

Distribution of elements in needles of *Pinus massoniana* (Lamb.) was uneven and affected by needle age

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*Pine needle sections as bioindicator for heavy metals and nutrient deficiency
particularly needle sheath for particle pollutants.*

Abstract

Macronutrients (P, S, K, Na, Mg, Ca), heavy metals (Fe, Zn, Mn, Cu, Pb, Cr, Ni, Cd) and Al concentrations as well as values of Ca/Al in the tip, middle, base sections and sheaths of current year and previous year needles of *Pinus massoniana* from Xiqiao Mountain were analyzed and the distribution patterns of those elements were compared. The results indicated that many elements were unevenly distributed among the different components of needles. Possible deficiency of P, K, Ca, Mn and Al toxicity occurred in needles under air pollution. Heavy metals may threaten the health of Masson pine. Needle sheaths were good places to look for particulate pollutants, in this case including Fe, Cu, Zn, Pb, Cr, Cd and Al.

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1. Introduction

Industrialization and urbanization result in the release of gaseous and particulate pollutants, such as sulphur and heavy metals. These have been reported to cause abnormalities in the nutrient status of conifers (Rautio et al., 1998) and also to reduce plant growth and development at high concentrations, causing death of plants in extreme cases (Greszta, 1982). Plants respond to these pollutants in many ways. Changes in calcium concentrations have been found to be a general physiological response of plants to metal toxicity (Nieminen and Helmisaari, 1996). Attention has been drawn to the development of analytical methods for measurement of pollutants in the environments (Vtorova and Markert, 1995). Chemical analysis of plants or plant parts is one of the most frequently used methods to monitor air pollutants. Various plants, such as mosses (Makinen,

1987; Rühling et al., 1987; Markert, 1993; Figueira et al., 2002), lichens and fungi (Svoboda et al., 2000) have shown a marked ability to accumulate certain pollutants. Pine needles have also been widely used as bioindicators for atmospheric pollutants (Kuhn et al., 1995; Kurczynska et al., 1997). Scots pine (*Pinus sylvestris* L.) (Grodzinska and Kazmierczakowa, 1977; Wentzel, 1982; Ewa et al., 1997; Giertych et al., 1997; Yilmaz and Zengin, 2004) and Norway Spruce (*Picea abies* (L.) Karst.) (Fober, 1976; Marschner et al., 1996; Tuomisto, 1988; Cape et al., 1990; Trimbacher and Weiss, 1999; Čeburnis and Steinnes, 2000) have been acknowledged as useful monitors due to their wide distribution and easy identification.

There is a growing public concern over the potential accumulation of pollutants in ecosystems in China owing to rapid urbanization and industrialization since the 1980s. Coupled with the rapid economic development, heavy metal contamination in the agricultural soils has become an increasingly serious problem in China (Chen et al., 1999). The Pearl River Delta, situated in the southern part of Guangdong Province, is one of the first regions that had experienced massive industrialization and urbanization in China over the past two decades. It has a total

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area of 41,600 km² with a population of over 25 million. After China's opening and reforming policy, the Delta region has undergone a rapid transition from a traditionally agriculture-based economy to an increasingly industry- and technology-based economy. The establishment of industrial operations and subsequent expansion of the population have considerably increased industrial and other emissions in the region (Guangdong Environmental Protection Bureau, 1996). Pollutants associated with the economic developments have already caused vegetation damage due to increased acidification and lack of pollution control (Wen et al., 2003; Luo et al., 2001). However, researchers have not provided sufficient information with regard to the pollutant distribution and the potential effects on plants. Reports on pollution-induced changes of element concentrations in plants are still limited from this area.

Although mean concentrations of elements in whole needles have been determined in earlier studies (Dmuchowski and Bytnerowicz, 1995; Rautio et al., 1998), results from whole needles may ignore element concentration difference in particular needle parts. It is important to identify which part of the needle was used for analysis, particularly when conducting bioindicator surveys. So far, only Jamrich (1972) and Giertych et al. (1997) have described the concentrations of several elements in different parts of needles injured by pollutants.

Masson pine (*Pinus massoniana* Lamb.), a pioneer species widely distributed in the Pearl River Delta, grows rapidly and is sensitive to air pollution (Liu, 1996; Huang et al., 1998). Its use as a bioindicator for air pollution has so far been rarely reported in China. Our objectives were to determine (1) whether there were any differences in element concentrations among the parts of different-aged healthy needles of Masson pine, (2) whether deficiency of nutrient elements or accumulation of heavy metals in the needles as a result of pollution, (3) which part(s) of the pine needle is best suitable for biomonitoring purposes and (4) the effectiveness of using the needle analysis as a bioindicator.

