 ± 0.3	26 ± 3
	102 (C-D)	0.29 ± 0.02	0.13 ± 0.02	0.50 ± 0.15	1.7 ± 0	4 ± 0	0.08 ± 0.03	0.08 ± 0.01	2.1 ± 0.4	6 ± 0	0.04 ± 0.00	9 ± 3	1.2 ± 0.1	26 ± 1
	158 (H-LR)	0.16 ± 0.04	0.08 ± 0.02	0.21 ± 0.01	1.0 ± 0	2 ± 0	0.04 ± 0.02	0.09 ± 0.01	1.4 ± 0.2	4 ± 0	0.02 ± 0.01	6 ± 1	0.8 ± 0.1	20 ± 2
	242 (H-HR)	0.35 ± 0.01	0.15 ± 0.01	0.19 ± 0.02	1.7 ± 0	6 ± 1	0.07 ± 0.01	0.16 ± 0.02	1.6 ± 0.2	3 ± 1	0.08 ± 0.02	5 ± 0	1.3 ± 0.1	19 ± 3
	Grand average	0.28 ± 0.1	0.13 ± 0.0	0.28 ± 0.2	1.6 ± 1	4 ± 2	0.07 ± 0.02	0.11 ± 0.0	1.9 ± 0.4	5 ± 2	0.05 ± 0.03	7 ± 2	1.1 ± 0.2	23 ± 4
R-1	52 (H-MR)	0.35 ± 0.06	0.16 ± 0.02	0.24 ± 0.03	3.9 ± 1	5 ± 1	0.08 ± 0.01	0.12 ± 0.02	2.3 ± 0.3	7 ± 1	0.07 ± 0.02	8 ± 1	1.3 ± 0.1	26 ± 3
	102 (C-D)	0.33 ± 0.05	0.14 ± 0.02	0.22 ± 0.03	1.6 ± 0	4 ± 0	0.04 ± 0.01	0.09 ± 0.01	2.2 ± 0.1	6 ± 2	0.04 ± 0.01	8 ± 1	1.1 ± 0.3	22 ± 3
	158 (H-LR)	0.34 ± 0.04	0.18 ± 0.05	0.27 ± 0.11	1.1 ± 0	3 ± 0	0.04 ± 0.01	0.09 ± 0.01	1.5 ± 0.2	7 ± 2	0.05 ± 0.02	8 ± 3	1.0 ± 0.0	28 ± 3
	242 (H-HR)	0.44 ± 0.04	0.19 ± 0.06	0.18 ± 0.01	2.8 ± 1	5 ± 1	0.12 ± 0.02	0.17 ± 0.02	1.6 ± 0.3	5 ± 1	0.10 ± 0.01	6 ± 1	1.2 ± 0.1	18 ± 3
	Grand average	0.36 ± 0.1	0.17 ± 0.0	0.23 ± 0.0	2.4 ± 1	4 ± 1	0.07 ± 0.04	0.12 ± 0.0	1.9 ± 0.4	6 ± 1	0.07 ± 0.03	8 ± 1	1.1 ± 0.1	24 ± 4
R-2	52 (H-MR)	0.29 ± 0.04	0.11 ± 0.01	0.23 ± 0.01	2.2 ± 0	5 ± 1	0.09 ± 0.01	0.11 ± 0.01	1.9 ± 0.4	7 ± 0	0.06 ± 0.03	8 ± 1	1.1 ± 0.1	24 ± 2
	102 (C-D)	0.23 ± 0.01	0.12 ± 0.02	0.20 ± 0.02	2.5 ± 1	4 ± 0	0.05 ± 0.01	0.11 ± 0.03	2.4 ± 0.6	5 ± 1	0.09 ± 0.01	7 ± 0	1.0 ± 0.1	22 ± 1
	158 (H-LR)	0.28 ± 0.04	0.22 ± 0.03	0.23 ± 0.01	<MDL	3 ± 0	0.04 ± 0.02	0.08 ± 0.01	1.4 ± 0.5	6 ± 1	0.05 ± 0.02	6 ± 1	0.8 ± 0.1	29 ± 3
	242 (H-HR)	0.36 ± 0.05	0.15 ± 0.02	0.14 ± 0.05	1.8 ± 1	4 ± 1	0.09 ± 0.05	0.11 ± 0.03	1.2 ± 0.2	4 ± 0	0.08 ± 0.02	6 ± 3	1.0 ± 0.2	17 ± 1
	Grand average	0.29 ± 0.1	0.15 ± 0.0	0.20 ± 0.0	1.8 ± 1	4 ± 1	0.07 ± 0.03	0.10 ± 0.0	1.7 ± 0.5	6 ± 1	0.07 ± 0.02	7 ± 1	1.0 ± 0.1	23 ± 5
