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Spatial distribution and isotopic signatures of N and C in mosses across Europe

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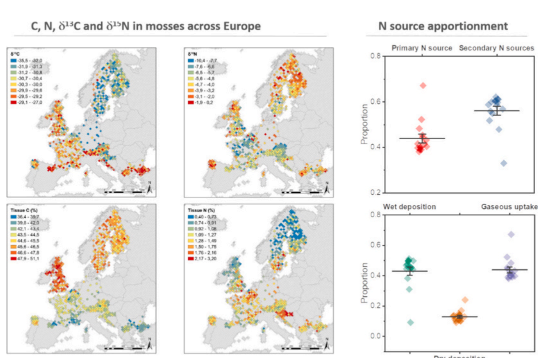
HIGHLIGHTS

- Spatial distribution of N, C, C/N ratio, in mosses across Europe
- Isotope-derived quantitative overview of atmospheric N sources on a European scale
- Isotopic analysis enhances pollution source attribution and environmental monitoring
- $\delta^{15}N$ and $\delta^{13}C$ analysis complements information obtained in European moss surveys

GRAPHICAL ABSTRACT



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A B S T R A C T

The accumulation of nitrogen (N) in moss tissue has proven to be a reliable marker of increasing N deposition. However, this measurement does not offer additional data about the origin of pollution. In this respect, the analysis of the N isotopic ratios might be a helpful tool in providing supplementary information about the nature of the nitrogenous species in biomonitoring surveys. Furthermore, isotopic signatures have been extensively used in the study of N and carbon (C) biogeochemical cycles. The main purpose of this study was to determine N and C elemental contents and their stable isotopes in mosses to investigate atmospheric pollution patterns across Europe. We aimed at identifying the main N polluted areas and evaluating the potential use of isotopic signatures in the attribution of pollution sources at a regional scale. With these objectives in mind, >1300 samples from 15 countries from Europe, all of them participants of the ICP-Vegetation programme 2005–2006, were analyzed for their C and N contents and $\delta^{15}N$ and $\delta^{13}C$. The results were compared to those derived from EMEP model, which provided modeled deposition and emission data, as well as to the predominant land uses at the sampling sites (based on CORINE Land Cover). This evaluation suggests that additional measurements of stable C and N isotopes in mosses could be a valuable tool in European environmental surveys. Such measurements not only provide useful information for identifying probable pollution sources but also enable the quantification of their contributions, serving as biological indicators of significant environmental processes. This study presents the first quantitative assessment of major atmospheric nitrogen (N) sources based on stable isotope analysis on a European scale, establishing a framework for evaluating historical changes in N across the region.

1. Introduction

Nitrogen (N) has historically been recognized as the primary limiting nutrient in many natural and semi-natural ecosystems (Fay et al., 2015; Vitousek et al., 2010). However, in the last decades, the availability of nitrogen has significantly increased, thus modifying the global nitrogen cycle (Fowler et al., 2013; Galloway et al., 2008). Anthropogenic activities, largely through agriculture, but also through industry and the burning of fossil fuels, have had a huge impact on the nitrogen budget of the Earth, causing serious impacts on biodiversity and the functioning of ecosystems, climate, water quality, human health and even the rate of population growth in developing countries (Erisman et al., 2013, 2008; Fowler et al., 2015; Godfray et al., 2010).

In Europe, several regulatory policies have been established to mitigate the negative impact of N pollution, including protocols such as the UNECE's Convention on Long-range Transboundary Air Pollution (CLRTAP) Gothenburg protocol or regulation such as the National Emission Ceiling Directive (Oenema et al., 2011; Winiwarter et al., 2015). In this context, the European Monitoring and Evaluation Programme (EMEP), operating under the framework of CLRTAP, aims at addressing transboundary air pollution problems through the collaborative efforts of five expertise centers (http://www.emep.int). This programme compiles annual emission data on atmospheric pollutants from different European countries to facilitate the analysis and modeling of atmospheric transport and deposition patterns (Fagerli and Aas, 2008; Harmens et al., 2014, 2011). The data generated by the models are subsequently validated using measurements from EMEP stations. Unfortunately, the coverage of this network is limited in certain regions, especially in southern Europe (García-Gómez et al., 2014; Harmens et al., 2011).

Complementing conventional monitoring sites, bioindicators can be valuable tools for assessing emission and deposition patterns of several pollutants, including N (Boltersdorf et al., 2014; Dołęgowska et al., 2021; Du et al., 2023; Harmens et al., 2014; Lequy et al., 2022; Sardans and Peñuelas, 2005). Because of their particular characteristics and special sensitivity, mosses are among the most used organisms in biomonitoring surveys, providing site-based information on atmospheric N concentrations, N deposition and N-related ecological impacts (Arróniz-Crespo et al., 2008; Harmens et al., 2014; Lazo et al., 2022; Meyer et al., 2015). In this context, the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP-Vegetation) conducts periodic monitoring surveys using mosses. These surveys offer an indirect and time-integrated information for assessing atmospheric pollutant deposition to ecosystems, reducing the need for extensive precipitation collector networks and covering areas where EMEP stations are unavailable (Harmens et al., 2015a). Since the 2005/2006 survey, this biomonitoring European network includes N among its target compounds, enabling the mapping of the spatial distribution of atmospheric N deposition across Europe (Harmens et al., 2015b, 2011).