2. Materials and methods

2.1. Site description

The study site was located on Xiqiao Mountain (112°58'E, 22°55'N) at Nanhai county, about 15 km from the industrial center of Foshan and 85 km from Guangzhou city (Fig. 1). At this area in south China, new industries including electroplating, aluminum and copper refining factories, and ceramic manufacturing have developed. Air monitoring data showed that annual mean concentrations of atmospheric SO₂ in this area were 0.082 mg m⁻³ in 2000, 0.077 mg m⁻³ in 2001, 0.056 mg m⁻³ in 2002 and 0.060 mg m⁻³ in 2003. The annual mean pH value of precipitation was 4.91 in 2000, 4.48 in 2001, 4.34 in 2002 and 4.45 in 2003. Emissions of SO₂ in 2000 reached 42,438 tons a⁻¹, and dusts, 2359 tons a⁻¹ (Nanhai Environmental Protection Bureau, 2000–2003).

2.2. Plant material

Six trees of *P. massoniana* (Lamb.), facing the industrial center without obvious injury, were selected and cut down from Xiqiao Mountain at the end of the growing season in December 2002. All these trees experienced nearly the same level of pollution 15 km from Foshan and 5 km from Nanhai. The sample trees, over 40 years old, were selected by a distance of at least 100 m from each other, and considered as the representative across this site.

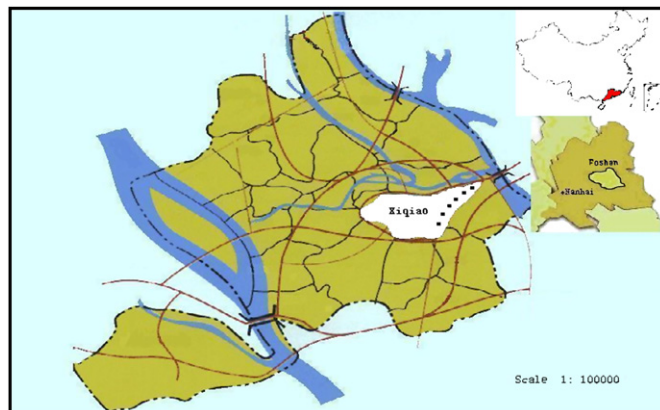


Fig. 1. Map of Xiaqiao and the sampling sites.

2.3. Needle sampling and preparation

The current year (2002, C) and previous year (2001, C + 1) needles were randomly sampled from branches at the upper, middle and lower crown in east, south, west and north directions of each tree, respectively. The needles were pooled to form a sample including 300 fascicles for each age class per tree. Samples were transported in clean polyethylene bags to the laboratory. The whole fresh needle was divided into the sheaths, and three needle sections, tip (T), middle (M), and base section (B), proportional to the length. During sampling and preparation, polypropylene gloves were used to avoid contamination. All needles were dried for 24 h at 65 °C, ground to a fine powder and stored in plastic vials for chemical analyses.

2.4. Chemical analyses

After wet digestion with nitric and perchloric acid, the total P was tested through molybdenum–antimony colorimetry, and total S by barium sulphate nephelometry. S and P standard solutions, supplied by WAKO Pure Chemical Industries Ltd. (Japan), were used to obtain six working standard solutions (0.0, 0.25, 0.5, 0.75, 1.0, 2.0 mg L⁻¹ for P and 0.0, 2.5, 5.0, 10.0, 15.0, 20.0 mg L⁻¹ for S), covering the range detected in samples, for calibration. Values of the P and S were converted into percentage of dry mass. Concentrations of total potassium (K), magnesium (Mg), calcium (Ca), sodium (Na), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn) were determined by atomic absorption spectrometry (AAS, GBC932AA, Australia), cadmium (Cd) and chromium (Cr) by graphite furnace atomic absorption spectrometry (GFAAS, ZEENIT 60, Germany), and lead (Pb) and aluminum (Al) by inductively coupled plasmas emission spectrometry (ICP, PS-1000AT, USA). These elements were expressed as parts per million (ppm = mg kg⁻¹) in dry matter.

In AAS analyses, calibration graphs were obtained by a linear calibration model using eight working elemental standard solutions (WAKO Pure Chemical Industries Ltd., Japan). The obtained calibration graphs were all of excellent quality, always presenting the correlation coefficient $r^2 > 0.999$.

