

# ATMOSPHERIC INPUT OF ELEMENTS TO FOREST ECOSYSTEMS OF THE KAMPINOSKI NATIONAL PARK

KAROL J. KRAM

Polish Academy of Sciences Centre for Ecological Research in Dziekanów Leśny, ul. Konopnickiej 1, 05-092 Lomianki, Poland; e-mail: karolkram@wp.pl

## Abstract

Kram K.J.: Atmospheric input of elements to forest ecosystems of the Kampinoski National Park. *Ekologia (Bratislava)*, Vol. 31, No. 2, p. 125–137, 2012.

This study was carried out in the Kampinoski National Park in central Poland during the 1998 and 2000 vegetative seasons of April to October. Standard rain collectors were used and traps equipped with artificial foliage of 2, 6 and 12 m<sup>2</sup> m<sup>-2</sup> surface area were employed to estimate aerosol-gaseous input. The input of most elements (N-NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, S-SO<sub>4</sub><sup>2-</sup>, P-PO<sub>4</sub><sup>3-</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup>) was found to increase significantly with increased artificial foliage area., with only the H<sup>+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> ions deviating from this trend. This result confirmed that ecosystems with large foliage area receive a greater nutrient pool than those with a smaller area. However, due to similar increment in anionic and cationic input with the leaf area index (LAI), the proportions between anions and cations remained unchanged at different foliage areas.

*Key words:* bulk precipitation, aerosol-gaseous input of elements, macroelements, heavy metals, leaf area index, artificial foliage

## Introduction

The amounts of elements reaching ecosystems from the atmosphere form a basic issue in contemporary ecology. Studies on the elemental budget in plants and on soil processes are unimaginable without knowing these amounts. In some cases, as in coastal ecosystems, the atmosphere can be the sole source of nutrients. In other cases the atmosphere may be the source of pollutants leading to decreased biodiversity or to forest death. Therefore, studies on this subject have been carried out for a long time. While finding relevant data is relatively easy in open areas, studies in forest grounds pose some problems. It has been noted that elements reach the ecosystems not only with rain but also in the form of gases and aerosols which settle on surfaces such as leaves, branches and trunks. While these rain and aerosol-gaseous inputs account for the greatest percentage of atmospheric input of elements to ecosystems, insoluble dust-fraction settling, also containing aerosols and gases,

can be an additional source of various elements on the foliage surface (Lindberg, Turner, 1988; Likens et al., 1994). Forests form an ecosystem with a relatively large trapping area, and they are particularly capable of increasing this input. This results in a marked increase in the total pool of elements in the atmospheric input (Van Breemen et al., 1982; Lovett, Kinsman, 1990; Fenn, Kiefer, 1999). Moreover, it has been demonstrated that the intensity of this increase varies depending on the investigated element, with the aerosol-gaseous inputs of very important elements such as sulphur and nitrogen being quite remarkable (Lovett et al., 1985; Lindberg et al., 1986; Stachurski, Zimka, 2000). Studies of the remaining elements have produced contrasting results. According to Bobbink, the dry deposition of calcium and magnesium is intensive, but potassium is not (Bobbink et al., 1992). Although Stachurski and Zimka reported that the aerosol-gaseous fraction did not increase the inputs of sodium or potassium (Stachurski, Zimka, 2000), other studies showed an increase of atmospheric input associated with aerosols and gases of all important elements including sodium and potassium (Kram, 2001, 2005).

This work aims to estimate the atmospheric input of elements with the consideration of their aerosol-gaseous fraction, to find which elements are significantly important in this fraction and to determine how aerosol-gaseous input can increase the element pool reaching five different forest ecosystems in the Kampinoski National Park.

## Study area and methods

### Study area

Studies were carried out in the Kampinoski National Park in 1998 and 2000 during the vegetative season of April to October. Sampling sites were located in the small village of Granica (52°17' N and 20°27' E) in the southern part of this park (Fig. 1). There are only local roads in this neighbourhood, which is situated 30 km from Warsaw. According to data collected at the meteorological post in this village, precipitation in 1998 was 556.5 mm, in keeping with the long-term average for this area, and it was a rather warm year with a mean annual air temperature of 8.5 °C. This contrasted sharply with conditions in 2000, which recorded one of the highest mean annual temperatures of 9.4 °C, and the lowest precipitation since 1990, at 413.9 mm (Andrzejewska, 2003).

The foliage surface area was measured in the following five tree stands; pine – *Pinus sylvestris*, birch – *Betula pendula*, locust tree – *Robinia pseudoacacia*, alder – *Alnus glutinosa* and oak – *Quercus robur*. Results from atmospheric input were obtained from these stands which were all located at a distance no further than 5 km from the atmospheric deposition sampling sites.

### Sampling methods

According to current views, the reliable measurement of atmospheric input of elements in a given ecosystem should consider aerosol-gaseous inputs. Standard rain collectors do not measure this form of input, which means that the total actual input can be several times undervalued (Lindberg et al., 1986; Ross, Lindberg, 1994). In response to this problem, many methods have been developed to measure the input of elements in the form of aerosols and gases (Bytnerowicz et al., 1987; Krupa, 2002; Raymond et al., 2004; Alonso et al., 2005). In the present study, the method of “artificial foliage” was selected. This method enables a simple, but precise measurement of the amount of rain and aerosol-gaseous deposits. It consists of using modified rain collectors equipped with artificial foliage



Fig. 1. Location of the study site.

of a known surface area situated above the trap (Stachurski, Zimka, 2000). Since the shape of the artificial leaves appeared to have no effect on the results obtained (Stachurski, Zimka, 2000), only one type of artificial foliage was used, and this was similar in shape to coniferous tree branches. Four types of traps were used:

- Variant "0" – a typical rain collector without artificial foliage. This trap is constructed from a plastic canister with a funnel collecting the rainfall. It is protected from above by a net to catch the larger impurities and animal organisms in a nylon filter with 10  $\mu$  resolution at the end of the funnel. This enabled the separation of dust pollutants and other small particles, such as herbivore faeces (Fig. 2a).
- Variant "1s" – a trap equipped with artificial foliage of 2  $m^2$  per  $m^2$  area.
- Variant "3s" – 6  $m^2$  per  $m^2$ .
- Variant "6s" – 12  $m^2$  per  $m^2$  (Fig. 2b).