Nevertheless, despite the effectiveness of mosses as indicators of N deposition, the analysis of total N content in moss tissue does not offer insight into the origin of the pollutants or the environmental processes that influence N accumulation. This limitation can be addressed through the use of stable isotopes, which have gained popularity in ecological and pollution studies over the past few decades (Bragazza et al., 2005; Díaz-Álvarez and Barrera, 2018; Du et al., 2023; Felix et al., 2016; Guerrieri et al., 2015).

Considering N pollution surveys, measurements of N stable isotopes have proved to be particularly useful for identifying emission sources (Boltersdorf and Werner, 2014; Liu et al., 2008a; Pearson et al., 2000; Zhao et al., 2019). The method is based on the differences in N isotopic signatures of the nitrogenous compounds, which are ultimately reflected in the tissues of mosses. A key aspect is that, generally, anthropogenic emissions of oxidized forms have a more positive $\delta^{15}N$ value (^{15}N isotopic composition) than the reduced forms (Felix et al., 2016, 2014; Heaton, 1986). Therefore, analysing the spatial variations of N isotopic signatures and correlating them with atmospheric components or the main N emitters could provide an integrated approach to identifying N pollution sources. In this regard, a dominance of N-NH_y forms in deposition is expected to result in more negative $\delta^{15}N$ values in mosses, whereas higher N-NO_x concentrations in deposition would correspond to less negative $\delta^{15}N$ value in plant tissues (Gerdol et al., 2014; Zechmeister et al., 2008). In the case of carbon (C), its ^{13}C isotopic composition ($\delta^{13}C$) serves as an indicator of photosynthetic efficiency (Liu et al., 2008b). As a recorder of CO_2 fixation, changes in $\delta^{13}C$ signatures may reflect potential CO_2 emission sources or reveal variations in environmental conditions that ultimately influence C metabolism (Díaz-Álvarez and Barrera, 2020; Liu et al., 2008b; Skrzypek et al., 2007; Zambrano Garcia et al., 2009). In recent decades, the $\delta^{13}C$ signal in moss species has been shown to be highly sensitive to changes in temperature, as well as to other parameters such as water availability and altitude gradients within ecosystems (Deane-Coe et al., 2015; Liu et al., 2008b; Skrzypek et al., 2007). Consequently, these factors may pose significant limitations to the use of this signal in air quality studies. However, limited research has been conducted on the interactions between these environmental parameters and N deposition in non-vascular plants. While some studies suggest that N deposition can enhance C fixation in mosses through a fertilizing effect (Liu et al., 2010), other findings indicates that

N deposition can induce nutritional imbalances (evidenced by lower C/N ratios) and impaired photosynthesis (reflected in higher $\delta^{13}C$ values) (Gerdol et al., 2007; Munzi et al., 2013; Pintó-Marijuan et al., 2013).

This study hypothesizes that the spatial distribution patterns of nitrogen (N) and carbon (C) tissue contents, together with their $\delta^{15}N$ and $\delta^{13}C$ isotopic signatures in mosses, can provide valuable insights into regional N and C source contributions and associated ecological processes across Europe. These patterns are expected to offer complementary information to that obtained in the existing European moss surveys. Specifically, the objectives of the study are to: 1) determine whether stable isotopic signatures in mosses can identify primary N hot-spot areas within the study region, 2) evaluate the effectiveness of moss $\delta^{13}C$ and $\delta^{15}N$ signatures in tracing and quantifying major N and C sources across European landscapes, and 3) explore the potential of isotopic signatures as indicators of critical ecological processes at a regional scale.

Although previous studies have assessed tissue N contents, to the best of the author's knowledge, this is the first time that tissue C concentrations, along with N and C stable isotopes, are analyzed at a European scale.

2. Material and methods

2.1. Material selection

In 2005/2006, approximately 3000 moss samples across 16 European countries were collected during the ICP-Vegetation moss survey (Harmens et al., 2011). Of these, 1313 samples, provided by 15 countries, were selected for the analysis of nitrogen and carbon concentrations and their respective stable isotopes (^{15}N and ^{13}C) (Fig. 1).

The most frequently selected species were *Hypnum cuppressiforme* Hedw. (34 %), *Pleurozium schreberi* (Brid.) Mitt. (23 %), *Hylocomium splendens* (Hedw.) Schimp. (22 %) and *Scleropodium purum* (Hedw.) Limpr. (8 %). The remaining 13 % of the samples consisted of other eight moss species, making a total of 12. Both the sampling procedure and the subsequent preparations for analysis were performed in accordance to the guidelines described in the protocol for the 2005/2006 survey (Harmens et al., 2006).