2.5. Statistical analysis

The mean and standard error of the mean (SE) of the elements for each needle section sample were calculated by SPSS program. Paired sample *t*-test is performed to compare the difference of element concentration in different needle sections at the confidence level of 95%.

3. Results

3.1. Mean concentrations of elements

The C + 1 needles had 10–100% lower concentrations of each element of P, S, K, Na and Al than the C needles, but

33–120% higher for Ca, Mn, Zn, Fe and Pb. No significant difference for Mg, Ni, Cd, Cr and Cu was observed between the two needle age classes. The Ca/Al ratio in the C + 1 needles was 4.5-fold higher than that in C needles (Table 1).

Elements in sheaths differed with the needle age. Mean values of S, Fe, Cr and Pb in the C + 1 sheaths were 35–64% higher than those in the C sheaths. Levels of each Mg, P, Al, Na, Mn, Zn and Cu in both C and C + 1 needles were nearly same, while Cd and Ni in the C + 1 sheaths were 2- and 7.5-fold higher, and K and Ca were 52% and 13% lower than that in the C sheaths, respectively. Ca/Al ratio in C sheath was 34% higher than that in C + 1 sheath (Table 1).

3.2. Element concentrations in different needle areas

Total sulphur (S) was within the range of 0.04–0.07% in C + 1 needles, and 0.06–0.08% in C needles, and had a general trend of increase from the tip to base section in both types of needles (Fig. 2). Statistical differences were not observed among the sections in either C or C + 1 needles. Total P decreased on the sequence of the tip, mid, base sections and sheath in the C needles, but increased in the C + 1 needles. Statistical difference of P between the sheath and the tip section was found in C + 1 needles, while the significant differences were found between the sheath and the middle, as well as between the sheath and tip section in C needles. The same sections were significantly lower in C + 1 needles than in C needles except the sheaths (Fig. 2).

Mg followed a similar distribution pattern in both needle types that they increased from tip section to sheath, and the sheath had significantly higher concentrations than any of the other three parts. Statistical differences between the same sections in C vs. C + 1 needles were not found (Fig. 3). Values of Al in the sheaths of C and C + 1 needles were significantly higher than those in tip, middle and base.

Table 1
Mean \pm SE values of element concentrations and Ca/Al ratio in whole needles (excluding sheaths) and in sheaths only

Element	C		C + 1	
	Needle means	Sheaths	Needle means	Sheaths
S	0.06 \pm 0.05	0.07 \pm 0.02	0.03 \pm 0.02	0.05 \pm 0.02
P	0.06 \pm 0.02	0.05 \pm 0.01	0.03 \pm 0.01	0.05 \pm 0.01
K	2973.7 \pm 205.3	2887.3 \pm 240.8	1950.8 \pm 618.2	1899.4 \pm 269.5
Mg	1384.7 \pm 356.0	2039.4 \pm 324.0	1395.1 \pm 602.9	1971.5 \pm 425.2
Na	316.0 \pm 65.9	286.0 \pm 80.8	289.3 \pm 64.4	274.0 \pm 32.2
Ca	373.3 \pm 137.4	1761.7 \pm 518.2	1492.1 \pm 654.2	1565.4 \pm 142.7
Al	274.9 \pm 84.0	497.6 \pm 41.3	216.9 \pm 32.2	532.6 \pm 78.7
Mn	170.6 \pm 56.9	223.2 \pm 32.2	226.1 \pm 119.5	215.9 \pm 24.6
Zn	54.5 \pm 9.2	97.4 \pm 7.0	65.0 \pm 20.6	104.6 \pm 11.7
Cu	13.3 \pm 5.0	18.1 \pm 2.8	11.2 \pm 3.2	19.0 \pm 3.4
Fe	81.6 \pm 22.4	278.0 \pm 32.8	110.2 \pm 26.2	393.2 \pm 44.6
Pb	0.12 \pm 0.10	22.9 \pm 0.9	1.39 \pm 0.74	30.8 \pm 2.8
Cr	0.91 \pm 0.33	2.29 \pm 0.82	0.97 \pm 0.31	3.64 \pm 0.79
Cd	0.26 \pm 0.15	0.24 \pm 0.2	0.26 \pm 0.16	0.50 \pm 0.19
Ni	0.53 \pm 0.45	0.13 \pm 0.01	0.46 \pm 0.15	0.98 \pm 0.22
Ca/Al	1.48 \pm 0.66	3.9 \pm 1.5	7.11 \pm 2.05	2.9 \pm 0.4

The elements are presented as ppm, except S and P, which are presented as percentage of dry mass.