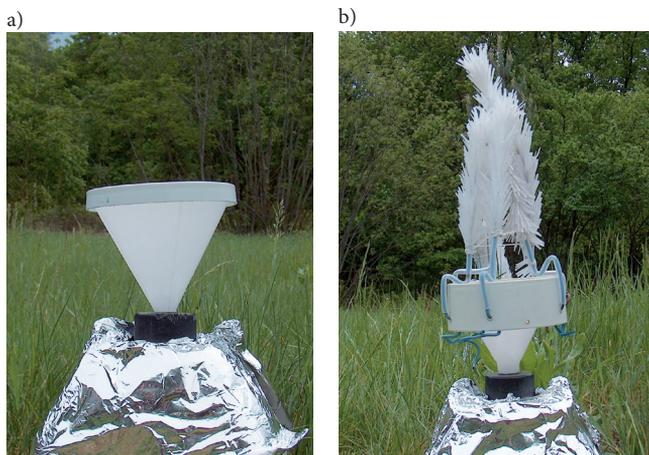


Fig. 2. Types of rain collectors:  
 2a. Typical rain collector.  
 2b. Rain collector with artificial foliage of an area of 12  $m^2 m^{-2}$ .

The gradient of surface areas fell within the range of the foliage cover found in forest ecosystems (Gower, Norman, 1991; Kram, 1998). Three traps of each variant were placed in an open area. Once every three weeks, the trapped water was collected and the nylon filters and plastic canisters were replaced with clean ones. The amount of water in each trap was measured in the field, and samples from each canister were collected and analyzed separately.

Dust sedimentation was estimated from the difference between the weight of the clean filter and that taken from the funnel after sampling. Both measurements were performed after drying the filter for 48 hours at 60 °C. At the end of the season, dust sedimentation was increased by dust settling on the internal walls of the funnels and on the artificial leaves. Artificial foliage was not cleaned nor exchanged during the entire sampling season. This meant that it resembled natural foliage which was also covered by dust in the vegetative season.

Each canister was wrapped in aluminium foil to protect the water from the sun's rays and from the development of algae and other micro-organisms.

### *Methods of measuring leaf area in forest ecosystems*

In order to determine the actual input of elements into the five studied ecosystems, one must know their intercepting area. This area is very similar to the leaf area index (LAI) which determines foliage area per unit area of the ground, and this is usually expressed in m<sup>2</sup> per m<sup>2</sup>. The LAI was measured in each studied tree-stand by the Li-Cor LAI-2000 optical device, which allows fast and relatively accurate measurements (Chason et al., 1991; Dufrière, Bréda, 1995). The measurements were performed in both study years in August, during the presumed period of largest foliage area.

According to Gower and Norman (1991) Li-Cor LAI-2000 undervalues the measurements of coniferous foliage area by 30 to 40%. Therefore, results obtained from pine forests were multiplied by a factor of 1.5, as has been calculated by cited authors for similar pine species. In deciduous forests, the leaf area index was also estimated based on measurements of the leaves which had fallen in autumn (Stachurski, Zimka, 1990).

In all the LAI records, all trees and shrub species present in a given ecosystem were considered, not only the dominant tree species.

### *Laboratory methods*

The pH was measured potentiometrically by the ion meter Orion Analyser 940 USA and the ROSS Sure-Flow electrode of Thermo Orion (USA).

Concentrations of the Na<sup>+</sup>, N-NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> cations and the Cl<sup>-</sup>, N-NO<sub>3</sub><sup>-</sup> and S-SO<sub>4</sub><sup>2-</sup> anions were determined in two analytical cycles by the Metrohm IC System 690, Switzerland, ion chromatograph. Water samples were filtered through 0.45 µm Teflon filters prior to analysis.

The concentrations of zinc, lead, cadmium and copper were analyzed by the inverse voltamperometric method (DPASV) using the Metrohm 646 VA Processor equipped with Metrohm 675 VA Sample Changer (Switzerland). Before this analysis, water samples were filtered through 0.45 µm Teflon filters, acidified with HNO<sub>3</sub> (Aristar, BDH, UK) and mineralized in ultraviolet for 7 hours.

The concentration of P-PO<sub>4</sub> was determined colorimetrically by the molybdenum-blue method using a UV-VIS Shimadzu (Japan) spectrophotometer.

### *Statistical methods*

Since the study period in every year was slightly different, for comparative reasons the element inputs obtained during the vegetative season were calculated, using "30 day months". Calculations were performed separately for each stand, so that 3 results were obtained in a season for each trap variant, and atmospheric input for a given variant was calculated as the arithmetic mean of these results.

Regressions of the relationship between the LAI and the magnitude of the atmospheric input of elements were calculated based on results from the open area obtained in the traps with and without artificial foliage. This resulted in a total of 24 data, composed of 4 variants at 3 sites for 2 seasons.

The  $Q_{10}$  index was also calculated for elements which were described by statistically significant ( $p < 0.05$ ) regression equations. This index demonstrates how the dependent variable of atmospheric input increases as the independent variable (LAI) increases by 10 units, which is also the difference in LAI between the open site and ecosystems with a large area of leaves.

Regressions of the input of particular elements on the various foliage areas, and the actual foliage area measured in the field, were requisite for the calculation of the total atmospheric input of elements to particular ecosystems.

