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COMPARISON BETWEEN THE PARAMETERS OF THROUGHFALL AND BULK DEPOSITION MEASURED IN TWO LABORATORIES USING THE SAME METHODS

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Abstract: *Among the main concerns of the researchers is the comparability of the analysis methods, in order to highlight possible errors. Several statistical approaches and graphical tools are available to investigate sources of analytical error and for decision-making. In this article, we present an operative protocol for the comparison of the precision for two laboratories with the same quantitative analytical methods. This paper describes the importance of achieving sequential stages, including experimental design, familiarization with the method of optimal research analysis, quality evaluation, selection of sample, definition of acceptability criteria. Sample measurement, data analysis and evaluation, final decision and reporting are also discussed and exemplified.*

The reason for performing a comparison experiment is to estimate the type and magnitude of systematic error between two laboratories with the same method and to judge if the two laboratories are identical within the inherent imprecision methods or within preset analytical quality specifications. Finally, the purpose was to check if same ranges of concentrations and fluxes of pollutants are obtained using the same methods of analysis, but in two different labs.

Key words: *Validation, analytical error, pollutants*

1. Introduction

Atmospheric deposition of pollutants and nutrients are usually important factors in environmental monitoring, enabling mass-budget studies, and evaluations of element cycling within terrestrial and aquatic ecosystems, reconstruction and prognosis of environmental biogeochemical trends [1]. Statistical comparison of two analytical methods or laboratories is a persistent task and one of the most important steps in the method of validation process.

An important question is why and in which way a correction can be made in case when a systematic error is indicated in the performed method comparison study. In order to receive harmonized results, it is than necessary to make a correction of the results obtained by one analyzer with respect to another [2].

When a new measurement method or device is developed it is important to test its agreement with other standardized or already established methods. The agreement is considered adequate when we might replace the old method with the new one. To test for agreement, the same samples are measured using both new and

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old method. In the case of destructive methods or where there are other reasons which prevent repeatability of measurement on the same samples (space and time variability), a larger number of samples is measured from the same population. Within the measurement comparison approaches the agreement is evaluated by testing for significant systematic differences. The differences or bias can be fixed (same shift across the range of values) or proportional (shift related to the magnitude of a measured variable). What is sought for in method comparison studies is actually not the agreement but the bias [3] which results from the statistical foundations itself.

A comparison between the inferential method and the throughfall method [4,5] is a cost-effective way to evaluate the inferential method; however, this procedure is limited to forest vegetation. In this procedure, the required measurements other than the inferential method related are wet-only deposition, throughfall, and stemflow. It is, therefore, desired that this procedure should be performed at a site where monitoring both for wet and dry deposition is conducted.

While foliar extraction methods address processes on the scale of leaves, throughfall and watershed mass balance methods are needed to address deposition to individual trees, forest stands and small catchments. To the extent that deposited material is washed from the canopy by rain, the flux of an ion below the canopy in throughfall provides some information on dry deposition.

Throughfall methods are generally limited in space to forest plots or small catchments (<100 of m^2). If locations exist where deposited SO_4^{2-} is a conservative ion within an entire watershed, hydrologic mass balance methods may be used to derive mean deposition rates over larger spatial and possibly longer time scales. These calculations require that the hydrologic cycle of the system be well characterized and that significant sources and sinks of SO_4^{2-} do not exist within the system, or are well quantified [6,1].

From a series of laboratory experiments, Takenaka developed simple relationships illustrating that the fraction of the volatile ions emitted was dependent on the ratio of the difference between non-volatile cations and anions and the volatile ion concentrations [7]. The total mass reemitted and their rates were then dependent on the volume of the surface wetness and rate of drying. Wentworth demonstrated the role of dew as a temporary reservoir for NH_3 by measuring its volume and ion balance along with the dynamics of wetting and drying of the surface in relation to 62 atmospheric NH_3 concentrations in a grass field. At their site, dew composition suggested that nearly all of NH_4+ in the dew was emitted to the atmosphere as NH_3 during evaporation [8]. Studies of dew chemistry and reemission continues of volatile compounds should consider the modeling framework of Burkhardt and, to the practical extent, include chemical analyses that will allow for extension of the results to this cuticular modeling framework [9].

