USING LICHEN AS BIO-INDICATOR OF HEAVY METAL POLLUTION AT THE NATIONAL HERITAGE PARK, RURAL AREA AND SOME PUBLIC PARKS IN BANGKOK

Chaiwat Boonpeng,[1,]* Tunsinee Jhampasri,[2] Chutima Sriviboon,[2] Kansri Boonpragob[1]
[1]Lichen Research Unit, Department of Biology, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand
[2]Deparment of Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand
*e-mail: chaiwat_u@hotmail.com

Abstract: Lichens have been wildly used as biomonitors for assessing airborne particulates throughout several past decades because they are inexpensive and provide reliable results. Accordingly the objectives of this study were to accesses quantities of heavy metals in the atmosphere in ten public parks in Bangkok. The study was performed by transplanting the lichen *Parmotrema tinctorum* from unpolluted site in Khao Yai National Park to rural site in Ban Sang, and to ten public parks in Bangkok. Eight heavy metals in lichen thalli were analyzed prior and after transplantation at 45th, 140th and 210th days. The results showed that after transplantation mean concentration of Zn^{2+} averaged from rural and polluted sites had the highest accumulation noted for 2 folds greater than the baseline concentration. Subsequently lower accumulations of Ni^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+} and Co^{2+} accounted for 1.8, 1.3, 1.2, 0.7 and 0.6 respectively were recorded. The maximum increased of each heavy metal at the polluted sites were 1-6 folds greater than its baseline concentration averaged from the reference and control sites. The highest and subsequently lower magnitude of the maximum increases were observed from Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Mn^{2+} of which their maximum concentrations were 7, 6, 6, 3, 2 and 1folds higher than the baseline concentration. Lead and cadmium were undetectable, however new technique is underway to improve analyzing capability. The highest accumulations of heavy metals were mostly found after 140 days of transplantation, and declined at 210 days because of rainfalls, which leached the accumulated pollutants from the lichen thalli. Most of the heavy metals came from heavy traffic in Bangkok, and anthropogenic activities. This study underpinned the efficiently of lichen be used as biomonitoring of heavy metal pollutants.

Introduction: Lichens have been used extensively as bioindicators and bioaccumulators for assessing air pollution as it is inexpensive and provide reliable information.[3,5,12,17,19] They absorb dry and wet deposition from the atmosphere and use them as sources of minerals and nutrients. In general, excess atmospheric elements are toxic to mankind, plants and lichens but those suitable concentrations can be benefit.[22] Using lichens as bioaccumulators of heavy metals as effective method was used for long time because they powerfully trapped with air particulates especially heavy metals, subsequently accumulated in their thalli.[6] However, some species have special mechanism to detoxify or remove those pollutants. Thereby, they can live in polluted sites for long time and they will be a good tool for assessing heavy metals in that area.[13,15] More importantly, Bari et al. (2001) observed the correlation of airborne particulates in the atmosphere and those accumulated in lichen thalli. However, lichens are generally disappeared from the polluted areas. Therefore transplanted lichens have been employed for such monitoring.[9,14,18] This study is part of the project on using lichens to assess air quality of ten pubic parks in Bangkok, of which the other aspects of the studies were previously reported.[4] The aim of this study was to monitor kinds and quantities of heavy metals in ten public parks in Bangkok, rural site and clean-air site by using the transplanted lichen *Parmotrema tinctorum* (Nyl.) Hale.

Methodology: Lichen thalli of *P. tinctorum* from dry evergreen forest at Khao Yai National Park, were transplanted to polluted sites at ten public parks in Bangkok, rural site at Ban Sang district, Prachinburi province and also within the unpolluted site or control site at Khao Yai National Park (Figure 1). Methods for transplantation and sample collections for biological and chemical analysis were described by Boonpeng (2011). Prior to and after transplantation ten heavy metals in lichen thalli were analyzed by using Ion Chromatography according to Saejia (2005) by Chemical Analysis Group, Department of Chemistry, Faculty of Science, Ramkhamhaeng University. Moreover, lichen thalli grew in natural habitats at the control site were also performed for comparing amounts of heavy metals accumulated in transplanted thalli and non-transplanted thalli at unpolluted site, it's called Reference site.