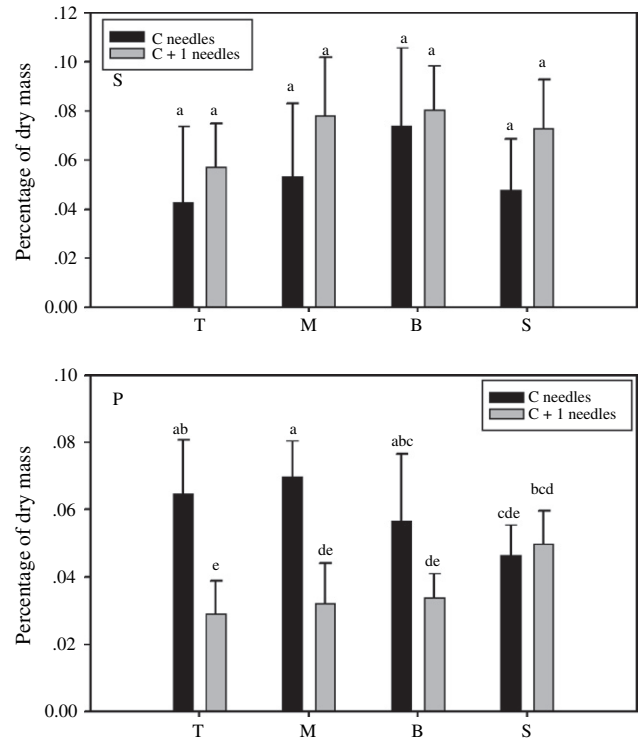


Fig. 2. Mean \pm SE contents of total S and P in different needle sections of the C and C + 1 needles of Masson pine ($n=6$). The significant differences among the sections between the needles were marked in the bars with different letters according to the Paired Sample *t*-test. The significance is set at 0.05 level. T = tip, M = middle, B = base and S = sheath.

Among the four parts, only the sheath was different statistically between the C and C + 1 needles. Furthermore, statistical differences among the sections were not found for K in the C needles, whereas differences between tip, middle and base sections were found in the C + 1 needles. Concentrations of Na were significantly different only in the middle section of the C and C + 1 needles; statistically highest concentrations appeared in the base section of C + 1 needle, whereas in the C needle it appeared in the middle section. Concentrations of Ca significantly peaked in C + 1 tip section, as in C sheath. The values in the C + 1 tip, middle and base sections were statistically higher than those in the corresponding section of C needles. Ca/Al ratios declined sharply in C + 1 needles from tip to base section, but it increased slightly in C needles. Tip Ca/Al values were significantly higher than any of the other sections in C + 1 needles, while in C needle, Ca/Al at the sheath was significantly higher than that in the tip and base section. The pattern of Ca/Al in the corresponding section between the aged needles was similar to the pattern of Ca (Fig. 3).

The concentrations of Cu and Fe increased from the tip towards the sheath of the C and C + 1 needles and were almost identical in both needle age classes, respectively. The concentrations of Fe (278 ppm in C needles and 393 ppm in C + 1 needles) and Cu (18 ppm in C needles and 19 ppm in C + 1 needles) were highest in the sheaths, which were significantly higher than those in the other needle sections (Fig. 4).

Mn concentrations ranged from 176 to 286 ppm in the C + 1 needles, and 158 to 223 ppm in the C needles did not