Other researchers have studied conventional throughfall collection methods that are labor intensive and analytically expensive to implement at broad scales. This study was conducted to test an alternative approach requiring infrequent sample collection and a greatly reduced number of chemical analyses. The major objective of the study was to determine nitrogen deposition measurements in bulk throughfall collected under pine (*Pinus* sp.) canopies and in forest clearings were compared between co-located conventional throughfall solution collectors and IER throughfall collectors using mixed bed IER columns [10].

Previous studies have reported considerable and site-specific differences between these methods, complicating the interpretation of results [11, 12, 13, 14]. For the estimate the deposition, many researchers used canopy budget and the inferential method with correction factors [15,16]. The authors noticed that high precipitation amounts partly explained remaining differences in wet deposition and larger discrepancies were observed when dry deposition estimates are compared between the emissions-based approach and the other two approaches. The authors noted that the remaining differences for wet deposits are correlated with some large amounts of precipitation. Larger discrepancies were also observed when dry deposition estimates are compared between the emission-based approach and the other two approaches. These differences occur due to weather conditions and their effects on tree species [17,18].

Other researchers applying different methods to distinguish between dry deposition and canopy leaching and to add to the almost non-existing deposition measurements for dissolved Cu, Pb, Mn, V, Zn, Ni and Cd in two Spanish forests differentially exposed to the urban and industrial environment. No significant differences in mean bulk deposition concentrations or fluxes were found between sites, indicating little differential effect of the urban/industrial environment on bulk precipitation chemistry. At both sites, throughfall and stemflow fluxes increased relative to bulk deposition for all elements, except for Zn and Cd. The relative contribution of leaching and dry deposition was evaluated through: the seasonal variability of throughfall, regressions of element fluxes on water flux in net throughfall [19, 20].

The authors also noted important aspects in the optimal estimation of the sample, related to the placement of the respective samples, the proper identification of the collection area. It was pointed out that the field intercomparison described by these researchers provided a good insight into the various aspects that contribute to the overall accuracy of measurements. [21].

A comparison study between two laboratories results of the same samples and methods is a new model research experiment. We purpose to study the constant systematic errors that are systematic deviations estimated as the average differences between laboratories. Proportional systematic error means that the differences between the 2 experiments are proportionally related to the level of measurements. The higher the values, the lower the error.

Estimates of random error may help in assessing validity of the measurements by the individual laboratories and help identify unexpected test results arising from sample mix-ups, transposition errors, and other mistakes.

The comparison between the values obtained in the two laboratories relates information concerning the comparability within the ICP Forests laboratories and not only.

2. Matherials and methods

Before the measurements are conducted, is important to know analytical error that is allowable without compromising the test. It usually is very helpful to collect and write down information relating to both the new method and the comparative method. Information on sample requirements, analytical process, reaction principles, calibration procedure, calculations, known interferences, and anticipated analytical performance is essential if unexpected or aberrant results occur.

In this phase, a working procedure is established. In practical terms this means that one establishes sufficient working the competence with the method so one can correctly prepare reagents, set up the analyzer, calibrate the method and obtain test results. The quantification limits are based on analytical quality specifications.

For quantitative and qualitative monitoring of atmospheric deposition, collectors were installed at 02.08.2018 and samples were collected during 16.08.2018– 03.08.2021, from the research area, located in the unit u.a. 35A, U.P. I, in the framework of Composesoratul Joseni Location of the studied pilot is found in figure 1. The description of the studied plod and stand is given in Table 1.