I-1	52 (H-MR)	0.41 ± 0.10	0.12 ± 0.04	0.29 ± 0.09	3.1 ± 1	5 ± 1	0.07 ± 0.02	0.16 ± 0.05	1.8 ± 0.4	8 ± 2	0.07 ± 0.02	11 ± 3	1.5 ± 0.4	25 ± 3
	102 (C-D)	0.42 ± 0.03	0.66 ± 0.20	0.31 ± 0.02	2.5 ± 1	5 ± 0	0.07 ± 0.01	0.18 ± 0.02	2.1 ± 0.3	19 ± 7	0.07 ± 0.02	10 ± 0	1.6 ± 0.1	38 ± 6
	158 (H-LR)	0.43 ± 0.05	0.24 ± 0.03	0.24 ± 0.03	1.3 ± 0	4 ± 1	0.03 ± 0.01	0.15 ± 0.02	1.9 ± 0.6	4 ± 0	0.06 ± 0.01	9 ± 1	1.1 ± 0.1	35 ± 6
	242 (H-HR)	0.77 ± 0.11	0.14 ± 0.01	0.21 ± 0.03	1.8 ± 0	5 ± 1	0.11 ± 0.03	0.17 ± 0.06	1.5 ± 0.3	5 ± 1	0.08 ± 0.03	7 ± 3	1.7 ± 0.4	26 ± 4
	Grand average	0.51 ± 0.2	0.29 ± 0.3	0.26 ± 0.1	2.2 ± 1	5 ± 0	0.07 ± 0.03	0.17 ± 0.0	1.8 ± 0.2	9 ± 7	0.07 ± 0.01	9 ± 2	1.5 ± 0.2	31 ± 7
I-2	52 (H-MR)	0.45 ± 0.04	0.17 ± 0.01	0.31 ± 0.04	2.6 ± 0	6 ± 1	0.10 ± 0.02	0.22 ± 0.04	2.5 ± 0.4	9 ± 2	0.07 ± 0.00	10 ± 2	1.6 ± 0.3	30 ± 6
	102 (C-D)	0.44 ± 0.04	0.44 ± 0.17	0.25 ± 0.05	1.9 ± 0	5 ± 1	0.10 ± 0.01	0.31 ± 0.08	2.5 ± 0.6	12 ± 4	0.11 ± 0.03	8 ± 1	1.4 ± 0.2	54 ± 2
	158 (H-LR)	0.39 ± 0.01	0.28 ± 0.01	0.24 ± 0.06	1.5 ± 0	4 ± 0	0.03 ± 0.01	0.34 ± 0.08	1.8 ± 0.2	5 ± 2	0.06 ± 0.02	9 ± 1	1.2 ± 0.2	41 ± 5
	242 (H-HR)	0.53 ± 0.05	0.15 ± 0.00	0.20 ± 0.04	3.2 ± 1	6 ± 1	0.15 ± 0.07	0.46 ± 0.03	1.9 ± 0.4	7 ± 2	0.11 ± 0.03	9 ± 1	1.6 ± 0.2	42 ± 4
	Grand average	0.45 ± 0.1	0.26 ± 0.1	0.25 ± 0.1	2.3 ± 1	5 ± 1	0.10 ± 0.05	0.33 ± 0.1	2.2 ± 0.4	8 ± 3	0.09 ± 0.03	9 ± 1	1.5 ± 0.2	42 ± 10[a]
I-3	52 (H-MR)	0.63 ± 0.39	0.16 ± 0.02	0.44 ± 0.21	3.3 ± 0	17 ± 1	0.11 ± 0.02	0.30 ± 0.19	4.0 ± 0.7	10 ± 1	0.10 ± 0.04	11 ± 3	2.0 ± 0.7	33 ± 4
	102 (C-D)	0.70 ± 0.03	0.54 ± 0.02	0.36 ± 0.03	2.1 ± 0	19 ± 2	0.12 ± 0.01	0.24 ± 0.02	2.7 ± 0.2	16 ± 2	0.19 ± 0.03	11 ± 1	1.7 ± 0.2	50 ± 2
	158 (H-LR)	0.29 ± 0.02	0.26 ± 0.01	0.26 ± 0.08	1.2 ± 0	5 ± 0	0.05 ± 0.00	0.16 ± 0.01	1.7 ± 0.1	7 ± 2	0.10 ± 0.01	9 ± 1	1.0 ± 0.0	43 ± 8
	242 (H-HR)	0.35 ± 0.04	0.20 ± 0.04	0.19 ± 0.02	2.7 ± 0	6 ± 1	0.14 ± 0.06	0.20 ± 0.01	1.5 ± 0.2	6 ± 2	0.10 ± 0.03	7 ± 1	1.5 ± 0.1	52 ± 9
	Grand average	0.49 ± 0.2	0.29 ± 0.2	0.31 ± 0.1	2.3 ± 1	12 ± 7[a]	0.11 ± 0.04	0.23 ± 0.1	2.5 ± 1.1	10 ± 5	0.12 ± 0.04	10 ± 2	1.6 ± 0.4	45 ± 8[a]