## Results

Calcium had the highest input in rain, found here in the traps without artificial foliage. Its mean input was  $0.607 \text{ kg ha}^{-1} \text{ month}^{-1}$  ( $0.532$  and  $0.682 \text{ kg ha}^{-1} \text{ month}^{-1}$  in 1998 and 2000, respectively). The second largest input was that of sulphur, with  $0.524 \text{ kg ha}^{-1} \text{ month}^{-1}$  ( $0.531$  and  $0.517$  respectively) and the third was ammonium-nitrogen with  $0.453 \text{ kg ha}^{-1} \text{ month}^{-1}$  ( $0.305$  and  $0.600$  respectively). Mean inputs were recorded for nitrate-nitrogen, potassium and chlorides at  $0.259$ ,  $0.258$  and  $0.244 \text{ kg ha}^{-1} \text{ month}^{-1}$ , respectively, while the deposition of sodium, magnesium and phosphorus was low, not exceeding  $0.2 \text{ kg ha}^{-1} \text{ month}^{-1}$ . The lowest inputs of analyzed elements were noted for hydrogen ions, and heavy metals registered from  $0.04 \text{ g ha}^{-1} \text{ month}^{-1}$  for cadmium to  $59.2 \text{ g ha}^{-1} \text{ month}^{-1}$  for zinc. The equivalent levels for anions were  $0.058 \text{ keq ha}^{-1} \text{ month}^{-1}$  ( $0.056$  in 1998 and  $0.060$  in 2000) and those for cations were  $0.082 \text{ keq ha}^{-1} \text{ month}^{-1}$  ( $0.066$  and  $0.098$  in 1998 and 2000, respectively). The inputs of these particular elements were delivered in a mean rainfall of  $45.9 \text{ mm month}^{-1}$ , with  $49.5$  and  $42.3$  in the respective years (Table 1).

Table 1. Monthly mean rainfall input of elements, water and dust in the Kampinoski National Park in the vegetative seasons of 1998 and 2000. Results were obtained from traps without artificial foliage (n=3).

Element		1998	± SD	2000	± SD	Average
dust	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	4.7	± 0.7	5.5	± 0.9	5.1
water	( $\text{mm month}^{-1}$ )	49.5	± 0.5	42.3	± 1.4	45.9
H <sup>+</sup>	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	15.8	± 2.8	4.0	± 2.2	9.9
Na <sup>+</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.153	± 0.011	0.154	± 0.024	0.153
N-NH <sub>4</sub> <sup>+</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.305	± 0.187	0.600	± 0.275	0.453
K <sup>+</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.216	± 0.111	0.300	± 0.102	0.258
Mg <sup>2+</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.064	± 0.015	0.077	± 0.015	0.070
Ca <sup>2+</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.532	± 0.066	0.682	± 0.018	0.607
Σ cations	( $\text{keq ha}^{-1} \text{ month}^{-1}$ )	0.066	± 0.018	0.098	± 0.023	0.082
Cl <sup>-</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.210	± 0.039	0.278	± 0.068	0.244
N-NO <sub>3</sub> <sup>-</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.243	± 0.024	0.276	± 0.033	0.259
S-SO <sub>4</sub> <sup>2-</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.531	± 0.038	0.517	± 0.048	0.524
P-PO <sub>4</sub> <sup>3-</sup>	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	0.075	± 0.039	0.092	± 0.040	0.083
Σ anions	( $\text{keq ha}^{-1} \text{ month}^{-1}$ )	0.056	± 0.005	0.060	± 0.007	0.058
Zn <sup>2+</sup>	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	50.9	± 4.2	67.6	± 5.5	59.2
Cd <sup>2+</sup>	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	0.04	± 0.01	0.04	± 0.01	0.04
Pb <sup>2+</sup>	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	0.8	± 0.1	0.3	± 0.1	0.6
Cu <sup>2+</sup>	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	2.7	± 0.5	3.8	± 0.2	3.3

The input differences between the years were small, with only hydrogen ions significantly different in 1998 with an almost four times higher level than in 2000, at 15.8 g ha<sup>-1</sup> month<sup>-1</sup> compared to 4.0 g ha<sup>-1</sup> month<sup>-1</sup> respectively (Table 1). While similar input decreases were also found for lead ammonium-nitrogen showed a reverse pattern with an increased input from 0.3 kg ha<sup>-1</sup> month<sup>-1</sup> in 1998 to 0.6 kg ha<sup>-1</sup> month<sup>-1</sup> in 2000.

There was a strong positive correlation between the atmospheric input of a given ion and the area of artificial foliage installed over the rain trap. This regularity was valid for most of the analyzed elements (Na<sup>+</sup>, N-NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, S-SO<sub>4</sub><sup>2-</sup>, P-PO<sub>4</sub><sup>3-</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup> as in Table 2). The increased input was a result of increased concentrations in the rain, because the amounts of water collected in the rain traps were similar irrespective of the area of artificial foliage.

The most intensive increase in atmospheric input in the area of artificial foliage, indicating the highest aerosol-gaseous input, was for cadmium. The increase in area of artificial foliage from 0 to 10 m<sup>2</sup> per m<sup>2</sup> provided double the amount of trapped cadmium (Q<sub>10</sub> = 2.54). The increase for other ions was smaller, varying from Q<sub>10</sub> = 1.54 for potassium to Q<sub>10</sub> = 2.21 for nitrate-nitrogen. The relationship between atmospheric input and the area of artificial foliage is presented in Fig. 3, where the nitrate ion is used as an example. The lowest, but statistically significant, value of Q<sub>10</sub> = 1.32 was found for copper (Table 2). However,

Table 2. Coefficients of the linear regression of element inputs on leaf area index (LAI in m<sup>2</sup> m<sup>-2</sup>) and values of the Q<sub>10</sub> index. Relationships are based on data obtained in the Kampinoski National Park in the years 1998 and 2000.