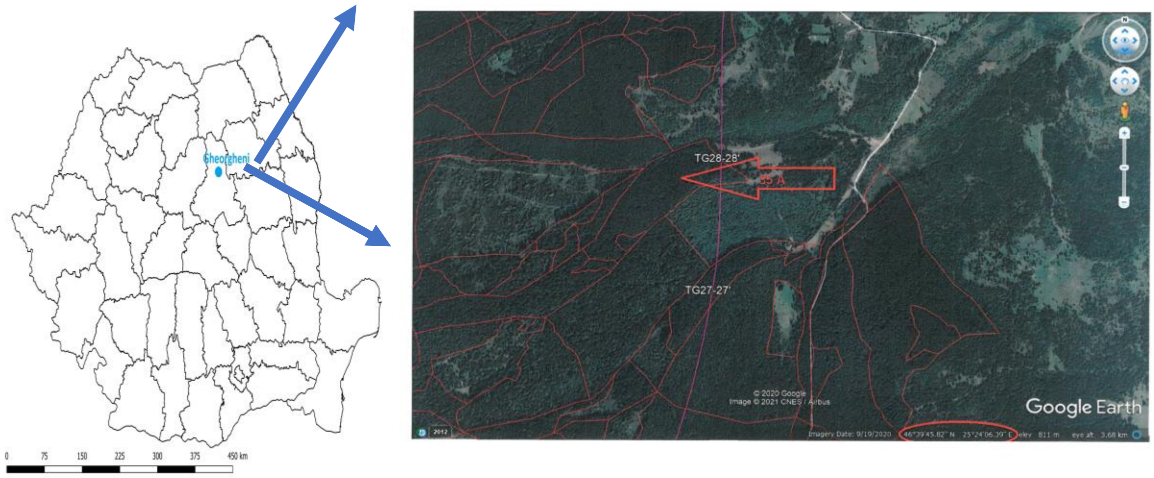

Fig. 1. Location of the studied plot (u.a. 35 A, U.P. I, Composesoratul Joseni)

Table 1.

Description of the studied plod and of the stand
(*Amenajamentul Ocolului Silvic De Regim Gheorgheni SA, UP, 2018-2021)

Studied plod	u.a. 35 A
Area	12.9 ha
GF	2-1B
SUP:A	TS:3333; TP:1211; SOL:3301
Side	Medium wave
NE Exhibition	INC.18G
Altitude	910-1010 m
Litter	Continue-normal
Flora type	Asparula-Oxalis. Natural fundamental superior productivity, relatively even aged trees
Current composition	6 MO 4BR (MO=Spruce, BR=Fir)
Sort	MO tick and very tick timber, BR tick and very tick
exploitable age	110 years
Stand age	80 years

According to Barbu and Iacoban [22], from INCDS Marin Drăcea, the working methodology consist of installation of collectors for precipitation in the open field and under the forest canopy. Nine collectors for atmospheric deposition were installed. Out of the 9 collectors, 3 were installed in open land and 6 under the canopy. Because the monitoring of atmospheric depositions was also carried out during the winter period, two types of collectors were used. The summer collectors are made of PVC gutters, equipped at one end with a collecting funnel, which directs liquid precipitation into a collection PE bag. Each of them had an exposure surface of 0.1 m^2. The gutters were fixed with a slope of approximately15 degrees, supported on wooden stakes, at a height of 0,8-1,0 m. A funnel was fixed at the lower end of the gutter, equipped with a hose, for collecting and directing the collected water in a bag installed in the ground, protected by a cover from the action of solar radiation. Winter catchers are made of a frame with a diameter of 17 cm that supp orts the collection bag, so that solid precipitation falls directly into the bag, without tipping over. The methodology was implemented at Ocolul Silvic de Regim Gheorgheni SA, in the field and in the laboratory.

Precipitation during the growing season were collected twice a month, and during the cold season once a month. The samples were stored at maximum +4°C, in order to avoid changes in the chemical composition of samples, before analysis. For this study, aliquots of precipitation samples were sent from Gheorgheni to the laboratory of INCDS "Marin Drăcea" Câmpulung Moldovenesc, in order to analyse the same parameters, with the same methods, in the two laboratories.

The analysis of physicochemical parameters of the precipitation samples pH, conductivity, concentrations of cations: Na^+, $N\text{-}NH_4^+$, K^+, Mg^{2+}, Ca^{2+} and anions: $S\text{-}SO_4^{2-}$, $N\text{-}NO_3^-$ și Cl^- was the one applied within the ICP Forests Program and is fully described by manny authors [22, 23].