I-4	52 (H-MR)	1.00 ± 0.09	0.64 ± 0.04	0.66 ± 0.09	3.1 ± 1	5 ± 1	0.36 ± 0.02	1.50 ± 0.11	6.1 ± 0.5	8 ± 1	0.37 ± 0.11	20 ± 3	3.4 ± 0.1	39 ± 5
	102 (C-D)	0.42 ± 0.01	0.41 ± 0.06	0.58 ± 0.05	2.9 ± 2	6 ± 0	0.11 ± 0.02	1.42 ± 0.39	3.5 ± 0.2	13 ± 1	0.17 ± 0.02	10 ± 1	1.7 ± 0.1	48 ± 3
	158 (H-LR)	0.31 ± 0.03	0.17 ± 0.02	0.25 ± 0.04	1.2 ± 0	4 ± 0	0.06 ± 0.01	0.55 ± 0.05	1.9 ± 0.2	5 ± 1	0.08 ± 0.02	9 ± 1	1.0 ± 0.0	36 ± 8
	242 (H-HR)	0.36 ± 0.03	0.17 ± 0.04	0.21 ± 0.02	2.8 ± 0	5 ± 2	0.09 ± 0.02	0.59 ± 0.06	1.5 ± 0.1	4 ± 0	0.11 ± 0.03	7 ± 2	1.4 ± 0.1	29 ± 4
	Grand average	0.52 ± 0.3	0.35 ± 0.2	0.43 ± 0.2	2.5 ± 1	5 ± 1	0.16 ± 0.14	1.02 ± 0.5[a]	3.2 ± 2.1	8 ± 4	0.18 ± 0.13[a]	12 ± 6	1.9 ± 1.1	38 ± 8[a]
I-5	52 (H-MR)	1.20 ± 0.19	0.55 ± 0.07	0.61 ± 0.07	4.8 ± 0	5 ± 1	0.39 ± 0.06	1.20 ± 0.10	6.3 ± 1.5	9 ± 2	0.33 ± 0.13	18 ± 1	3.3 ± 0.2	43 ± 3
	102 (C-D)	0.75 ± 0.03	0.54 ± 0.06	0.79 ± 0.22	2.0 ± 0	6 ± 0	0.07 ± 0.01	0.70 ± 0.05	4.6 ± 1.6	14 ± 1	0.15 ± 0.01	9 ± 1	1.8 ± 0.1	45 ± 4
	158 (H-LR)	0.35 ± 0.04	0.20 ± 0.03	0.24 ± 0.06	1.2 ± 0	4 ± 0	0.05 ± 0.01	0.38 ± 0.06	1.6 ± 0.1	6 ± 2	0.07 ± 0.02	8 ± 1	1.1 ± 0.1	38 ± 4
	242 (H-HR)	0.54 ± 0.14	0.17 ± 0.04	0.15 ± 0.02	2.7 ± 0	5 ± 1	0.11 ± 0.02	0.62 ± 0.09	1.2 ± 0.3	6 ± 2	0.08 ± 0.03	7 ± 1	1.6 ± 0.2	36 ± 3
	Grand average	0.71 ± 0.4[a]	0.37 ± 0.2	0.45 ± 0.3	2.7 ± 2	5 ± 1	0.16 ± 0.16	0.73 ± 0.4[a]	3.4 ± 2.5	9 ± 4	0.16 ± 0.12	10 ± 5	1.9 ± 0.9	41 ± 4[a]
I-6	52 (H-MR)	1.22 ± 0.16	0.55 ± 0.03	0.53 ± 0.07	3.7 ± 1	5 ± 0	0.38 ± 0.06	0.60 ± 0.10	5.2 ± 0.6	8 ± 1	0.29 ± 0.01	17 ± 5	2.5 ± 0.2	48 ± 4
	102 (C-D)	0.64 ± 0.17	0.58 ± 0.18	0.40 ± 0.03	1.9 ± 0	5 ± 0	0.09 ± 0.02	0.29 ± 0.01	5.3 ± 0.4	12 ± 3	0.10 ± 0.01	9 ± 1	1.3 ± 0.1	51 ± 3
	158 (H-LR)	0.52 ± 0.11	0.28 ± 0.02	0.24 ± 0.06	1.7 ± 0	4 ± 0	0.05 ± 0.00	0.32 ± 0.03	1.5 ± 0.3	8 ± 1	0.07 ± 0.01	10. ± 2	1.1 ± 0.2	46 ± 2
	242 (H-HR)	0.58 ± 0.11	0.18 ± 0.02	0.13 ± 0.05	2.0 ± 1	4 ± 1	0.08 ± 0.04	0.40 ± 0.16	1.0 ± 0.3	6 ± 1	0.05 ± 0.01	8 ± 1	1.2 ± 0.3	41 ± 5