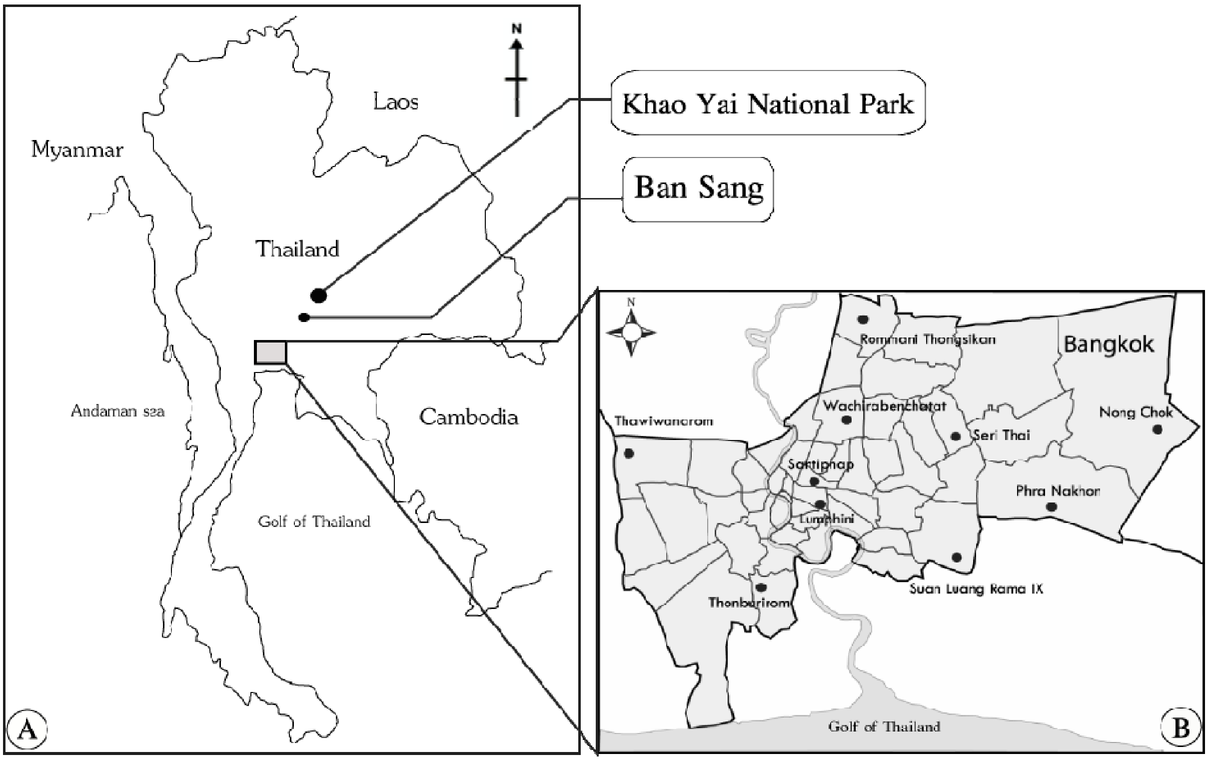

Figure 1. Locations of the study sites (A) and locations of ten public parks in Bangkok (B).

Results, Discussion and Conclusion:

Heavy metals in lichen thalli

Zinc seems to have the highest magnitude of accumulation on the average basis and the second on the maximum basis. The concentration in lichens continually increased in the rural and ten public parks after transplantation. The concentration remained high even after rainfall. The highest concentration of 290 µg g^{-1} dw. was recorded from Lumphini at 210 days after transplantation, whereas the reference and control site were 45 and 62 µg g^{-1} dw during the same period (Table 3). Lichens in urban areas in Switzerland and Sweden have Zn^{2+} 159-259 µg g^{-1} dw.,[11] whereas those from the rural areas in Israel have 49.4 µg g^{-1} dw.[10] Traffic and anthropogenic activities were the causes of this pollutant in urban environment.[9,14]