In order to implement the ICP Forests methodology in the Ocolul Silvic de Regim Gheorgheni SA laboratory, reagents of analytical grade and prepared standards for instruments calibration were sent from the INCDS "Marin Drăcea" Câmpulung Moldovenesc laboratory.

A separate sub-sample was taken, prior filtration, for the determination of pH and conductivity (as stated in ISO 10523 and ISO 7888). Standardized analytical methods and procedures were used, preferably ISO, specified by ICP Forests, in the two laboratories.

For the determination of ion concentrations of Cl^-, $S\text{-}SO_4^{2-}$, $N\text{-}NO_3^-$, Na^+, $N\text{-}NH_4^+$, K^+, Mg^{2+} and Ca^{2+} from precipitation, an ion chromatography system Dionex ICS-3000, and an ion chromatography system Dionex ICS-5000+, respectively, were used. The two instruments were equipped with systems for the simultaneous analysis of anions and cations. A total number of 110 samples was analysed: 56 bulk deposition and 54 throughfall samples. All reagents used were of high purity (Merck or Fluka). The determination of pH and conductivity were performed as soon as possible, after the sample's reception in labs. Samples were filtered and the concentrations of cations and anions were measured. Comparative analytical methods and devices used are presented in table 2.

Internal clues of controlling and ensuring the quality of the analyses in the laboratory, according to the ICP Forests methodology, are: comparing the calculate conductivity with the measured conductivity, cheking the cation-anion balance, verifying that Na/Cl ratio is in the 0.5-1.5 range (but no more than 4.0); using of control charts for samples of known concentrations.

The quality assurance and control (QA/QC) procedures further include the use of control charts for internal reference material to check long-term comparability within national laboratories, as well as participation in periodic laboratory ring tests [24] and field inter-comparisons [25; 26] to check the international comparability.

Table 2.

Parameters, analytical methods and equipment used in the experiment

	INCDS Marin Drăcea Campulung		**Ocolul Silvic de Regim Gheorgheni SA**		**Analytical methods/standards**
No.	**Parameter (UM)**	**Equipment**	**Parameter (UM)**	**Equipment**	
1.	pH	**SIAnalyticsTitrolineEasy Titrator**, TZ3230 type, with 20 ml burette, N62 electrode, range 0-14 pH units (-5...+100 °C)	pH	**WTW pH Meter**, InoLab type 7310, SenTix 41 electrode, range: 0-14 pH units	ISO 10523
2.	Conductivity (µS/cm)	**WTW Conductivity Meter** InoLab 730P, with conductivity cell TetraCon 325, Range: 0-1000 µS/cm; 0-100 mS/cm	Conductivity (µS/cm)	(0 - 50ºC).	SR EN 27888:1997
3.	K^+ (mg/l)	DIONEX Ion chromatography dual system ICS3000, for simultaneous determination of cations and anions with DP (dual pump), DC (compartement detector), and Autosampler. The pumps IC work at a flow rate of 0,001 to 1,0 ml/min and operating pressures up to 41 Mpa (6000 psi), recommended 35 MPa (5000 psi).	K+ (mg/l)	DIONEX Ion chromatography dual system ICS-5000+ ThermoScientific), with DP (dual pump), EG (eluent generator), DC (compartement detector), and Autosampler. The capillary pumps IC work at a flow rate of 0,001 to 3,0 ml/min and operating pressures up to 41 Mpa (6000 psi), recommended 35 MPa (5000 psi).	EN 27888
4.	Ca^{2+} (mg/l)	Dionex ion cromatograf ICS3000	Ca2+ (mg/l)	WTW Conductivity Meter, InoLab 7110 with conductivity cell TetraCon 325, Range: 0-1000 µS/cm	EN ISO 7980
5.	Mg^{2+} (mg/l)	Dionex ion cromatograf ICS3000	Mg2+ (mg/l)	DIONEX Ion chromatography dual system ICS-5000+	EN 15309
6.	Na^+ (mg/l)	Dionex ion cromatograf ICS3000	Na+ (mg/l)	DIONEX Ion chromatography dual system ICS-5000+ (	EN 15309
7.	$N\text{-}NH_4^+$ (mg/l)	Dionex ion cromatograf ICS3000	N-NH4+ (mg/l)	Ion cromatograf DIONEX ICS5000+ (ThermoScientific),	EN ISO 1491
8.	Cl^- (mg/l)	Dionex ion cromatograf ICS3000	Cl- (mg/l)	Ioncromatograf DIONEX ICS5000+ (ThermoScientific),	EN ISO 10304
9.	$N\text{-}NO_3^-$ (mg/l)	Dionex ion cromatograf ICS3000	N-NO3- (mg/l)	Ioncromatograf DIONEX ICS5000+ (ThermoScientific),	EN ISO 10304
10.	$S\text{-}SO_4^{2-}$ (mg/l)	Dionex ion cromatograf ICS3000		Ioncromatograf DIONEX ICS5000+ (ThermoScientific),	EN ISO 10304