Element		a	b	±SE	r	p	Q <sub>10</sub>
dust	(kg ha <sup>-1</sup> month <sup>-1</sup> )	5.3	-0.032	0.045	-0.15	NS	-
water	(mm month <sup>-1</sup> )	44.9	0.015	0.249	0.01	NS	-
H <sup>+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	11.3	-0.099	0.385	-0.05	NS	-
Na <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.157	0.012	0.003	0.68	<0.001	1.80
N-NH <sub>4</sub> <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.602	0.039	0.015	0.49	<0.05	1.65
K <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.315	0.017	0.005	0.58	<0.01	1.54
Mg <sup>2+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.078	0.007	0.001	0.89	<0.001	1.85
Ca <sup>2+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.624	0.044	0.005	0.87	<0.001	1.70
Σ cations	(keq ha <sup>-1</sup> month <sup>-1</sup> )	0.095	0.007	0.001	0.76	<0.001	1.68
Cl <sup>-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.258	0.021	0.004	0.73	<0.001	1.81
N-NO <sub>3</sub> <sup>-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.294	0.035	0.002	0.96	<0.001	2.21
S-SO <sub>4</sub> <sup>2-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.558	0.037	0.004	0.89	<0.001	1.66
P-PO <sub>4</sub> <sup>3-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.111	0.011	0.003	0.64	<0.001	1.95
Σ anions	(keq ha <sup>-1</sup> month <sup>-1</sup> )	0.063	0.005	0.000	0.93	<0.001	1.86
Zn <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	57.6	0.227	0.396	0.12	NS	-
Cd <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	0.04	0.006	0.001	0.87	<0.001	2.54
Pb <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	0.60	0.008	0.014	0.12	NS	-
Cu <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	3.58	0.115	0.040	0.53	<0.01	1.32

Notes: a – constant, b – inclination of the regression line, SE – standard error, r – correlation coefficient, p – significance, NS – non-significant (p > 0.05), Q<sub>10</sub> – coefficient that informs how will the dependent variable (atmospheric input) change when the independent variable (LAI) changes by 10 units; n = 24

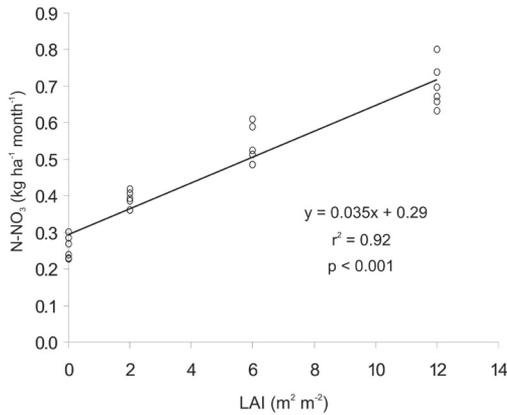


Fig. 3. Relationship between the artificial foliage area and atmospheric input of nitrates. Regression was based on data obtained in the Kampinoski National Park in the years 1998 and 2000.  $n = 24$ .

no statistically significant relationship of the type described above was registered for dust, hydrogen ions, zinc or lead.

Increased intercepting area similarly increased the input of both cations and anions, as calculated by the sum of their equivalents. The  $Q_{10}$  index was 1.86 for anions and 1.68 for cations (Fig. 4). Due to the similar increase, the proportions between cations and anions did not change with varying areas of leaves. The parallel increase in both ions could be the reason for the above mentioned lack of positive relationship between foliage surface area and the input of hydrogen ions.

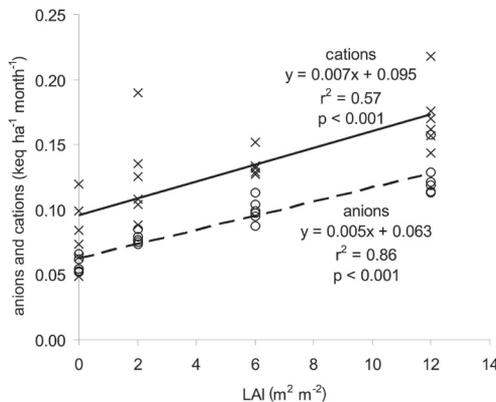


Fig. 4. Relationship between the input of anions and cations and the artificial foliage area. Regressions are based on data from the Kampinoski National Park in the years 1998 and 2000. The input of cations is a sum of equivalents of:  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ; that of anions is a sum of:  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ .  $n = 24$ .

Although the effect of artificial foliage on inputs was more evident in 1998 than in 2000, the input increase with increasing artificial foliage area was confirmed for the majority of ions in both study seasons (Table 3).

The highest leaf area index in the five studied forest ecosystems in both study seasons was established in the oak tree stand at  $LAI = 6.29 \text{ m}^2 \text{ m}^{-2}$  (Table 3). This was lower in the alder stand at  $LAI = 3.88 \text{ m}^2 \text{ m}^{-2}$ , and the remaining three stands of pine, birch and locust trees registered low LAIs of 1.97, 2.50 and  $2.52 \text{ m}^2 \text{ m}^{-2}$ , respectively (Table 4).

The input of elements for particular tree stands was calculated. based on the leaf area of the ecosystem, and the relationship between element input and foliage area is shown in Table 4. It is apparent that the oak forest had the highest LAI, and that this received

Table 3. Coefficients of the linear regression of element inputs on leaf area index (LAI in  $\text{m}^2 \text{ m}^{-2}$ ) and values of the  $Q_{10}$  index. Relationships are given separately for two study seasons. Explanations as in Table 2.