2.2. Elemental and isotopic analysis

Approximately 4 mg of dried moss samples were weighted and analyzed for N and C content (%) and their isotopic signatures, $\delta^{15}N$ and $\delta^{13}C$ (‰). The analyses were conducted using an elemental analyzer (Vario MICRO Cube, Elementar, Hanau, Germany) coupled to an isotope ratio mass spectrometer (IsoPrime 100, Cheadle, UK), following the methodology described in Delgado et al. (2013). Quality control of the analytical method was performed using moss reference material M2 and M3 (Steinnes et al., 1997) and international isotopic standards (IAEA, Vienna, Austria). Both accuracy and precision were found to be lower than 2 % for total C and N concentration and within 0.1 ‰ and 0.3 ‰ for the isotopic signatures of ^{13}C and ^{15}N, respectively.

Isotope data were reported as $\delta^{13}C$ and $\delta^{15}N$ values, which represent the relative difference expressed in per mil (‰), between the isotopic composition of the sample and that of a standard: Vienna Pee Dee Belemnite (V-PDB) for carbon and atmospheric N_2 for nitrogen:

$$\delta^{13}C\ (‰ vs.V-PDB) = \left[\left(R_{sample}/R_{standard}\right) - 1\right] \times 1000$$

$$\delta^{15}N\ (‰ vs.atm-air) = \left[\left(R_{sample}/R_{standard}\right) - 1\right] \times 1000$$

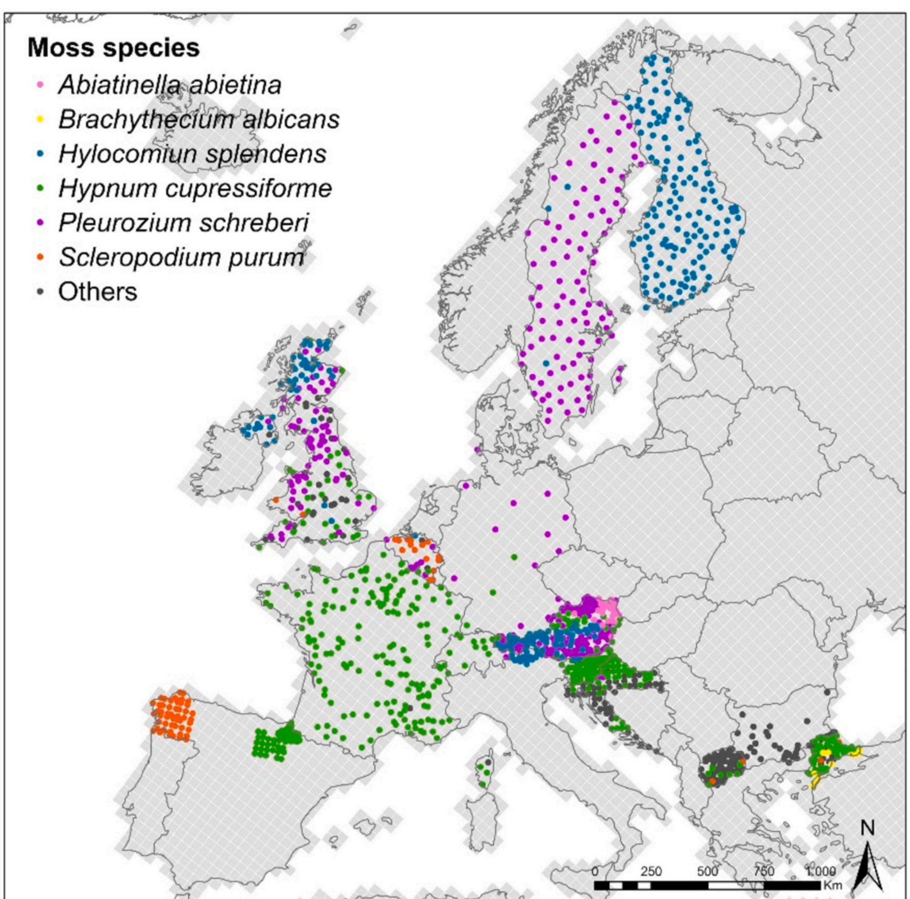

Fig. 1. Moss species collected at each sampling point and representation of the EMEP 50 km × 50 km grid using for this study.

where R_{sample} is the isotope ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$ and $R_{standard}$ is the isotope ratio for the standard.

2.3. Statistical analysis

Relationships between N and C concentrations in mosses, along with their isotopic signatures ($\delta^{15}N$ and $\delta^{13}C$), and a set of potential predictor variables –including precipitation, altitude, distribution of land use (based on the Corine Land Cover 2006 ("CLC," 2006)), and EMEP modeled N deposition and air concentrations data 2005 ("EMEP/CEIP," 2014)- were explored. As the moss variables did not follow a normal distribution, the nonparametric Spearman's correlation test was applied. All statistical analyses were performed employing the SPSS v. 15.0 software package (SPSS Inc., Chicago, IL, USA).