3. Results and discussion

Precipitation is the most effective process in removing and transporting different ionic compounds, pollutants, and soluble gases from the atmosphere to the earth's surface [27] and helps to understand the relative contribution of different sources of atmospheric pollutants. The composition of rainwater varies from site to site and region to region due to the difference of the local and remote emission sources [28] and reflects all the characteristics of air pollutants [29].

The amount of precipitation collected in the open field and under the forest canopy was calculated considering the reception surface of collectors.

For this study, samples were split and half stored at the Ocolul Silvic de Regim Gheorgheni SA laboratory and half sent to the INCDS "Marin Drăcea" Câmpulung Moldovenesc laboratory. For 2018 and 2021, the periods of collection don't cover all the years, so the calculated values of concentrations (fig.2) and fluxes (fig.3) are mean annual only for 2019 and 2020. Calculating TF and BD ($Q \cdot c \cdot 10^{-2}$, in kg ha^{-1}) by multiplication of the precipitation quantity (Q, in L m^{-2}), the concentrations (c, in mg L^{-1}) and the unity conversion factor 10^{-2}.

For the concentrations and fluxes of S-SO_4^{2} ion, the results obtained are lower in Gheorgheni, but are comparable to those obtained at Campulung. The values of the concentrations and fluxes of Ca^{2+} ion measured and calculated in the two laboratories are comparable, except for 2018, under the canopy, when higher results were obtained in Campulung than in Gheorgheni.