Table 3 (continued)

Site	Days after exposure (climatic condition)	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Ti	V	Zn
	Grand average	0.74 ± 0.3[a]	0.40 ± 0.2	0.33 ± 0.2	2.3 ± 1	5 ± 0	0.15 ± 0.15	0.40 ± 0.1	3.3 ± 2.3	8 ± 2	0.13 ± 0.11	11 ± 4	1.5 ± 0.7	47 ± 4[a]
I-7	52 (H-MR)	0.80 ± 0.06	0.49 ± 0.07	0.53 ± 0.06	3.6 ± 1	6 ± 2	0.29 ± 0.07	0.65 ± 0.02	6.5 ± 0.2	8 ± 0	0.28 ± 0.01	14 ± 1	2.8 ± 0.4	30 ± 0
	102 (C-D)	0.80 ± 0.04	0.51 ± 0.05	0.25 ± 0.02	1.9 ± 0	5 ± 0	0.06 ± 0.01	0.29 ± 0.02	4.7 ± 0.7	16 ± 3	0.16 ± 0.01	9 ± 0	2.0 ± 0.1	39 ± 3
	158 (H-LR)	0.40 ± 0.03	0.37 ± 0.09	0.19 ± 0.03	1.5 ± 0	4 ± 0	0.05 ± 0.02	0.26 ± 0.03	2.3 ± 0.1	9 ± 2	0.08 ± 0.02	11 ± 1	1.6 ± 0.2	38 ± 12
	242 (H-HR)	0.49 ± 0.09	0.13 ± 0.02	0.20 ± 0.06	2.3 ± 1	7 ± 2	0.11 ± 0.07	0.32 ± 0.09	1.7 ± 0.5	5 ± 2	0.10 ± 0.04	7 ± 1	2.1 ± 0.6	34 ± 5
	Grand average	0.62 ± 0.2	0.38 ± 0.2	0.29 ± 0.2	2.3 ± 1	6 ± 1	0.13 ± 0.11	0.38 ± 0.2	3.8 ± 2.2	9 ± 5	0.15 ± 0.09	10 ± 3	2.1 ± 0.5[a]	35 ± 4[a]
I-8	52 (H-MR)	0.87 ± 0.18	0.55 ± 0.13	0.60 ± 0.15	3.7 ± 1	5 ± 0	0.26 ± 0.03	0.47 ± 0.07	5.3 ± 0.3	8 ± 2	0.27 ± 0.00	19 ± 5	2.5 ± 0.6	32 ± 6
	102 (C-D)	0.98 ± 0.07	0.46 ± 0.06	0.27 ± 0.07	2.0 ± 0	5 ± 1	0.05 ± 0.01	0.16 ± 0.04	4.3 ± 0.5	7 ± 0	0.11 ± 0.01	8 ± 1	1.5 ± 0.3	31 ± 3
	158 (H-LR)	0.27 ± 0.05	0.40 ± 0.05	0.12 ± 0.03	1.3 ± 0	3 ± 0	0.04 ± 0.01	0.17 ± 0.04	1.4 ± 0.2	4 ± 1	0.08 ± 0.04	7 ± 0	1.1 ± 0.1	25 ± 4
	242 (H-HR)	0.43 ± 0.22	0.14 ± 0.01	0.19 ± 0.10	2.5 ± 1	4 ± 1	0.15 ± 0.07	0.19 ± 0.09	1.4 ± 0.3	5 ± 0	0.14 ± 0.08	8 ± 3	1.3 ± 0.7	25 ± 13
	Grand average	0.64 ± 0.3	0.39 ± 0.2	0.30 ± 0.2	2.4 ± 1	4 ± 1	0.13 ± 0.10	0.25 ± 0.2	3.1 ± 2.0	6 ± 2	0.15 ± 0.08	11 ± 6	1.6 ± 0.6	28 ± 4