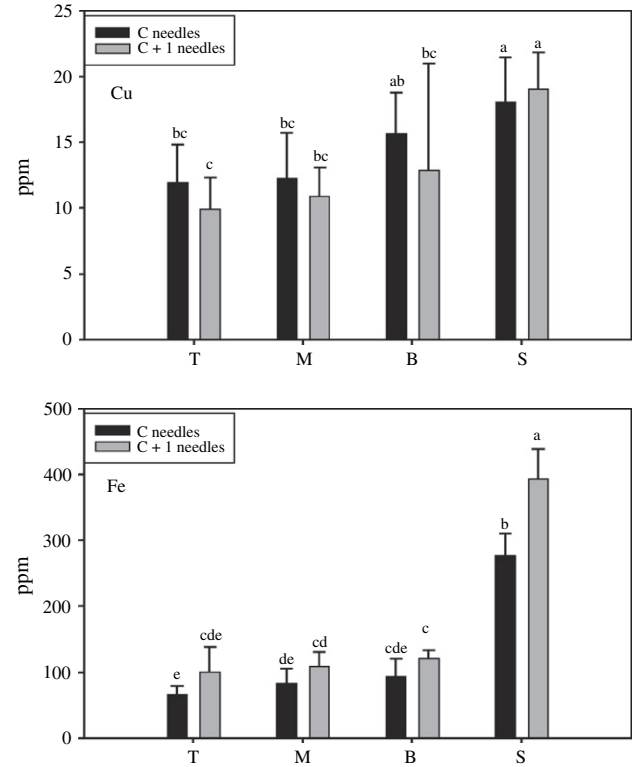
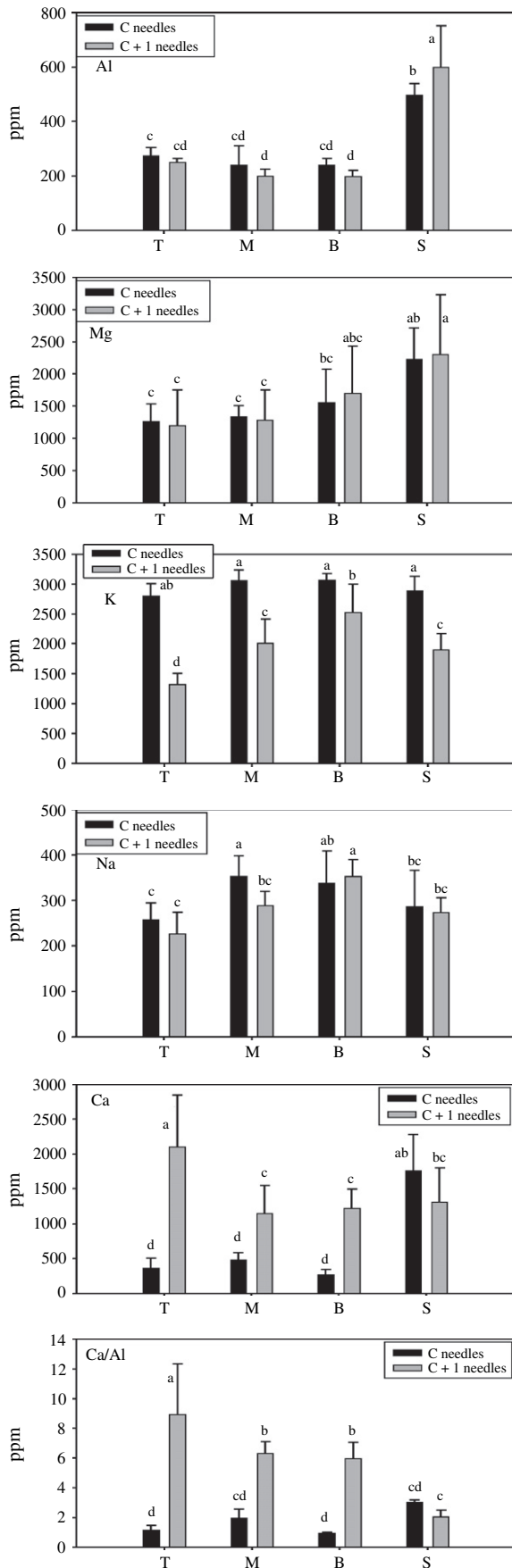


Fig. 4. Mean \pm SE concentrations of Cu and Fe in different needle sections of the C and C + 1 needles of Masson pine ($n = 6$). The significant differences among the sections between the needles were marked in the bars with different letters according to the Paired Sample t -test. The significance is set at 0.05 level. T = tip, M = middle, B = base and S = sheath.

show statistical difference both in C and C + 1 needles. Concentrations of Zn varied from 52 to 97 ppm in the C needles and 47 to 104 ppm in the C + 1 needles. It increased generally from the tip to the sheath in both the C and the C + 1 needles. In the C + 1 needles, base and sheath Zn statistically differed from that in the tip and middle sections, while in C needles, only sheath Zn was statistically higher than that of the other sections; no significant differences were observed among tip, middle and base sections (Fig. 5).