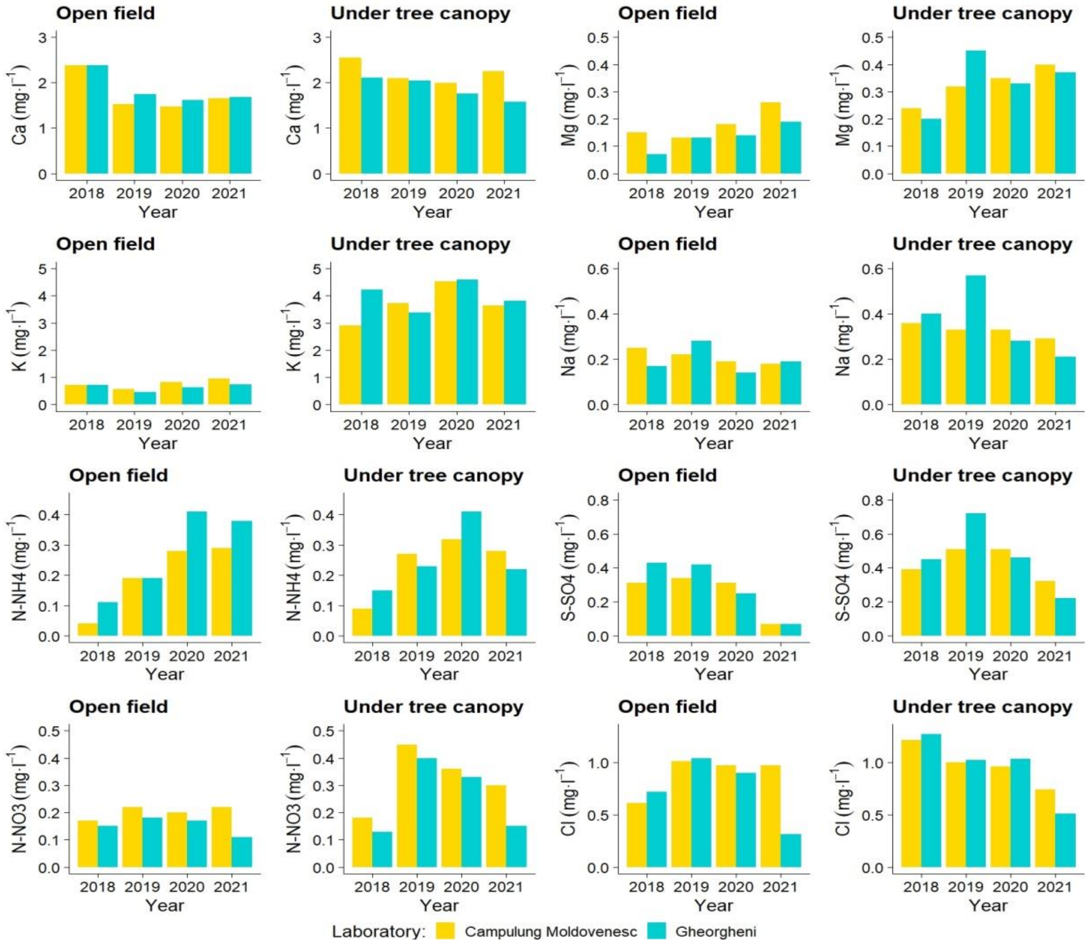

Fig. 2. Mean period concentrations of cations and anions determined in the same bulk deposition and throughfall samples in two laboratories from Romania for the period 2018-2021

The values of the concentrations and fluxes of ions calculated under the forest canopy, for the ion of Na^{2+} are comparable, except in 2019 under the canopy, when higher results were obtained in Gheorgheni than in Campulung. For Mg^{2+} the values of the concentrations and fluxes are equal or lower in Gheorgheni, except for 2019, under the canopy.

Higher values were highlighted for the $N\text{-}NH_4^+$ ion at Gheorgheni, due to the low stability of this ion. The tendency to transform to other compounds (N_2, by reduction or NO_3^-, by oxidation) is high for ammonium ions. The highest differences are found in the years 2018, 2019 and 2021, for the results obtained in the open field, at Gheorgheni, because the analysis was performed before those from Campulung.