52 days (October 18, 2013–December 8 2013; H-MR = hot-medium rain), 102 days (December 9, 2013–January 27, 2014; C-D = cool-dry), 158 days (January 28, 2014–March 24, 2014; H-LR = hot-light rain), and 242 days (March 25, 2014–June 16, 2014; H-HR = hot-heavy rain)

<*MDL* below the method detection limit

[a] The grand average value is significantly different from that at the control site by one-way ANOVA with Duncan's multiple range test at $p < 0.05$, $n = 4$

lichen *P. furfuracea* was significantly higher during the wet period. In addition to the effect of rainwater, element contents in lichens vary depending on physiological processes, the affinity of the elements, and climatic conditions (Bargagli and Mikhailova 2002; Godinho et al. 2008; Wolterbeek 2002).

The average concentrations of each element in the lichen at the control site were similar to or lower than those reported for several lichens elsewhere (Table 6). Even though trace elements in lichens from unpolluted habitats vary among species, these values are considered as background levels (Bargagli and Mikhailova 2002; Bergamaschi et al. 2004; Darnajoux et al. 2015). Therefore, it is reasonable to use the concentrations of elements in *P. tinctorum* at the control site as the background.

Element concentrations were evidently higher in the petrochemical industrial area than at the rural and control sites. Similar findings were also observed in other regions. Nadal et al. (2009) reported that in the petrochemical area of Tarragona County (Spain), V in vegetation (*Piptatherum*), had a significantly higher concentration than in an unpolluted site. The peak concentrations of Ni and Pb in the lichen *Dirinaria picta* from Singapore were associated with the chemical and petrochemical industries (Ng et al. 2005), and high levels of airborne metal deposits in the lichen *Xanthoria parietina* in Kocaeli Province (Turkey) were associated with petroleum refineries, coal and oil combustion, and metal-related industries (Demiray et al. 2012).