Lead concentrations along the needle length followed a similar pattern in both the C and C + 1 needles. It increased gradually from the tip to the base, and accumulated acutely in the sheath. The concentrations of Pb varied from 0.11 to 22.9 ppm in C needles, and from 2.2 to 30.8 ppm in the C + 1 needles, both with the maximum in the sheath. Cr increased from the tip to the base and significantly accumulated in the sheath of the C + 1 needles, while in the C needles no general pattern was observed except for the Cr accumulation in C sheath. Ni peaked in the C sheaths and varied from 0.3 to 1.3 ppm

Fig. 3. Mean \pm SE concentrations of Al, Mg, P, K, Na, Ca and the values of Ca/Al ratio in different needle sections of the C and C + 1 needles of Masson pine ($n = 6$). The significant differences among the sections between the needles were marked in the bars with different letters according to the Paired Sample t -test. The significance is set at 0.05 level. T = tip, M = middle, B = base and S = sheath.

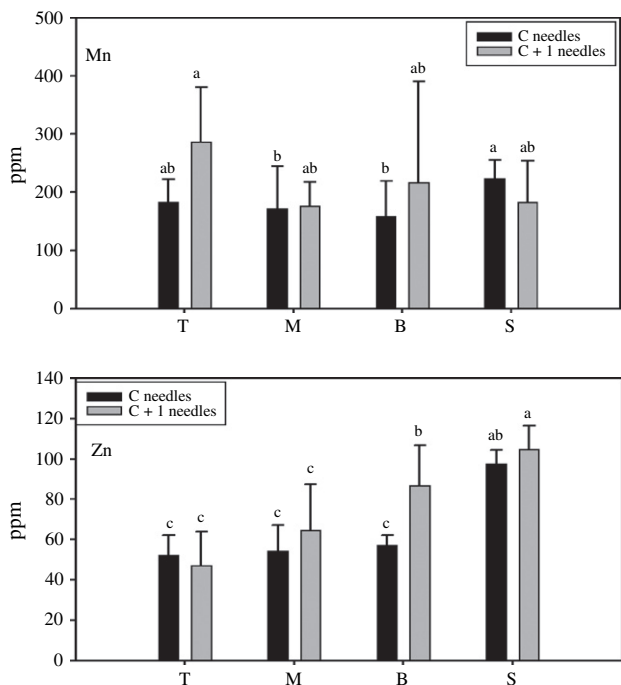


Fig. 5. Mean ± SE concentrations of Mn and Zn in different needle sections of the C and C + 1 needles of Masson pine (n = 6). The significant differences among the sections between the needles were marked in the bars with different letters according to the Paired Sample t-test. The significance is set at 0.05 level. T = tip, M = middle, B = base and S = sheath.

along the needle. The differences among tip, middle and base sections were not significant. The lowest Ni concentrations in needles were seen both in tip section of the C and the C + 1 needles. Values of Pb, Cr and Cd in the C + 1 sheaths were statistically higher than those in the C sheaths, but values of Ni were not significantly different from that in the C and C + 1 sheaths (Fig. 6).

4. Discussion

The mean concentration of elements differed intrinsically between the C and C + 1 needles and was related with element types. Several studies have shown that element concentration in needles can be used to diagnose nutrient deficiency or excess, particularly under pollution stress (Smidt, 1988; Zöttl and Hüttl, 1989; Dmuchowski and Bytnerowicz, 1995). Dmuchowski and Bytnerowicz (1995) established that the total S within the range of 0.06–0.07% is normal for Scots pine needles. Based on this, S deficiency may occur in the C + 1 needles indicated by its relatively lower content.

Normal levels for elements in plants were defined as 0.11–0.17% for P (Smidt, 1988), 3500–6600 ppm for K (Zöttl and Hüttl, 1989), 2300–5000 ppm for Ca and 500–1300 ppm for Mg (Smidt, 1988). In the present study, the mean concentrations of P, K and Ca in both C and C + 1 needles were far below the lower limits presented in the above studies, suggesting that nutrient deficiency for these elements may occur in Masson pine. This may cause prolonged abnormality in the growth