The proportional contributions of atmospheric N sources to mosses was estimated by using a Bayesian mixing model (Parnell et al., 2010) applied to the isotopic signatures of the samples. This analysis was conducted with the MixSIAR package in R software (Stock and Semmens, 2016). The source apportionment approach is based on the premise that the isotopic signature in moss tissues reflects the isotopic signal of all nitrogen forms taken from the atmosphere, whether through dry or wet deposition or gaseous uptake. To focus on a better understanding of the direct uptake of nitrogen by mosses, isotope fractionation during secondary processes was deliberately excluded from the analysis (see more details in Text S1). Thus, the $\delta^{15}N$ of total N in mosses samples was used as the unique isotope and the MixSIAR model was run selecting the Markov Chain Monte Carlo (MCMC) run length set to 'very long', without priors for the proportion of sources, no isotope concentration dependence and no factor enrichment (Stock and Semmens, 2016). Country was included as a factor that generates fixed effects. For this study, 7 sources of N were included: 1) NH_3 from Livestock waste ($\delta^{15}N = -28.00 \pm 11.00$ ‰, $n = 17$, (Du et al., 2023)), 2) NO_x from Vehicle exhaust ($\delta^{15}N = -7.30 \pm 7.80$ ‰, $n = 151$, (Du et al., 2023)), 3) NO_x from Biomass burning ($\delta^{15}N = 1.00 \pm 4.10$ ‰, $n = 24$, (Du et al., 2023)), 4) NH_4^+ from Dry deposition ($\delta^{15}N = 10.27 \pm 11.87$ ‰, $n = 200$, (Park et al., 2018; Xu et al., 2019; Zheng et al., 2018)), 5) NO_3^- from Dry deposition ($\delta^{15}N = 6.21 \pm 2.58$ ‰, n = 200, (Park et al., 2018; Xu et al., 2019)), 6) NH_4^+ from Wet deposition ($\delta^{15}N = -6.42 \pm 4.40$ ‰, n = 200, (Ciezka et al., 2016; Xu et al., 2019)) and 7) NO_3^- from Wet deposition ($\delta^{15}N = 1.94 \pm 3.62$ ‰, n = 200, (Xu et al., 2019)). The definition of nitrogen sources and the additional assumptions on which this selection is based are described in the Supplementary material (Text S1 and Fig. S1).

All geographical analyses and mapping were performed using ArcGis for Desktop v. 10.2. software package, with the EMEP 50 km × 50 km grid as the reference.

To generate maps of N, C; the C/N ratio, $\delta^{15}N$, $\delta^{13}C$ and temperature, mean values were calculated and displayed for each grid cell. For N deposition and air concentrations of the different nitrogenous species considered, modeled data from the EMEP network for 2005 were selected and similarly displayed ("EMEP/CEIP," 2014). Additionally, for each EMEP cell, the percentage of specific land cover types provided in the CORINE Land Cover 2006 inventory was estimated and mapped ("CLC," 2006). Temperature data correspond to the annual mean temperatures for 2004, 2005, and 2006, which were downloaded from the 'Global Climate database' (https://www.globalclimatemonitor.org/).

3. Results and discussion

3.1. N elemental contents and $\delta^{15}N$ signatures

Considering all available data from the 15 participating countries, the mean N content in moss tissues was 1.27 %, ranging from 0.40 to 3.95 % (Table 1). The highest N concentrations were detected in Croatia, Slovenia and Belgium, and locally in parts of UK (southeast), Sweden (south), Bulgaria and Switzerland. On the contrary, the lowest values were recorded in Finland, Sweden (center and north) and the UK. In these latter countries, a clear north-south gradient was observed, with the northernmost areas exhibiting the lowest N concentrations (Fig. 2A). These findings agree with those of Poikolainen et al. (2009), who observed the same pattern in a moss survey carried out in Finland. Indeed, the spatial distribution patterns of N across Europe in our study closely resemble those reported by Harmens et al. (2011), thereby corroborating that the subsample selected (35 % of the total samples) is statistically representative of the moss survey conducted in 2005. Furthermore, this study also includes data from Sweden, Croatia (Špirić et al., 2014) and Macedonia (Stafilov et al., 2020) for the same year, which were not included in the ICP-Vegetation 2005/2006 survey. The results from the subsequent moss survey (2010/2011 campaign) showed that central and western areas continued to be among the most exposed to high N deposition, as evidenced by moss N contents (Harmens et al., 2015b). However, not all participants of the 2005/2006 campaign provided data in 2010, and new countries were incorporated in the 2010/2011 survey. Moreover, the number of sampling sites per country also varied, with significant differences observed in countries such as France or Slovenia (Harmens et al., 2015b). These discrepancies prevented further comparisons.