In the Map Ta Phut area, four elements (Mo, Sb, Cd, and Cu) were present at heavy contamination levels (CF ≥ 3). Molybdenum was the most prominent, occurring at five industrial sites, i.e., I-2, I-4, I-5, I-6, and I-7. The two highest CF values, ten- and sevenfold higher than at the control site, were observed at I-4 and I-5, respectively. Molybdenum is widely used as a catalyst in the chemical and petrochemical industries (Rojas-Rodríguez et al. 2012) and is emitted by coal-fired power plants (Adriano 2001). Although this is an essential trace element and has relatively low toxicity in humans, it can be toxic, particularly for copper-deficient persons (Vyskocil and Viau 1999). Antimony was the second most predominant element found at the four industrial sites, i.e., I-4, I-5, I-7, and I-8. A high concentration of Sb was observed in areas near petrochemical and chemical industrial locations and heavy traffic areas (Achotegui-Castells et al. 2013; Canha et al. 2014; Lucadamo et al. 2016). This element can affect the cardiovascular and respiratory systems in humans (ATSDR 1992), and antimony trioxide is a possible human carcinogen (Sundar and Chakravarty 2010). The third most prevalent element was cadmium, observed at three industrial sites, i.e., I-6, I-7, and I-8. Emission sources of cadmium are associated with many industrial processes, e.g., metallurgical plants, fossil fuel combustion, phosphate fertilizer, electroplating, and polyvinyl chloride plastics (Bargagli and Mikhailova 2002; WHO 2010), as well as traffic (Bari et al. 2001; Demiray

Table 4 Contamination factors and pollution load indexes calculated using the grand averages of the elements accumulated in the transplanted lichens

Monitoring site	CF													PLI
	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Ti	V	Zn	
C	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
R-1	1.3	1.3	0.8	1.4	1.1	1.0	1.1	1.0	1.3	1.4	1.2	1.0	1.0	1.1
R-2	1.0	1.2	0.7	1.1	1.0	0.9	1.0	0.9	1.1	1.4	1.0	0.9	1.0	1.0
I-1	1.8	2.3	0.9	1.3	1.2	1.0	1.6	1.0	1.9	1.4	1.4	1.3	1.4	1.4
I-2	1.6	2.1	0.9	1.4	1.3	1.3	3.2	1.2	1.7	1.7	1.4	1.3	1.8	1.5
I-3	1.7	2.3	1.1	1.4	*3.0*	1.5	2.1	1.3	*2.0*	2.4	1.5	1.4	2.0	1.8
I-4	1.9	2.8	1.5	1.5	1.2	2.2	*9.7*	1.7	1.6	*3.7*	*1.8*	1.7	1.7	2.1
I-5	2.5	2.9	*1.6*	*1.6*	1.3	*2.2*	6.9	1.8	1.8	3.2	1.6	1.8	1.8	2.1
I-6	*2.6*	*3.2*	1.2	1.4	1.2	2.1	3.8	1.7	1.7	2.6	1.7	1.4	*2.1*	1.9
I-7	2.2	3.0	1.0	1.4	1.4	1.8	3.6	*2.0*	1.9	3.1	1.5	*1.9*	1.6	1.9
I-8	2.3	3.1	1.0	1.4	1.0	1.8	2.3	1.7	1.3	3.0	1.6	1.5	1.2	1.7

The italicized numbers are the highest values, CF indication: <1.2 = no contamination; 1.2 ≤ CF < 2 = light contamination; 2 ≤ CF < 3 = medium contamination; ≥3 = heavy contamination; PLI indication: <0.9 = no pollution; 1 ± 0.1 = background level; 1.1 < PLI < 1.5 = low pollution; 1.5 ≤ PLI < 2.0 = moderate pollution; 2.0 ≤ PLI < 2.5 = high pollution; and ≥2.5 = very high pollution

CFs contamination factors, *PLIs* pollution load indexes

et al. 2012). This element is well known as a human carcinogen and is toxic to various systems, including kidneys and the respiratory, reproductive, and skeletal systems (Godt et al. 2006). Copper was at the fourth most highly contaminated level in the petrochemical area and was observed only at I-3, adjacent to an agricultural area for cassava and other cash crops. The remarkably high Cu concentration at this site might be associated with pesticide application (Nimis et al. 2000; Paoli et al. 2012) and/or to nearby road traffic (Giordano et al. 2013; Koz et al. 2010; Yemets et al. 2014). High concentration of Cu can potentially affect the respiratory and neurological systems (ATSDR 2004b). In addition, elements with CF values ranging from 2 to 3 should be carefully considered and frequently monitored, especially those with high toxicity, such as As, Hg, and Pb (ATSDR 2014).