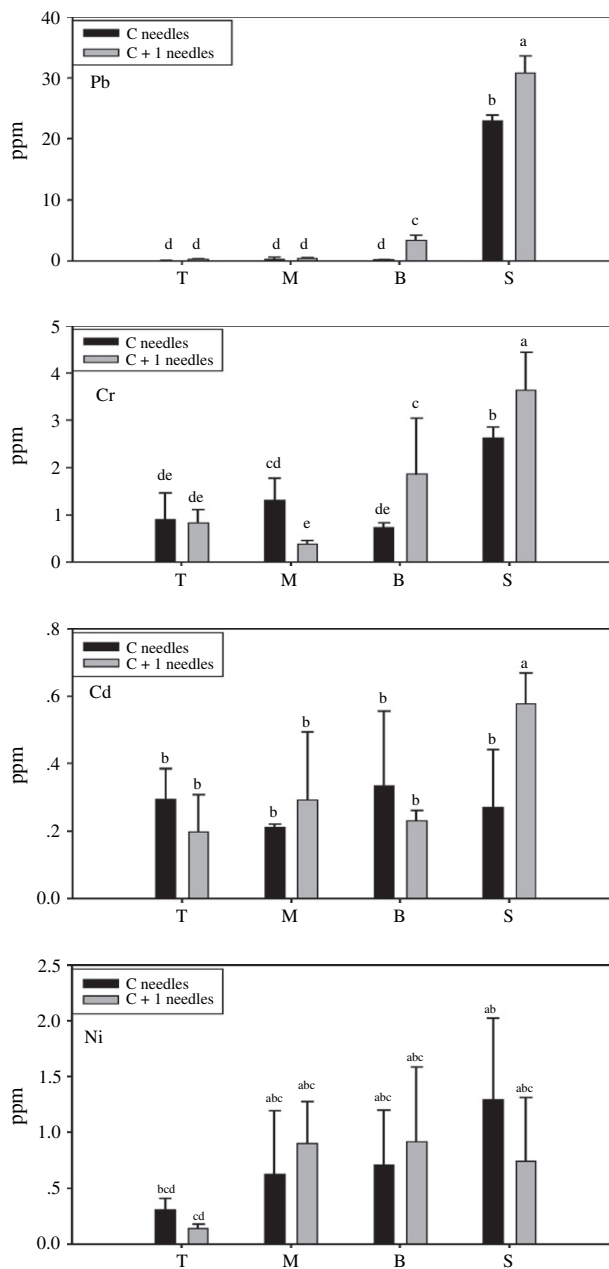


Fig. 6. Mean ± SE concentrations of Pb, Cr, Cd and Ni in different needle sections of the C and C = 1 needles of Masson pine (n = 6). The significant differences among the sections between the needles were marked in the bars with different letters according to the Paired Sample t-test. The significance is set at 0.05 level. T = tip, M = middle, B = base and S = sheath.

of needles, since the needle Mg, P and K levels have been shown to be closely related to needle longevity (Lamppu and Huttunen, 2003). Total P did not statistically differ among the tip, middle and base sections of the C and C + 1 needles. However, the P content in the three sections of C + 1 needles were lower than that in C needles, suggesting the efficiency of C + 1 needles (excluding sheath) as a bioindicator of P deficiency. Although no significant differences were observed for Al among tip, middle and base sections of the C and C + 1 needles, sheath Al was statistically higher than the other

three parts, implying more efficiency of sheaths as bioindicators for Al toxicity. Huettl (1989) reported that nutrient deficiency (and particularly Mg deficiency) was related to the decline of tree health. The Mg concentrations in the C and C + 1 needles were far below the levels presented by Smidt (1988). This indicated that the Masson pine growing under pollution stress may risk Mg insufficiency. The Ca/Al ratio in the foliage tissue was lower than 12.5, indicating 50% risk of Al-induced damage (Rengel, 1992). In our study, we noted that the ratio was 7.11 for the whole needle excluding sheath, 7.9 for tip, 6.2 for middle, and 6.0 for the base of the C + 1 needles, and the corresponding values were 1.48, 1.2, 2.0 and 0.8 of the C needles. Based on the values of the Ca/Al among the sections, the sheaths of C + 1 needles and the tip section of C needles are more suitable for diagnoses of Al toxicity than the other sections, because part of the Al is most likely to be on the needle surface (soil dust), and most likely sheath collects dust more than the other parts. The results implied that the decline of Masson pine forest at the moment in the Delta may be related to the Al toxicity.