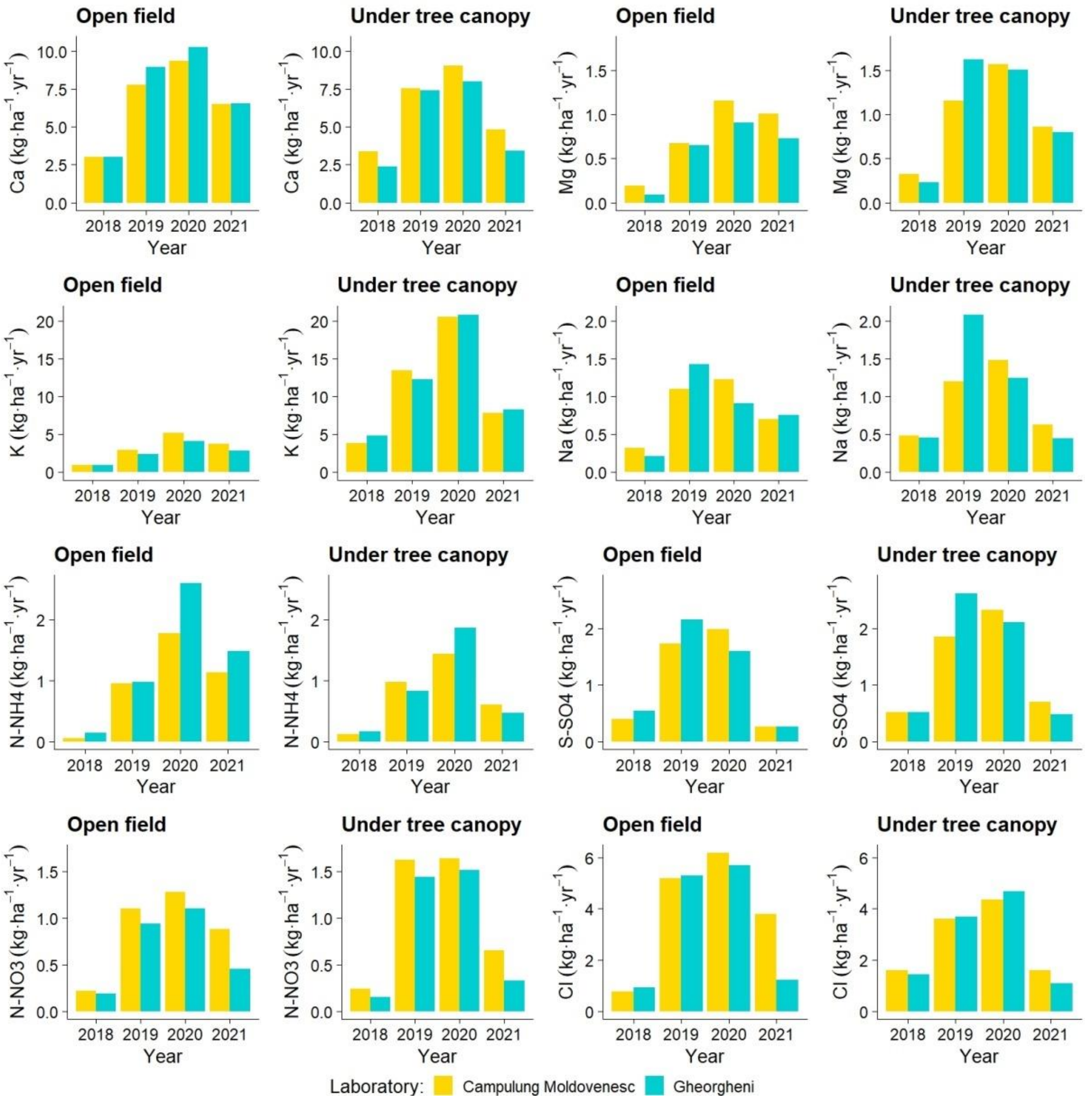

Fig. 3. Depositions of cations and anions determined using the same bulk deposition and throughfall samples analyzed in two laboratories from Romania for the period 2018-2021

The concentrations and fluxes of K^+ ion calculated at the two laboratories are very close, both in open field and under the canopy.

It is obvious that the results obtained at Gheorgheni, for the $N\text{-}NO_3$ ion are systematically lower both in bulk deposition and in throughfall. The samples collected under the canopy may also contain other compounds that may interfere and change the obtained values. In the NH_3–SO_2–liquid water system, NH_3 neutralizes the H^+ ions formed in the absorption of SO_2 and its subsequent oxidation to sulfate, and thus maintains the solubility of SO_2 and the rate of sulfate production. It also helps to maintain higher levels of pH, so the reaction of S (IV) with oxidizing agents, such as O_3 proceeds at a faster rate, compared to that at lower pH values [30].

The declining concentrations of SO_2 cause less acidic SO_4^{2-}, therefore, a reduction in the reactions with NH3 will occur [31]. This may also be an explanation to the increased NH3 concentrations. The values for Cl^- concentrations and fluxes are comparable excepting for 2021, when the results obtained at Campulung are three times higher than at Gheorgheni (0.97 comparing to 0.31 mg/l and 3.8 comparing to 1.2 kg/ha/year). This problem can be explained by the difficulties registered in the ion chromatograph operation from the anion's subsystem, at Gheorgheni laboratory.