Element		Year	a	b	$\pm$ SE	r	p	$Q_{10}$
dust	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	5.2	-0.011	0.056	-0.06	NS	-
		2000	5.4	-0.053	0.076	-0.21	NS	-
water	( $\text{mm month}^{-1}$ )	1998	49.0	0.191	0.129	0.42	NS	-
		2000	40.9	-0.160	0.141	-0.34	NS	-
$\text{H}^+$	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	1998	18.8	-0.100	0.321	-0.10	NS	-
		2000	3.8	-0.097	0.122	-0.24	NS	-
$\text{Na}^+$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.160	0.020	0.003	0.92	<0.001	2.26
		2000	0.154	0.005	0.001	0.77	<0.01	1.31
$\text{N-NH}_4^+$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.362	0.049	0.012	0.79	<0.01	2.36
		2000	0.843	0.029	0.021	0.40	NS	-
$\text{K}^+$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.247	0.026	0.006	0.82	<0.01	2.06
		2000	0.383	0.008	0.008	0.31	NS	-
$\text{Mg}^{2+}$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.070	0.008	0.001	0.94	<0.001	2.17
		2000	0.085	0.005	0.001	0.87	<0.001	1.58
$\text{Ca}^{2+}$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.601	0.058	0.007	0.94	<0.001	1.96
		2000	0.646	0.030	0.004	0.92	<0.001	1.47
$\Sigma$ cations	( $\text{keq ha}^{-1} \text{ month}^{-1}$ )	1998	0.075	0.009	0.001	0.90	<0.001	2.15
		2000	0.116	0.004	0.002	0.64	<0.05	1.38
$\text{Cl}^-$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.226	0.031	0.007	0.83	<0.001	2.38
		2000	0.290	0.011	0.003	0.77	<0.01	1.37
$\text{N-NO}_3^-$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.284	0.037	0.004	0.95	<0.001	2.29
		2000	0.303	0.034	0.003	0.97	<0.001	2.13
$\text{S-SO}_4^{2-}$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.560	0.046	0.004	0.96	<0.001	1.81
		2000	0.556	0.028	0.003	0.94	<0.001	1.50
$\text{P-PO}_4^{3-}$	( $\text{kg ha}^{-1} \text{ month}^{-1}$ )	1998	0.098	0.016	0.003	0.84	<0.001	2.60
		2000	0.124	0.005	0.004	0.40	NS	-
$\Sigma$ anions	( $\text{keq ha}^{-1} \text{ month}^{-1}$ )	1998	0.062	0.006	0.001	0.94	<0.001	2.03
		2000	0.065	0.004	0.000	0.96	<0.001	1.69
$\text{Zn}^{2+}$	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	1998	50.8	1.005	0.332	0.69	<0.05	1.20
		2000	64.4	-0.550	0.616	-0.27	NS	-
$\text{Cd}^{2+}$	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	1998	0.046	0.007	0.001	0.93	<0.001	2.52
		2000	0.032	0.006	0.001	0.87	<0.001	2.88
$\text{Pb}^{2+}$	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	1998	0.86	0.013	0.008	0.48	NS	-
		2000	0.34	0.003	0.007	0.16	NS	-
$\text{Cu}^{2+}$	( $\text{g ha}^{-1} \text{ month}^{-1}$ )	1998	3.14	0.202	0.070	0.68	<0.05	1.64
		2000	4.02	0.027	0.022	0.36	NS	-

Table 4. Theoretical input of elements to particular ecosystems calculated from LAI of particular tree stands and regression equations (Table 2) of elemental input on artificial foliage area. Results were based on data from the Kampinoski National Park in vegetative seasons of the years 1998 and 2000.

Element		Open area	Pine	Birch	Stands Locust tree	Alder	Oak
LAI	(m <sup>2</sup> m <sup>-2</sup> )	0.00	1.97	2.50	2.51	3.88	6.29
dust	(kg ha <sup>-1</sup> month <sup>-1</sup> )	5.3	5.3	5.3	5.3	5.3	5.3
water	(mm month <sup>-1</sup> )	44.9	44.9	44.9	44.9	44.9	44.9
H <sup>+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	11.3	11.3	11.3	11.3	11.3	11.3
Na <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.157	0.181	0.187	0.187	0.204	0.232
N-NH <sub>4</sub> <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.602	0.679	0.700	0.700	0.753	0.847
K <sup>+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.315	0.348	0.358	0.358	0.381	0.422
Mg <sup>2+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.078	0.092	0.096	0.096	0.105	0.122
Ca <sup>2+</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.624	0.711	0.734	0.734	0.795	0.901
Σ cations	(keq ha <sup>-1</sup> month <sup>-1</sup> )	0.095	0.109	0.113	0.113	0.122	0.139
Cl <sup>-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.258	0.299	0.311	0.311	0.339	0.390
N-NO <sub>3</sub> <sup>-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.294	0.363	0.382	0.382	0.430	0.514
S-SO <sub>4</sub> <sup>2-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.558	0.631	0.651	0.651	0.702	0.791
P-PO <sub>4</sub> <sup>3-</sup>	(kg ha <sup>-1</sup> month <sup>-1</sup> )	0.111	0.133	0.139	0.139	0.154	0.180
Σ anions	(keq ha <sup>-1</sup> month <sup>-1</sup> )	0.063	0.073	0.076	0.076	0.082	0.094
Zn <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	57.6	57.6	57.6	57.6	57.6	57.6
Cd <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	0.040	0.052	0.055	0.055	0.063	0.078
Pb <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	0.60	0.60	0.60	0.60	0.60	0.60
Cu <sup>2+</sup>	(g ha <sup>-1</sup> month <sup>-1</sup> )	3.58	3.81	3.87	3.87	4.03	4.30

a markedly larger pool of elements than the open areas and the pine, birch and locust tree stands which registered lower LAI. This was particularly significant for elements with the highest  $Q_{10}$  index, whose input increased substantially with foliage area. These elements in the study area included cadmium, nitrate-nitrogen, phosphorus and magnesium. Their pool delivered a high LAI to ecosystems. For example, the oak tree stand pool was almost twice that supplied to open areas, and this was 30–50% higher than that delivered to pine tree stands which had low LAI (Table 4). Respective differences in the nitrate-nitrogen pool were 0.220 and 0.151 kg ha<sup>-1</sup> month<sup>-1</sup>, and this led to 1.3 kg more nitrogen delivered to the oak stand than to non-vegetated grounds, and 0.9 kg more than that supplied to the pine forest, during the 180 day vegetative period.