Table 1
Summary statistics of total N concentration (%, dry weight) in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Country	Number of sites	Mean	Standard deviation	Minimum	Maximum
Austria	219	1.21	0.25	0.76	2.00
Belgium	27	1.66	0.50	0.52	2.82
Bulgaria	31	1.34	0.29	0.88	2.16
Croatia	90	1.93	0.67	0.97	3.95
Finland	150	0.89	0.27	0.52	1.73
France	166	1.36	0.29	0.74	2.10
Germany	17	1.36	0.31	0.92	1.90
Italy	20	1.16	0.16	0.77	1.50
Macedonia	72	1.36	0.32	0.82	2.34
Slovenia	55	1.84	0.47	0.82	2.82
Spain	115	1.30	0.33	0.78	2.30
Sweden	100	1.02	0.42	0.40	2.32
Switzerland	10	1.25	0.41	0.64	2.10
Turkey	72	1.26	0.29	0.78	2.40
UK	169	1.06	0.35	0.59	2.76
Europe	**1313**	**1.27**	**0.45**	**0.40**	**3.95**

In the last years, several studies have demonstrated that N concentration in moss tissues is a good bioindicator of atmospheric N deposition (Boltersdorf et al., 2014; Boltersdorf and Werner, 2014; Du et al., 2022; Hicks et al., 2000; Izquieta-Rojano et al., 2016; Pitcairn et al., 2006). In the present work, the spatial distribution patterns of N contents in mosses (Fig. 2A) showed a strong correlation with the spatial trends of N deposition modeled by EMEP (Fig. S2), so that mosses collected in areas with high levels of N deposition also have the highest N content and vice versa ($r = 0.553$ $p < 0.01$, Table S1). These results confirm that the differences in tissue chemistry can be used as sensitive indicators of N deposition at a regional scale, in accordance with previous findings of Schröder et al. (2010) and Harmens et al. (2015b, 2011), who also assessed the exposure-response relationship between mosses and EMEP-modeled deposition loads across Europe. However, although the correlations between tissue N and EMEP-modeled deposition values were highly significant (Table S1), regression models showed considerable scatter and the coefficient of determination was moderate (Fig. S3). Harmens et al. (2015b) found a similar behaviour when plotting N concentration in mosses against EMEP deposition loads. These authors observed that after excluding grid cells with only one to three moss samples, the scatter was significantly reduced. Therefore, the observed scatter in this study may be related to an insufficient sample size for some of the EMEP cells studied, suggesting that future research

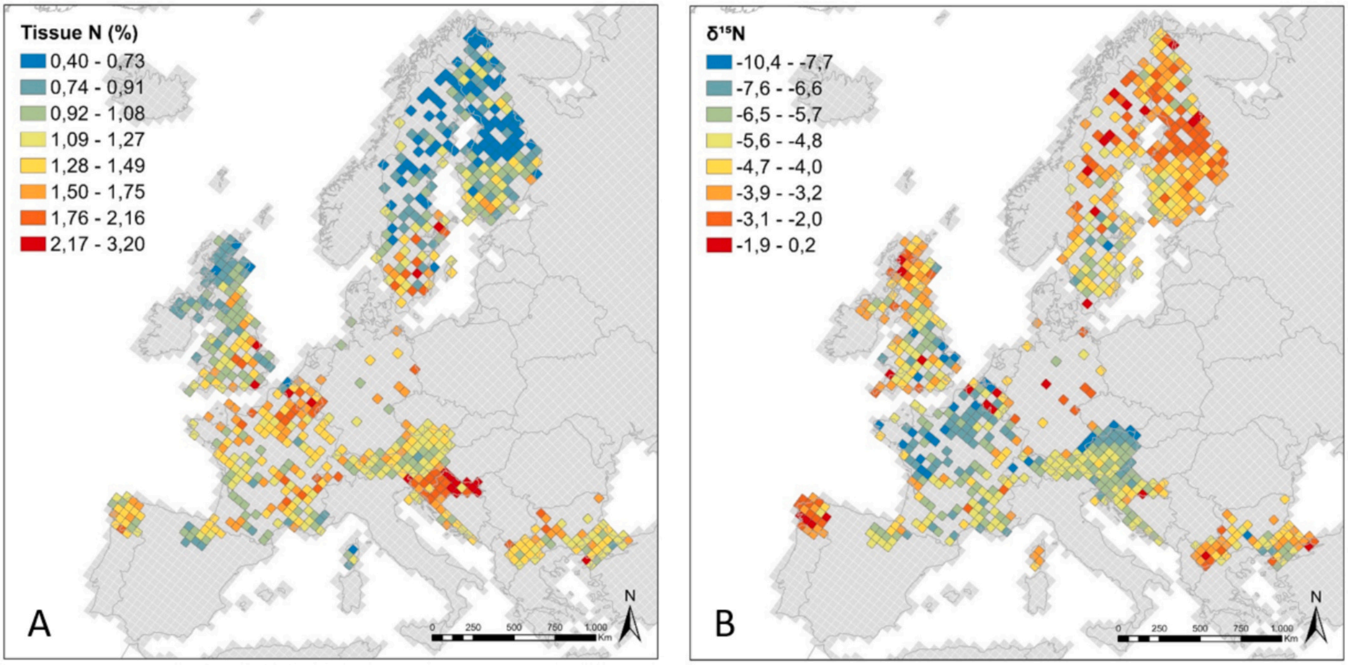

Fig. 2. Mean concentration of N (A) and δ^{15}N (B) per EMEP grid cell in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

should focus on cells with a sufficient number of sampling sites.