Elevated concentrations of heavy metals in plant tissues generally indicate contamination associated with these elements (Guderian, 1977), and needle longevity has been reported to decrease linearly with the increase in heavy metal concentrations (Lamppu and Huttunen, 2003). Although no significant differences were found for Mn among the sections of both C and C + 1 needles, our results demonstrated that Mn concentrations both in C and C + 1 needles were far below the background level (977.5 ppm) of the Masson pine needles in the study area (Li and Zheng, 1989). This deficiency may cause abnormality in the growth of Masson pine in the future. The levels of Fe ranged from 66.6 to 277.9 ppm in C needles, and 100.3 to 393.2 ppm in C + 1 needles were higher than its background value of 97.6 ppm in the pine needle in the area (Li and Zheng, 1989). An excessive supply of copper can cause symptoms of chlorosis that are similar to the symptoms of Fe deficiency (Bergman, 1983). Several authors reported that the normal concentration of Cu in most plants is in the range of 4–13 ppm (Kabata-Pendias and Piotrowska, 1984), and about 11.0 ppm in Masson pine of the Pearl River Delta (Li and Zheng, 1989). Excessive Cu may destroy sub-cellular structure of plants (Sresty and Madhava, 1999). In our study, higher levels of Cu in the range of 9.9–19 ppm in the C + 1 needles and 11.9–18.0 ppm in the C needles might induce negative effects on the studied Masson pine forests. The concentrations of Zn in both C and C + 1 needles were also above the normal range of Zn in the Masson pine needles, which is 40.0 ppm in the area (Li and Zheng, 1989). Ni is essential for plants in low concentrations (Salisbury and Row, 1992). Concentration of 10–15 ppm of Ni in plants has been reported to be the toxic limit (Marschner, 1995). Ni concentrations among various sections in both C and C + 1 needles were far below the toxic levels, implying no Ni risk occurred in Masson pine in the Delta. Although some accumulations were found in the needle sheath, differences of Ni concentrations among the sections both in C and C + 1

needles were not significant, and it is hard to determine which part of the needle could be recommended as bioindicator to Ni contamination. Pb is well known as a pollutant of airborne particulates. Normal concentrations of Pb in plants are less than 10 ppm (Kabata-Pendias and Piotrowska, 1984). Allen et al. (1974) even proposed that lower than 3 ppm of Pb was the normal level for plants. Our results showed that the Pb concentrations along the length of C + 1 needles were close to the normal levels given by Allen et al. (1974). Although the Pb concentrations in needle parts did not exceed the normal level, the sheath Pb in C needles (22.9 ppm) and C + 1 needles (30.8 ppm) were far above the normal levels presented by Kabata-Pendias and Piotrowska (1984) and Allen et al. (1974), implying that Pb could be potentially harmful on local vegetation and environments in the future if the emission of pollutants is not controlled effectively.

Cadmium, one of the most dangerous pollutants for organisms, is mainly derived from anthropogenic sources and can be actively absorbed by plant roots, and easily transported within plants. Our results demonstrated that the current Cd level was 0.31–1.30 ppm in C needles and 0.14–0.92 ppm in C + 1 needles, which exceeded the level of 0.01–0.3 ppm from unpolluted natural stands reported by Allen et al. (1974) and the normal range of 0.05–0.5 ppm presented by Kabata-Pendias and Piotrowska (1984). According to the statistical results, only the sheath of C + 1 needles could be used as bioindicator to Cd contamination.

Significant accumulation of Al, Fe, Cu, Zn, Cr and Pb in the sheaths of both C and C + 1 needles was found, and that of Cd was found in the sheaths of C + 1 needles. The possible reasons for this may include the following: (1) sheath has relatively rougher surface than needles, (2) sheath may be more effective in binding elements and with heavy metals by the secretions or exudates such as turpentine and wax than needles, and (3) the special structures of sheath in capturing dust deposition and collecting pollutants in rainfall may allow it to be more effective as accumulator. These advantages make them in fact better indicators than the needles for particular pollutants in atmospheric monitoring.

5. Conclusions

The present results indicated that most elements measured were unevenly distributed along the different parts of Masson pine needles. Possible deficiency of P, K, Ca and Mn in needles under air pollution stress may occur due to their concentration level being below the normal range for plant growth, and this may be accompanied by Al toxicity due to low Ca/Al ratio in all parts of needles. Ni seems not a serious problem due to its low concentration in pine foliage, while Fe, Cu, Zn, Cd and Pb may render negative impacts on the Masson pine trees under pollution stress since their concentrations were far above their normal ranges for plant growth. Our study confirmed the usefulness of needle sheaths as a good bioindicator for particulate pollution containing Fe, Cu, Zn, Pb, Cr, Cd and Al. The results from the present study may provide implications in developing monitoring drafts and protocols,

particularly in areas with high frequency of pollution. Further studies on the structural and functional aspects of the needle (especially the sheath) in collecting pollutants should be emphasized.

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