Nickel had the second highest magnitude of increase at the polluted sites based on the average and maximum categories. However, the concentrations were slightly declined after 45 days of transplantation at all sites, and partially increased after 140 days then declined after rain. The highest concentration of 24 µg g^{-1} dw. occurred in lichen at Seri Thai at 140 days after transplantation, comparing with 3 and 2 µg g^{-1} dw. of those from the reference and control site (Table 3). Nickel is the additive to fuel particular diesel, thus combustion from automobiles and industries could be major sources.[12,23] Reported concentrations of Ni^{2+} ranged from 2.6-667 µg g^{-1} dw from unpolluted and polluted sites around the world.[8]

Copper had the third highest magnitude of increasing of the mean concentration from the polluted sites, and the highest magnitude of increase of the maximum level among all sites. The highest concentration of 127 µg g^{-1} dw. was achieved at Bang sang the rural site after 140 days of transplantation, which was unusually high (Table 1). It was probably contamination form fungicide used in agriculture in this area or interference of other substance during chemical analysis. In addition, this pollutant was found high quantity at Seri Thai park, which probably caused by fungicide used in the park. Copper is usually found in high concentration in urban areas caused by heavy traffic; tires, brakes, engines and vehicle component wear off.[21] Reported concentration from else where are 1.1-84 µg g^{-1} dw.[8]

Iron was found in highest concentration in lichen thalli. It ranges from 129 – 520 µg g^{-1} dw. The mean concentration at the polluted site had the fourth magnitude of increasing comparing with that from the reference and control sites. The concentrations from most sites seem to increase after transplantation particularly at day 140 after transplanting which related to dry period.[5] The highest maximum concentration was observed from Lumphini park at 210 days after transplantation. After rain lichens from five polluted sites had declined concentration of Fe^{3+}, whereas those from the other half of the sites had increasing quantities (Table 2). Generally, Fe^{3+} had high proportion in earth crust therefore iron cumulative in thalli from both the unpolluted and polluted sites were probably contributed by geochemical sources. However, cars components and human activities could be sources of this pollutant in the public parks in Bangkok metropolitan, while wind-blown dust could be the source of Fe^{3+} in rural site.[13,19] Concentration of Fe^{3+} in lichens from several locations are 339-3,092 µg g^{-1} dw.[8]

Manganese had average concentration of from the polluted site lower than that at the control and reference sites before transplantation. Lichen from a few sites and sampling periods had relatively low concentration after transplantation. The concentration from all sites and sampling periods range from 4–103 µg g^{-1} dw, which was 18 folds difference. The highest accumulation was observed from Ban Sang of the rural site, and Rommani Thongsikan ranked the second (Table 2). The causes of this remain unresolved. This heavy metal is normally terrigenous element.[16,21] This study found the highest concentration at the rural site, which could contribute from soil dust. Ranges of concentration of Mn^{2+} in lichens reported from several sites are 13-137.1 µg g^{-1} dw.[8]

Cobalt was found in very low concentration in lichens from all sites. The highest content occurred at Lumphini park, whereas those from the other parks were nil (Table 1). This make the mean concentration in lichens from the polluted sites became lower than that at the reference and control site. Co^{2+} was contributed by earth crust, and could be originated from industries and car-manufacturing factories.[7]

Lead and cadmium were under detection capacity of the instruments used in this study. However it does not mean that they are not important. Improve analyzing capacity is needed for thoroughly examination of the atmospheric pollutants.

Table 1. Amounts of cobalt (Co^{2+}) and cupper (Cu^{2+}) in the lichen *P. tinctorum* before and after transplanted to all study sites (µg g^{-1} dw.; n=3)