The measured precipitation composition data were quality checked using the ionic balance method and the calculated conductivity.

The distribution of the measured pH and conductivity values showed that there are deviations of ± 10% reported to the values of the Campulung laboratory that participated in the intercalibration exercise (fig.4).

The rainwater pH of an unpolluted and clean atmosphere has a value around 5.6, as the dissolution of naturally existing CO_2 and other acidic species (NOx; SO_2) occurs in the cloud droplets [32]. Changes in the rainwater pH values, below or above this level, are mainly due to acidic or alkaline components.

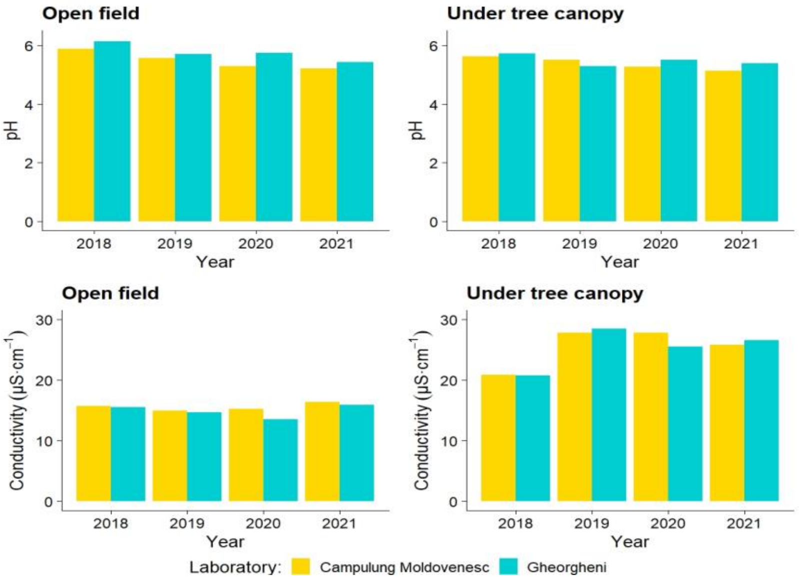

Fig. 4. Means weighted pH and conductivities, for the studied period 2018-2021

Acid precipitation with pH values less than 5.0 is likely due to the influence of anthropogenic emissions of H_2SO_4 and/or HNO_3 (Seinfeld et al. 2006). pH values greater than 6.0 indicate inputs of alkaline substances into rainwater, like NH4 + and terrigenous components (Ca^{2+}, Mg^{2+}) derived from limestones and dolomites. The process of neutralization is also related with the anthropic emissions of NH_3 and NH_4 which react with the SO_4 $^{2-}$ and NO3 − present in the atmosphere, and result in the forming of the ammonium sulfate $(NH_4)^2SO_4$, and nitrate, NH_4NO_3 [33].

4. Conclusion

This experiment was very useful for transferring the ICP Forests methodology concerning atmospheric deposition from the INCDS “Marin Dracea” Campulung Moldovenesc laboratory to that from to the Ocolul Silvic de Regim Gheorgheni SA.

Procedure comparison as such may be very beneficial. For instance, they may be used to highlight the importance of correct handling techniques and be an incentive to evaluate the correctness of procedures currently used.

Performing studies comparing methods of analysis or checking the results obtained by two or more laboratories for applying the same methods of analysis at the same time is a major task, but also a very difficult one. As noted in this study, if no attention is paid to the difference between the comparison method and the procedure, this may lead to erroneous conclusions in the final results obtained. A proper approach to these procedures can lead to more effective monitoring of the analyzes performed, provoke a review of procedures, detect errors and increase motivation for developing new methods.

The outcome of such an effort will be to ensure that harmozed results are reported. The results obtained revealed that the levels of concentrations and fluxes calculated with the values measured in the two laboratories are comparable and are within the same ranges considered at European level.

The databases obtained in this study represent a novelty of the monitoring of atmospheric deposits and can be used in future research as a reference base.

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