Table 5 Rotated component matrix and the total variance explained for the elements from the transplanted lichens

Element	Component	
	PC1	PC2
Hg	0.918	-0.008
V	0.898	0.216
Sb	0.889	0.199
Ti	0.823	0.262
As	0.786	0.318
Ni	0.780	0.360
Mo	0.746	0.199
Cr	0.689	0.010
Co	0.686	0.387
Pb	0.112	0.884
Zn	0.196	0.731
Cd	0.524	0.711
Cu	0.049	0.565
Eigenvalue	6.171	2.716
% of total variance	47.469	20.896
% of cumulative variance	47.469	68.364

Principal component analysis (PCA) with Varimax rotation, Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy = 0.885, the significance of Bartlett's sphericity test is <0.001, and factor loadings higher than 0.50 are considered to be significant variables (Hair et al. 2009)

PCA, a tool to identify possible sources of elements (Boamponsem et al. 2010; Zeng et al. 2015; Zhang et al. 2009), segregated the elements in this study into two components. The first component was positively correlated with ten elements with factor loadings higher than 0.50: Hg, V, Sb, Ti,

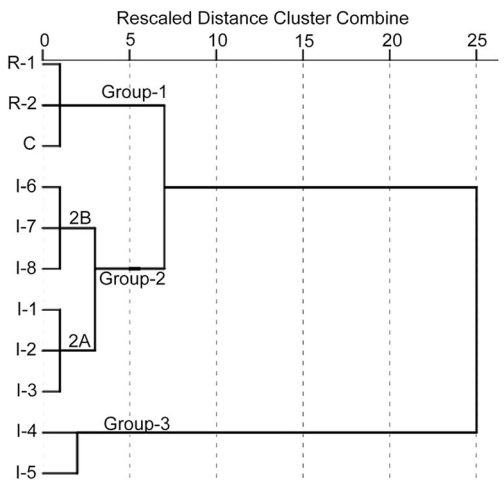

Fig. 2 Dendrogram of the sampling sites based on contamination factors. Three statistically significant groups are formed at (Dlink/Dmax) × 25 < 5

Table 6 Average background concentrations (μg/g) of trace elements in various lichens worldwide

Element	*Parmotrema tinctorum*		*Parmotrema reticulatum*[c]	Several lichen species[d]			Peltigeralean lichens[e]	*Usnea barbata*[f]	*Umbilicaria decussata*[g]	Range (different species and regions)
	This study[a]	Brazil[b]	China	Himalayas	Kenya	Italy	NE Canada	Tierra del Fuego	Antarctica	
As	0.27	–	0.47	0.20	0.10	0.30	–	0.73	–	0.10–0.73
Cd	0.11	0.10	–	0.02	0.02	0.08	0.08	0.17	0.10	0.02–0.17
Co	0.26	–	1.3	0.10	0.10	0.10	0.11	0.52	–	0.10–1.3
Cr	1.4	3.0	1.7	0.9	0.7	0.4	0.19	1.0	0.5	0.19–3.0
Cu	3.4	–	–	3.3	2.2	1.9	4.9	2.5	3.5	1.9–4.9
Hg	0.07	0.10	–	–	–	–	–	–	0.1	0.07–0.10
Mo	0.10	–	0.24	–	–	–	0.06	0.07	–	0.06–0.24
Ni	1.8	–	2.1	–	–	–	1.0	0.83	0.9	0.83–2.10
Pb	4.1	2.0	–	6.9	1.5	3.2	0.43	2.2	0.3	0.3–6.9
Sb	0.05	–	–	0.40	0.85	0.16	–	0.06	–	0.05–0.85
Ti	5.5	–	–	–	–	–	3.0	–	7.0	3.0–7.0
V	0.95	–	–	0.4	1.2	0.5	0.2	1.8	0.7	0.2–1.8
Zn	20	44	18	16	19	15	51	42	10	10–51

[a] Averaged from all collection periods, including pre-exposure

[b] Käffer et al. (2012)

[c] Zhang et al. (2002), mean values in the 1990s

[d] Bergamaschi et al. (2004), average values of the lowest concentrations

[e] Darnajoux et al. (2015), whole lichen concentrations

[f] Conti et al. (2009)

[g] Bargagli and Mikhailova (2002)