Regarding predominant land uses (Fig. S4), the N content in mosses (Fig. 2A) showed a positive correlation with the percentage of agricultural areas ($r = 0.494$, $p < 0.01$) and a negative association with the presence of forests ($r = -0.176$, $p < 0.01$) and wetlands ($r = -0.528$, $p < 0.01$) (Table S1). Other investigations have shown similar relationships, indicating that agriculture is one of the main drivers explaining variations in N concentrations in mosses (Boltersdorf and Werner, 2013; Pesch et al., 2008; Schröder et al., 2010). Additionally, the narrow association between wetlands and low N values in mosses might be expected, since the highest percentages of these areas are located in northern countries, where the lowest N deposition loads were estimated. Besides, although significant, the relationship between forested areas and N concentration was less pronounced. This could be explained by differences in the nitrogen deposition loads that forested areas experience. As shown in Fig. S4, two well-differentiated regions with >50–60 % forest coverage were identified: one in Finland and Sweden, and the other in Austria and Slovenia. In northern countries, forests received the lowest N deposition loads, but some forested areas in central Europe did not follow this pattern, exhibiting much higher tissue N concentrations according to the EMEP modeled fluxes (Fig. S2).

Despite the significant evidence mentioned above, there are other site-specific factors that may also contribute to variations in N concentrations in mosses. It has been demonstrated that mosses collected under the influence of the canopy drip are usually more N-enriched (Meyer et al., 2015; Skudnik et al., 2015). In forested areas of central and southern Europe, where temperature and moisture conditions highly differ from those of northern countries (Jones, 2004), it is often difficult to find suitable moss sampling sites that are not influenced by tree canopies (Gerdol et al., 2000; Špirić et al., 2012), which could lead to higher N content in the tissues. Indeed, the results of the 2010/2011 moss survey showed a clear decline in N content in mosses from Slovenia mainly due to an increased sampling effort rather than a true decrease in N deposition fluxes in those areas (Harmens et al., 2015b).

Similarly, factors such as altitude, precipitation, moss species selection, and proximity to local pollution sources have been shown to influence N concentrations in moss tissue (Arróniz-Crespo et al., 2008; Harmens et al., 2011; Hicks et al., 2000; Schröder et al., 2010; Stuart et al., 2021). In this respect, δ^{15}N signatures have been proposed as bioindicators of N sources in the environment, offering additional valuable information to that obtained from elemental analyses (Izquieta-Rojano et al., 2016; Skinner et al., 2006; Zechmeister et al., 2008). However, their utility at a European scale has yet to be validated.

The results of stable isotope signatures revealed that the European mean of δ^{15}N value was −4.85 ‰, ranging from −10.35 to 6.60 ‰ (Table 2). Spatially, mosses from eastern countries, northern UK, Finland, Sweden and Galicia (western Spain) showed the highest δ^{15}N values, whereas countries in the central belt of Europe were more depleted in the ^{15}N isotope (Fig. 2B). Regarding correlation relationships, δ^{15}N signatures were negatively associated with NH_y/NO_x deposition ratios modeled per EMEP grid cell (Fig. S5) (wet deposition ratios: $r = -0.465$, $p < 0.01$; dry deposition ratios: $r = -0.422$, $p < 0.01$) the proportion of agricultural lands ($r = -0.496$, $p < 0.01$) and atmospheric NH_3 concentrations ($r = -0.364$, $p < 0.01$) (Table S1 and Fig. S6). These relationships suggest that nitrogen in mosses is derived from multiple

Table 2
Summary statistics of δ^{15}N isotopic signatures (‰, dry weight) in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Country	Number of sites	Mean	Standard deviation	Minimum	Maximum
Austria	219	−6.04	1.28	−10.01	−2.45
Belgium	25	−4.21	4.26	−8.72	6.60
Bulgaria	31	−4.69	1.17	−8.71	−2.14
Croatia	90	−5.34	1.70	−9.18	1.63
Finland	150	−3.69	1.04	−6.69	−1.17
France	166	−6.00	1.33	−9.05	−2.10
Germany	17	−3.65	1.13	−6.17	−1.57
Italy	20	−5.62	0.83	−7.36	−3.96
Macedonia	72	−3.47	1.36	−6.03	−0.38
Slovenia	55	−6.15	1.20	−9.75	−3.70
Spain	115	−3.92	1.87	−7.25	1.85
Sweden	100	−4.17	1.50	−8.09	0.17
Switzerland	10	−6.75	1.90	−10.35	−4.80
Turkey	72	−4.43	1.64	−8.32	0.81
UK	169	−4.54	1.76	−8.89	3.64
Europe	**1311**	**−4.85**	**1.92**	**−10.35**	**6.60**

atmospheric pools.