Study sites	**Co^{2+} ± SD**				**Cu^{2+} ± SD**			
	0 (days)	45 (days)	140 (days)	210 (days)	0 (days)	45 (days)	140 (days)	210 (days)
Reference	3±2	0±0	0±0	0±0	23±3	3±0	1±0	4±1
Control	3±2	1±1	0±0	0±0	23±3	12±2	21±1	10±1
Ban Sang	3±2	0±0	1±0	0±0	23±3	12±3	127±3	7±2
Nong Chok	3±2	0±0	0±0	0±0	23±3	13±1	8±1	8±0
Phra Nakhon	3±2	0±0	0±0	0±0	23±3	15±0	8±1	10±0
Suan Luang Rama IX	3±2	0±0	0±0	0±0	23±3	6±1	14±5	19±4
Seri Thai	3±2	2±0	1±0	0±0	23±3	20±4	78±7	16±4
Lumphini	3±2	4±0	0±0	0±0	23±3	13±4	17±0	29±2
Santiphap	3±2	0±0	0±0	1±0	23±3	17±2	10±0	5±1
Wachirabenchatat	3±2	0±0	0±0	nd.	23±3	15±0	10±2	nd.
Rommani Thongsikan	3±2	2±1	0±0	0±0	23±3	42±3	8±0	8±1
Thonburirom	3±2	3±0	0±0	1±1	23±3	7±0	18±2	10±3
Thawiwanarom	3±2	0±0	0±0	0±0	23±3	20±8	15±2	11±3
Baseline: mean (ranges)	**0.9 (0-3)**				**12 (1-23)**			
Polluted sites: mean (ranges)	**0.5 (0-4)**				**16 (5-78)**			
Average increased at polluted sites	**0.6 folds**				**1.3 folds**			
Maximum increased at polluted sites	**4 folds**				**7 folds**			

Note. nd. = no data or not detect. Baseline concentrations were averaged from all of control and reference while mean concentrations at polluted sites were averaged from all of public parks in Bangkok after transplantation. Max. or maximum increased at polluted sites were calculated from *highest value at polluted site / baseline mean* and its mean followed *mean value at polluted site / baseline mean*.

Table 2. Amounts of iron (Fe^{3+}) and manganese (Mn^{2+}) in the lichen *P. tinctorum* before and after transplanted to all study sites (µg g^{-1} dw.; n=3)

Study sites	**Fe^{3+}** ± SD				**Mn^{2+}** ± SD			
	0 (days)	45 (days)	140 (days)	210 (days)	0 (days)	45 (days)	140 (days)	210 (days)
Reference	145±8	214±8	129±13	199±25	33±9	57±1	23±1	18±3
Control	145±8	141±9	168±2	276±7	33±9	51±3	57±9	23±2
Ban Sang	145±8	237±12	204±6	409±7	33±9	72±14	103±4	37±5
Nong Chok	145±8	145±1	139±2	232±1	33±9	61±26	30±11	5±0
Phra Nakhon	145±8	161±6	401±10	177±2	33±9	12±6	39±3	13±0
Suan Luang Rama IX	145±8	150±2	187±34	142±1	33±9	23±4	66±12	10±0
Seri Thai	145±8	152±15	297±1	178±1	33±9	31±12	38±17	12±0
Lumphini	145±8	162±4	261±10	520±35	33±9	7±5	16±9	71±10
Santiphap	145±8	163±2	291±0	264±2	33±9	6±2	23±4	8±0
Wachirabenchatat	145±8	206±9	176±20	nd.	33±9	4±0	42±4	nd.
Rommani Thongsikan	145±8	133±13	243±9	167±11	33±9	28±19	73±14	10±8
Thonburirom	145±8	156±22	216±3	192±0	33±9	14±2	13±5	17±3
Thawiwanarom	145±8	127±8	161±4	180±38	33±9	21±2	58±14	9±4
Baseline: mean (ranges)	**177 (129-276)**				**37 (18-57)**			
Polluted sites: mean (ranges)	**206 (127-520)**				**26 (4-73)**			
Average increased at polluted sites	**1.2 folds**				**0.7 folds**			
Maximum increased at polluted sites	**3 folds**				**2 folds**			

Note. nd. = no data or not detect. Baseline concentrations were averaged from all of control and reference while mean concentrations at polluted sites were averaged from all of public parks in Bangkok after transplantation. Max. or maximum increased at polluted sites were calculated from *highest value at polluted site / baseline mean* and its mean followed *mean value at polluted site / baseline mean*.