As, Ni, Mo, Cr, Co, and Cd. All of them were associated with industrial emissions, having high concentrations at the sites next to the main industrial area (Table 3). Mercury is emitted by coal-fired power plants, chemical manufacturing, chlor-alkali plants, and steel production (Demiray et al. 2012; Grangeon et al. 2012; Scerbo et al. 2002). Vanadium and nickel are good indicators of coal and oil combustion, being associated with oil refineries and the petrochemical industry (Adamo et al. 2003; Brunialti and Frati 2007; Nadal et al. 2009). Titanium is used for corrosion resistance in the chemical and petrochemical industries and as an alloying element in the steel industries (Boyer 2010; Malaspina et al. 2014). Arsenic originates from coal combustion, the smelting of metals, and steel production (Demiray et al. 2012). A high concentration of Cr near a petrol refinery was previously observed by Achotegui-Castells et al. (2013), and a small amount of Co may be released from coal-fired power plants or the use of cobalt alloys and chemicals (ATSDR 2004a).

The second component was correlated with four elements: Pb, Zn, Cd, and Cu. The first three elements are related to traffic emissions, while Cu could be associated with both traffic and agriculture (Odiwe et al. 2014; Olowoyo et al. 2011; Sorbo et al. 2008; Sujetoviene and Sliumpaite 2013). The highest concentrations of Pb and Cu occurred at I-3, while the maximum quantities of Cd and Zn were found at I-6 (Table 3). Both sites are near Sukhumvit Road (Fig. 1).

The cluster analysis segregated the sites into three groups, according to element concentrations. Group 1 included the control and rural sites, suggesting that atmospheric deposition of trace elements at the two rural sites was similar to the background level at the control site. The rural sites, which are 55 and 35 km away from the central industrial area, are typical small communities in a large area with a rubber plantation serving as a man-made protective barrier from airborne elements originating from Route 344. Group 2 could be separated into 2 sub-groups, 2A (I-1 to I-3) and 2B (I-6 to I-8). Based on the PLIs, all sites in this group had moderate pollution, except for site I-1 which had a low pollution level. The sites in sub-group 2A were located in the outer zone, more than 7 km from the main industrial area, whereas those in sub-group 2B were less than 5 km away. Lastly, group 3 consisted of I-4 and I-5, which had the highest PLI of 2.1, categorized as highly polluted. These sites, less than 4 km from the industrial center, were overloaded with Mo and Sb. Our results may suggest that the zone safe from airborne hazardous elements is ca. 10 km away from the main industrial area; however, further intensive studies are necessary.

Evidence obtained from this study confirms that the petrochemical industry can be a source of trace elements in the air. In addition, lichen is a cost-effective biomonitoring tool, providing contamination levels of airborne trace elements, as well as overall air pollution loads in study areas.

Conclusions

The present study allowed us to categorize the atmospheric deposition of trace elements near the petrochemical industrial complex into high (two industrial sites), moderate (five industrial sites), and low (one industrial site) levels, whereas values at the rural sites were comparable to the background level. Six elements, As, Cu, Mo, Sb, V, and Zn, had significantly higher concentrations at the industrial sites than at the control site. Four heavily contaminating elements, Cd, Cu, Mo, and Sb, are a matter of concern because they are toxic and affect human health, especially Cd and Sb. Most of the elements, i.e., As, Cd, Co, Cr, Hg, Mo, Ni, Sb, Ti, and V, were of industrial origin, but Cd, Cu, Pb, and Zn were related to vehicle emissions and agriculture.

This study fills a gap in knowledge about airborne trace element pollution by the petrochemical industry in Thailand. Since several toxic compounds are known to be discharged from petrochemical manufacturing processes, it is crucial to expand future studies to encompass other pollutants, such as polycyclic aromatic hydrocarbons (PAHs) for an overall assessment of environmental quality and human impact.

Although the degree of atmospheric deposition at most industrial sites was classified as moderate pollution, this could change in time with intensive industrial development and changes in climatic conditions. Thus, continuous and reliable monitoring is essential at Map Ta Phut during and beyond the lifetime of industrial activities.

Finally, the present study confirms that lichen can be used efficiently to evaluate levels of airborne elements, providing one of the best solutions when adequate air monitoring equipment cannot be obtained due to financial constraints.

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