## Discussion

Atmospheric delivery of sulphur to the Kampinoski forest was 0.524 kg S-SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> month<sup>-1</sup>, or 6.3 kg ha<sup>-1</sup> y<sup>-1</sup>. Considering aerosol-gaseous input, the oak tree stand had the largest intercepting area and it received 9.5 kg S-SO<sub>4</sub><sup>2-</sup> ha<sup>-1</sup> y<sup>-1</sup>. This proved to be a smaller input than

quoted in literature data. This same area of Kampinoski forest was previously supplied with  $12.4 \text{ kg S ha}^{-1} \text{ y}^{-1}$  from the atmosphere 20 years before (Zimka, 1989). In other regions of Poland, the input of sulphur ranged in 1993 from  $7.8 \text{ kg S-SO}_4^{2-}$  in the Czuluchów Forest in north-western Poland (Tarabuła, 1995) to  $17.1 \text{ kg ha}^{-1} \text{ y}^{-1}$  in Pogórze Wielickie in southern Poland between 1991 and 1995 (Szarek-Łukaszewska, 1999). There was, however, a slightly lower value of  $16.0 \text{ kg}$  given by Stachurski, Zimka (2000) for the Karkonosze Mts region, in data from 1996–1997. This latter value was enriched by aerosol-gaseous input, which accounted for as much as  $22.2 \text{ kg}$  of sulphur deposited per hectare on dying spruce forests (Stachurski, Zimka, 2000).

Such a low input of  $\text{S-SO}_4^{2-}$  obtained in this present study may be a result of a systematic decrease in the deposition of this ion recorded in Poland during the 1980's and 1990's (Szarek-Łukaszewska, 2003), and also in Western Europe (Fowler et al., 2005; Giannitrapani et al., 2006; Zimmermann et al., 2006). A systematic decrease in  $\text{SO}_2$  in the air was also observed by Adamski, Wawrzoniak (1998) and Szarek-Łukaszewska (2003).

The atmospheric input of nitrogen showed a different pattern, with literature data being more consistent. This present study showed deposit of  $3.1 \text{ kg N-NO}_3^-$  and  $5.4 \text{ kg N-NH}_4^+$ , at  $8.5 \text{ kg N ha}^{-1} \text{ y}^{-1}$ , together with an aerosol-gaseous input of  $6.2$  and  $10.2 \text{ kg}$  comprising a total of  $16.4 \text{ kg N ha}^{-1} \text{ y}^{-1}$ . Consideration of aerosol-gaseous forms in this study is important, because the total nitrogen input obtained in this way slightly exceeded the critical load assumed to be dangerous for ecosystems. Nitrogen loads of  $10\text{--}15 \text{ kg ha}^{-1} \text{ y}^{-1}$  for coniferous forests and  $15\text{--}20 \text{ kg ha}^{-1} \text{ y}^{-1}$  for deciduous forests are assumed to be at a critical level (Bobbink, Roelofs, 1995). Twenty years ago the Kampinoski forest received  $10.4 \text{ kg N}$  per ha per year, including organic nitrogen but excluding aerosol-gaseous forms, and this was one third less than now (Zimka, 1989). Similar loads of  $10.8 \text{ kg inorganic N ha}^{-1} \text{ y}^{-1}$  ( $7.5 \text{ kg N-NH}_4^+$  and  $3.3 \text{ kg N-NO}_3^-$ ) were also reported for Czuluchów forest by Tarabuła (1995). Higher atmospheric inputs were found, however, in Pogórze Wielickie at  $5.3 \text{ kg N-NO}_3^-$  to as much as  $15.1 \text{ kg N-NH}_4^+$  (Szarek-Łukaszewska, 1999). Therefore, inputs recorded in this present study and in the Karkonosze Mts, even counting the aerosol-gaseous fractions of  $10.2 \text{ kg N-NH}_4^+$  (Kampinoski forest) or  $11.3 \text{ kg N-NH}_4^+ \text{ ha}^{-1} \text{ y}^{-1}$  (the Karkonosze Mts – Stachurski, Zimka, 2000), were lower than those in Pogórze Wielickie. This input can be considered low compared with results obtained in Western Europe. Monitoring carried out between 1985 and 1995 throughout Europe demonstrated that the atmospheric input of nitrogen exceeded  $15 \text{ kg ha}^{-1} \text{ y}^{-1}$  in almost half the sampling sites (Erisman, De Vries, 2000). In contrast to sulphur, the atmospheric deposition of nitrogen has not recently changed, and remains at the same level or has even increased (Rodà et al., 2002; Fowler et al., 2005). This is despite the noted decrease in nitrogen dioxide concentrations in the air (Adamski, Wawrzoniak, 1998).

Some studies in other regions showed that the input of potassium, sodium or phosphorus might be independent of foliage area (Bobbink et al., 1992; Stachurski, Zimka, 2000), but for potassium and sodium our present results confirmed the earlier studies in the Pomerania region regarding the effect of foliage area on the atmospheric inputs of such elements (Kram, 2005). Deposition of aerosols and gases is known to depend on

geographic location. It is more intensive in coastal regions than in inland areas (Ferm et al., 2000) and it sometimes constitutes the main percentage of atmospheric input (Tarnay et al., 2001; Sanz et al., 2002). Other factors affecting deposits include land relief (Rodà et al., 2002) and the distance from pollution sources. In non-polluted areas, the contribution of dust and aerosols to nitrogen input is small, while in urban areas it becomes the main source (Lovett, Lindberg, 1993). Japanese studies showed a much larger input of nitrogen and sulphur onto the mountain slope facing urban areas than on the opposite slope of the same mountain (Chiwa et al., 2003).

In the Karkonosze Mts, the atmospheric input of many elements increased with foliage area, but the intensity of deposition was higher for anions than for cations. Consequently, ecosystems with very large foliage area received relatively more acidifying anions than alkalinizing cations. This in turn resulted in the acidification of rainfall that fell on spruce forests with large foliage area (Stachurski, Zimka, 2000). Acidification of Kampinoski forest did not occur, and the deposition of hydrogen ions was, contrary to other ions, the same irrespective of the foliage area. Deposits of all the main elements rose with the same intensity with increasing foliage area, and the high aerosol-gaseous acidifying input of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  was neutralised by equally high input of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ . Therefore, proportions between the elements, as well as acidification, remained the same irrespective of large or small foliage area in the ecosystems. This stable acidity and ionic proportion is important for the health of forest ecosystems in the Kampinoski National Park.