Considering that mosses take almost all their N from the atmosphere, $\delta^{15}N$ signatures in moss shoots are assumed to reflect the isotopic signatures of atmospheric compounds (Xiao et al., 2010). In this respect, several studies have linked more negative $\delta^{15}N$ values to predominant NH_3/NH_4^+ inputs, whereas slightly negative to positive values have been associated with NO_x fluxes. In other words, the greater the contribution of NH_4^+ as a nitrogen source for mosses, the more negative their $\delta^{15}N$ values, and conversely, when the oxidized species dominate, $\delta^{15}N$ values tend to be less negative or even positive (Boltersdorf et al., 2014; Du et al., 2023; Felix et al., 2016; Gerdol et al., 2014; Pearson et al., 2000; Stewart et al., 2002). Moreover, in many of these studies NH_y/NO_x ratios in deposition budgets are calculated to evaluate the influence of different N compounds on the stable isotopes of nitrogen. The spatial distribution of $\delta^{15}N$ signatures (Fig. 2B) and the bivariate correlation coefficients found in this study (Table S1 and Fig. S6) align well with these previous findings, suggesting a clear association between ^{15}N depletion in moss tissues and the dominance of reduced N species in deposition, as well as ^{15}N enrichment in mosses exposed to proportionally higher NO_x loads (Fig. S2). Therefore, these data confirmed that $\delta^{15}N$ isotopic signatures can be used to attribute N sources in biomonitoring surveys of atmospheric pollution at the European scale.

Nevertheless, it is important to highlight that while the most ^{15}N-depleted signatures were clearly related to agricultural lands and high N deposition loads of reduced compounds in central Europe, the relationship between slightly negative or positive signatures and NO_x fluxes was less clear. A deeper analysis of the spatial distribution patterns revealed two well-differentiated situations where $\delta^{15}N$ signatures showed ^{15}N enrichment.

On one hand, mosses from eastern countries (Macedonia and Turkey), Germany, Belgium and Galicia (Spain) were exposed to high N deposition fluxes, including significant loads of NO_x compounds (Fig. S2), and showed high tissue N concentrations (Fig. 2A). It is well-known that Germany has important industrial activity, and Galicia also houses considerable industrial centers. Indeed, both Germany and Spain failed to meet their NO_x emission ceilings in 2010 (EEA, 2014). Moreover, eastern countries have experienced high NO_x emissions because of a late industrial development and less strict implementation of regulatory policies (Gaigalis and Skema, 2015; Vestreng et al., 2009). As a result, the less negative $\delta^{15}N$ signatures observed in these countries seem to respond to the presence of important NO_x fluxes, according to the aforementioned premises.

On the other hand, mosses from northern UK, Finland and Sweden, despite also showing ^{15}N enrichment, were subjected to the lowest N deposition loads in Europe (Fig. S2) and exhibited the lowest N contents (Fig. 2A). In these cases, the less negative $\delta^{15}N$ signatures may be a sign of N-limitation in these ecosystems (Clarkson et al., 2005; Hyodo et al., 2013; McKee et al., 2002). This hypothesis was supported by the C/N ratio results (Gerdol et al., 2007; Munzi et al., 2013), which showed a positive correlation with $\delta^{15}N$ signatures ($r = 0.339$, $p < 0.01$; Table S1 and Fig. S6) and were extremely elevated in those areas of northern Europe as discussed later.

In addition, a significantly negative correlation between $\delta^{15}N$ signatures and tissue N content was found ($r = -0.346$, $p < 0.01$) (Table S1), indicating the important role of reduced nitrogenous species in nitrogen accumulation in mosses. This finding agrees with the work of Pitcairn et al. (2006), Solga and Frahm (2006) or Liu et al. (2013), who concluded that N concentrations in moss tissues are more responsive to NH_y exposure, thus providing a particularly reliable indicator of this type of atmospheric pollution. In this context, our data also revealed a weak but significant relationship between $\delta^{15}N$ and C ($r = 0.233$, $p < 0.01$) and $\delta^{13}C$ ($r = -0.187$, $p < 0.01$) (Table S1). These results suggest a decrease in C fixation and photosynthesis impairment associated with NH_y exposure (Du et al., 2014; Pintó-Marijuan et al., 2013).

3.2. N source apportionment

The proportional contributions calculated by the MixSIAR model reflect the combined effect of the $\delta^{15}N$ values of both primary and secondary nitrogen sources on the moss bulk nitrogen concentration. This approach allows us to quantitatively evaluate the relative contribution of each nitrogen pool, as the uptake of nitrogen into moss tissue does not introduce significant ^{15}N fractionation (Bragazza et al., 2005; Dawson et al., 2002). According to our results (Table S2), 38 to 52 % and 31 to 51 % of N in mosses across Europe can be attributed to gaseous uptake and wet deposition, respectively, while dry deposition accounted for only 9 to 17 %. These results are in line with the general consensus among researchers that dry N deposition does not dominate over wet N deposition in a large geographic region (Boltersdorf et al., 2014; Harmens et al., 2011; Xu et al., 2019). However, an exception to this pattern is observed in Belgium, where gaseous uptake dominates (67 %) over both wet (9 %) and dry (24 %) deposition (Table S2). In this case, the high proportion of gaseous uptake was almost exclusively due to NO_x emission from vehicles and biomass burning (55 %, Fig. 3), which is consistent with the elevated NO_x loads modeled by EMEP across most of this country (Fig. S2).