Table 3. Amounts of nickel (Ni^{2+}) and zinc (Zn^{2+}) in the lichen *P. tinctorum* before and after transplanted to all study sites (µg g^{-1} dw.; n=3)

Study sites	**Ni^{2+}** ± SD				**Zn^{2+}** ± SD			
	0 (days)	45 (days)	140 (days)	210 (days)	0 (days)	45 (days)	140 (days)	210 (days)
Reference	9±2	2±0	3±1	3±1	46±5	41±3	42±2	45±4
Control	9±2	3±0	2±0	2±0	46±5	55±2	54±1	62±2
Ban Sang	9±2	3±2	3±0	4±0	46±5	67±3	58±2	62±5
Nong Chok	9±2	4±2	10±6	3±0	46±5	63±2	64±2	84±0
Phra Nakhon	9±2	4±1	17±2	6±0	46±5	63±1	86±9	100±3
Suan Luang Rama IX	9±2	6±1	5±1	5±0	46±5	66±4	98±5	100±4
Seri Thai	9±2	5±2	24±1	4±0	46±5	77±4	150±3	125±4
Lumphini	9±2	3±0	7±1	18±1	46±5	70±4	116±4	290±5
Santiphap	9±2	4±0	6±1	5±1	46±5	72±1	94±1	107±2
Wachirabenchatat	9±2	12±1	8±0	nd.	46±5	63±1	101±3	nd.
Rommani Thongsikan	9±2	4±2	10±8	6±4	46±5	65±6	105±1	73±15
Thonburirom	9±2	5±0	2±0	4±1	46±5	84±4	107±3	106±1
Thawiwanarom	9±2	3±0	4±0	3±0	46±5	75±1	110±1	104±0
Baseline: mean (ranges)	**4 (2-9)**				**49 (41-62)**			
Polluted sites: mean (ranges)	**7 (2-24)**				**97 (63-290)**			
Average increased at polluted sites	**1.8 folds**				**2 folds**			
Maximum increased at polluted sites	**6 folds**				**6 folds**			

Note. nd. = no data or not detect. Baseline concentrations were averaged from all of control and reference while mean concentrations at polluted sites were averaged from all of public parks in Bangkok after transplantation. Max. or maximum increased at polluted sites were calculated from *highest value at polluted site / baseline mean* and its mean followed *mean value at polluted site / baseline mean*.

Total concentrations of heavy metals in the study sites

Concentrations of all heavy metals accumulated in thalli after transplantation 140 days (prior having rainfall events) were sum for comparing levels of air pollution among the study sites. The total pollutants in Bangkok public parks except Nong Chok park, clearly demonstrated higher amounts than those at unpolluted site, Control and Reference. Nong Chok park showed lower concentration than control but there had higher than reference. More data and information are needed to elucidate this situation.

Total concentration of heavy metals at the rural site show higher than those from some public parks in Bangkok. It possibly caused by terrigenous elements especially Fe^{3+} and Mn^{2+}. These elements came from wind-blown dust or soil aerosols which are usually dense in this area. In addition, this site had relatively dry condition therefore dust was easily deposited in thalli, whereas watering twice a day are practiced in public parks in Bangkok.

In summary, heavy traffic and anthropogenic activities including industries were major sources of heavy metal pollutants in public parks in Bangkok. While terrigenous elements such as Fe^{3+}, Zn^{2+} and Mn^{2+} were major pollutants in rural site and unpolluted site. In addition, pesticides could be source of copper pollutant in some parks particularly the rural site. Higher total heavy metals accumulated in lichens transplanted to public parks in Bangkok than those found at unpolluted site reconfirm that lichens can be effectively use as bioaccumulators, bioindicators or biomonitors for assessing air quality caused by heavy metal pollutants.

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Acknowledgements: We would like to thank members of the Lichen Research Unit and members of the Analytical Group from Ramkhamhaeng University, Office of Public Park and Office of Environment, Bangkok and Khao Yai National Park for assistance field and laboratory works. This work was supported by Thai Government, and Human Resource Development in Science Project (Science Achievement Scholarship of Thailand, SAST).

Keywords: Lichen, Bioindicator, Bangkok, Heavy metals, Public Parks