Although the applied method was relatively simple and inexpensive, it enabled satisfactory results to be obtained. Demonstrating the importance of aerosol-gaseous input for element-cycling in forest ecosystems suggests that the methods for analyzing this input are indispensable in studies of the type presented here. Only through these means can a reliable assessment of atmospheric ionic deposition be obtained, and processes during their passage through the forest canopy evaluated.

## Conclusion

1. In the Kampinoski forest, larger foliage area resulted in higher atmospheric deposition of:  $\text{N-NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ . This increased input was invalid only for hydrogen ion, zinc and lead.
2. The relationship between foliage area and this input ensured that the ecosystems with large intercepting areas received a much larger pool of nutrients and toxic elements than those with smaller area.
3. Due to a similar increase in the input of anions and cations, the proportions between particular ions did not change along the gradient of foliage area.

*Translated by the author  
English corrected by R. Marshall*

## Acknowledgements

The author wishes to express his gratitude to A. Stachurski and J. Zimka for scientific supervision and invaluable advice, and to K. Zielska for her help in chemical analysis. The author also wishes to thank L. Kufel for his help in preparing the English version of this manuscript.

## References

- Adamski, L., Wawrzoniak, J., 1998: Air pollution research in four selected regions in Poland (in Polish). Prace Instytutu Badawczego Leśnictwa, seria A, 863: 5–34.
- Alonso, R., Bytnerowicz, A., Boarman, W.I., 2005: Atmospheric dry deposition in the vicinity of the Salton Sea, California – I: Air pollution and deposition in a desert environment. *Atmos. Environ.*, 39: 4671–4679. <http://dx.doi.org/10.1016/j.atmosenv.2005.04.016>
- Andrzejewska, A., 2003: Climate of the Kampinoska forest (in Polish). In Andrzejewski, R. (ed.), *Kampinoski Park Narodowy*, Tom I, pp. 41–68.
- Bobbink, R., Heil, G.W., Raessen, M.B.A.G., 1992: Atmospheric deposition and canopy exchange processes in heathland ecosystems. *Environ. Pollut.*, 75: 29–37. [http://dx.doi.org/10.1016/0269-7491\(92\)90053-D](http://dx.doi.org/10.1016/0269-7491(92)90053-D)
- Bobbink, R., Roelofs, J.G.M., 1995: Nitrogen critical loads for natural and semi-natural ecosystems: the empirical approach. *Water Air Soil Pollut.*, 85: 2413–2418. <http://dx.doi.org/10.1007/BF01186195>
- Bytnerowicz, A., Miller, P.R., Olszyk, D.M., 1987: Dry deposition of nitrate, ammonium and sulfate to a *Ceanothus crassifolius* canopy and surrogate surfaces. *Atmos. Environ.*, 21: 1805–1814. [http://dx.doi.org/10.1016/0004-6981\(87\)90121-1](http://dx.doi.org/10.1016/0004-6981(87)90121-1)
- Chason, J.W., Baldocchi, D.D., Huston, M.A., 1991: A comparison of direct and indirect methods for estimating forest canopy leaf area. *Agric. For. Meteorol.*, 57: 107–128. [http://dx.doi.org/10.1016/0168-1923\(91\)90081-Z](http://dx.doi.org/10.1016/0168-1923(91)90081-Z)
- Chiwa, M., Oshiro, N., Miyake, T., Nakatani, N., Kimura, N., Yuhara, T., Hashimoto, N., Sakugawa, H., 2003: Dry deposition washoff and dew on the surfaces of pine foliage on the urban- and mountain-facing sides of Mt. Gokurakuji, western Japan. *Atmos. Environ.*, 37, 3: 327–337. [http://dx.doi.org/10.1016/S1352-2310\(02\)00889-0](http://dx.doi.org/10.1016/S1352-2310(02)00889-0)
- Dufrène, E., Bréda, N., 1995: Estimation of deciduous forest leaf area index using direct and indirect methods. *Oecologia*, 104: 156–162. <http://dx.doi.org/10.1007/BF00328580>
- Erisman, J.W., De Vries, W., 2000: Nitrogen deposition and effects on European forests. *Environ. Rev.*, 8: 65–93. <http://dx.doi.org/10.1139/a00-006>
- Fenn, M.E., Kiefer, J.W., 1999: Throughfall deposition of nitrogen and sulphur in a Jeffrey pine forest in the San Gabriel Mountains, Southern California. *Environ. Pollut.*, 104: 179–187. [http://dx.doi.org/10.1016/S0269-7491\(98\)00195-X](http://dx.doi.org/10.1016/S0269-7491(98)00195-X)
- Ferm, M., Westling, O., Hultberg, H., 2000: Atmospheric deposition of base cations, nitrogen and sulphur in coniferous forests in Sweden – a test of a new surrogate surface. *Boreal Env. Res.*, 5: 197–207.
- Fowler, D., Smith, R.I., Muller, J.B.A., Hayman, G., Vincent, K.J., 2005: Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. *Environ. Pollut.*, 137: 15–25. <http://dx.doi.org/10.1016/j.envpol.2004.12.028>
- Giannitrapani, M., Bowman, A., Scott, M., Smith, R., 2006: Sulphur dioxide in Europe: Statistical relationship between emissions and measured concentrations. *Atmos. Environ.*, 40: 2524–2532. <http://dx.doi.org/10.1016/j.atmosenv.2005.12.052>
- Gower, S.T., Norman, J.M., 1991: Rapid estimation of leaf area index in conifer and broad-leaf plantations. *Ecology*, 72: 1896–1900. <http://dx.doi.org/10.2307/1940988>
- Kram, K.J., 1998: Influence of species composition and forest age on leaf area index. *Pol. J. Ecol.*, 46: 75–88.
- Kram, K.J., 2001: Influence of leaf area on atmospheric input of elements to the ecosystems of the Kampinos National Park (central Poland). *Pol. J. Ecol.*, 49: 327–337.
- Kram, K.J., 2005: Bulk deposition and aerosol-gaseous input of elements in the forested area of coastal region (Pomerania, North Poland). *Pol. J. Ecol.*, 53: 261–268.
- Krupa, S.V., 2002: Sampling and physico-chemical analysis of precipitation: a review. *Environ. Pollut.*, 120: 565–594.

- Likens, G.E., Driscoll, C.T., Brusco, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Ryan, D.F., Fahey, T., Reiners, W.A., 1994: The biogeochemistry of potassium of Hubbard brook. *Biogeochemistry*, 25: 61–125. <http://dx.doi.org/10.1007/BF00000881>
- Lindberg, S.E., Lovett, G.M., Richter, D.D., Johnson, D.W., 1986: Atmospheric deposition and canopy interactions of major ions in a forest. *Science*, 231: 141–145. <http://dx.doi.org/10.1126/science.231.4734.141>
- Lindberg, S.E., Turner, R.R., 1988: Factors influencing atmospheric deposition, stream export, and landscape accumulation of trace metals in forested watersheds. *Water Air Soil Pollut.*, 39: 123–156. <http://dx.doi.org/10.1007/BF00250954>
- Lovett, G.M., Lindberg, S.E., Richter, D.D., Johnson, D.W., 1985: The effects of acidic deposition on cation leaching from three deciduous forest canopies. *Can. J. For. Res.*, 15: 1055–1060. <http://dx.doi.org/10.1139/x85-171>
- Lovett, G.M., Kinsman, J.D., 1990: Atmospheric pollutant deposition to high-elevation ecosystems. *Atmos. Environ.*, 24A, 11: 2767–2786.
- Lovett, G.M., Lindberg, S.E., 1993: Atmospheric deposition and canopy interactions of nitrogen in forests. *Can. J. For. Res.*, 23: 1603–1616. <http://dx.doi.org/10.1139/x93-200>
- Raymond, H.A., Yi, S.-M., Moumen, N., Han, Y.J., Holsen, T.M., 2004: Quantifying the dry deposition of reactive nitrogen and sulfur containing species in remote areas using a surrogate surface analysis approach. *Atmos. Environ.*, 38: 2687–2697. <http://dx.doi.org/10.1016/j.atmosenv.2004.02.011>
- Rodà, F., Avila, A., Rodrigo, A., 2002: Nitrogen deposition in Mediterranean forests. *Environ. Pollut.*, 118: 205–213. [http://dx.doi.org/10.1016/S0269-7491\(01\)00313-X](http://dx.doi.org/10.1016/S0269-7491(01)00313-X)
- Ross, H.B., Lindberg, S.E., 1994: Atmospheric chemical input to small catchments. In Moldan, B., Černý, J. (eds), *Biogeochemistry of small catchments*. Scope 51. Wiley, Chichester, p. 55–84.
- Sanz, M.J., Carratalà, A., Gimeno, C., Millán, M.M., 2002: Atmospheric nitrogen deposition on the east coast of Spain: relevance of dry deposition in semi-arid Mediterranean regions. *Environ. Poll.*, 118, 2: 259–272. [http://dx.doi.org/10.1016/S0269-7491\(01\)00318-9](http://dx.doi.org/10.1016/S0269-7491(01)00318-9)
- Stachurski, A., Zimka, J.R., 1990: Methods of studies on forest ecosystems: evaluation of nitrogen accumulation in leaf litter in the association *Pino-Quercetum*. *Ekol. Pol.*, 38: 383–398.
- Stachurski, A., Zimka, J.R., 2000: Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors. *Environ. Pollut.*, 110: 345–356. [http://dx.doi.org/10.1016/S0269-7491\(99\)00290-0](http://dx.doi.org/10.1016/S0269-7491(99)00290-0)
- Szarek-Łukaszewska, G., 1999: Input of chemical elements to the forest ecosystem on the Carpathian Foothills (S Poland). *Pol. J. Ecol.*, 47: 191–213.
- Szarek-Łukaszewska, G., 2003: Sulphur input to the Niepołomice Forest: changes during 30 years (Southern Poland). *Pol. J. Environ. Stud.*, 12, 2: 239–244.
- Tarabula, T., 1995: Preliminary results of studies on the effect of chemical soil treatment on element flux in rain water in a Scots pine forest. *Fol. Forest. Pol. Series A - Forestry*, 37: 73–88.
- Tarnay, L., Gertler, A.W., Blank, R.R., Taylor, G.E. Jr., 2001: Preliminary measurements of summer nitric acid and ammonia concentrations in the Lake Tahoe Basin air-shed: implications for dry deposition of atmospheric nitrogen. *Environ. Pollut.*, 113, 2: 145–153. [http://dx.doi.org/10.1016/S0269-7491\(00\)00168-8](http://dx.doi.org/10.1016/S0269-7491(00)00168-8)
- Van Breemen, N., Burrough, P.A., Velthorst, E.J., van Dobben, H.F., de Wit, T., Ridder, T.B., Reijnders, H.F.R., 1982: Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. *Nature*, 299: 548–550. <http://dx.doi.org/10.1038/299548a0>
- Zimka, J.R., 1989: Analysis of processes of element transfer in forest ecosystems. *Pol. Ecol. Stud.*, 15: 135–212.
- Zimmermann, F., Matschullat, J., Brüggemann, E., Plessow, K., Wienhaus, O., 2006: Temporal and elevation-related variability in precipitation chemistry from 1993 to 2002, Eastern Erzgebirge, Germany. *Water Air Soil Pollut.*, 170: 123–141. <http://dx.doi.org/10.1007/s11270-006-2860-2>