Areas with intense road traffic or near extensive agricultural regions, where ambient gaseous N compounds are abundant, are expected to show higher contributions from both dry deposition and gaseous uptake (Pearson et al., 2000; Xu et al., 2019). Indeed, similar trends of higher gaseous uptake were observed in Spain (52 %, with 45 % attributed to NO_x from combustion sources), the UK (48 %, with 41 % from combustion sources), Switzerland (45 %, with 33 % from combustion sources), Austria (44 %, with 31 % from combustion sources) and Turkey (43 %, with 36 % from combustion sources). Several of these regions also experienced high loads of NO_x emissions, as noted earlier. Globally, exhaust NO_x emission from vehicles was the second most important N source across Europe (10 to 51 % of the total N contributions, Fig. 3), representing between 27 and 76 % of the total estimated gaseous uptake. NO_x from biomass burning contributed between 4 and 19 % of the total N in mosses. On the contrary, primary gaseous contributions from livestock waste emissions accounted for <14 % of the total moss N across the surveyed European countries (Fig. 3). However, this source along with others such as fertilized soils (see Text S1 for more details) is probably the main contributor to the NH_4^+ in wet depositions.

For wet deposition, NH_4^+ was the dominant N form (5 to 43 % of the total N contributions), representing >60 % of wet deposition across Europe. This is largely due to the faster transfer rate of atmospheric NH_3 (e.g., from nearby agricultural areas) compared to NO_x (Hanson and Lindberg, 1991; Sutton et al., 1993), as well as the high relative humidity in forested areas and the relatively low NO_x emissions in these zones, which favor NH_3 absorption. In addition, N concentrations in moss tissues appear to respond more effectively to NH_y exposure (Liu et al., 2013; Pitcairn et al., 2006; Solga and Frahm, 2006). This result aligns with the significant correlation previously observed between $\delta^{15}N$ signatures and NH_y/NO_x wet deposition ratio, as well as between $\delta^{15}N$ signatures and the proportion of agricultural lands (Table S1 and Fig. S6). The highest NH_4^+ wet deposition contributions were estimated in Croatia (43 %) and France (40 %), while the lowest were recorded in Belgium (5.4 %), Spain (22 %) and in Finland and the UK (both with ~30 %) (Fig. 3). Wet NO_3^- deposition, on the other hand, contributed only 4 to 17 % of the total nitrogen in mosses. Similarly, NH_4^+ in dry deposition (4 to 21 % of the total N in mosses) appears to be more readily absorbed by mosses than NO_3^- (3 to 11 % of the total N in mosses).

In summary, nitrogen in moss samples across Europe appears to come mainly from secondary sources, accounting for >55 % in most countries, and is mainly derived from wet deposition (typically >70 % of the secondary contribution). In contrast, primary nitrogen mainly originates from combustion sources, and predominantly in its oxidized form. Notably, only in Belgium (67 % for primary and 33 % for secondary N) and Spain (52 % for primary and 48 % for secondary N)

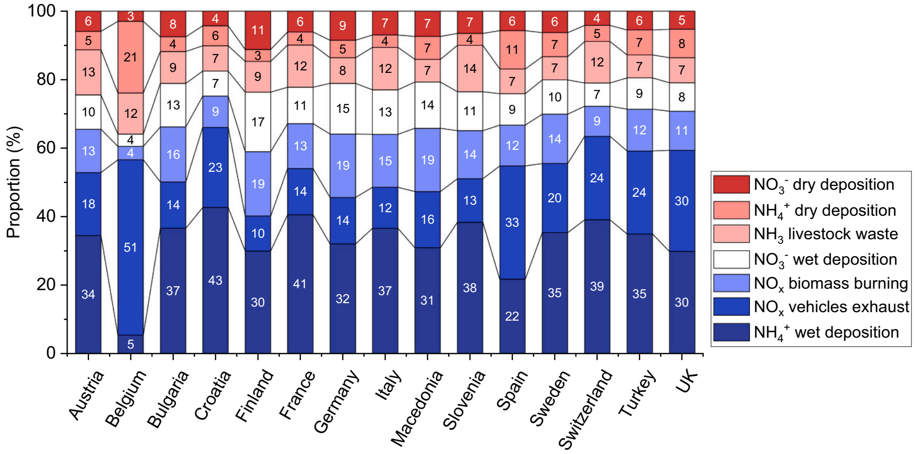

Fig. 3. Relative proportional N contributions (%) by European countries calculated by MixSIAR model.

primary nitrogen were predominant, while in the UK (48 % for primary and 52 % for secondary N), near balanced contributions from these two pools of atmospheric nitrogen was estimated. This first isotope-derived quantitative overview of the main atmospheric nitrogen sources for mosses offers a new perspective, facilitating the assessment of historical changes in nitrogen deposition contributors on a European scale (from 2005–2006 to the present), and providing a novel and important aspect to the European moss surveys conducted under the ICP Vegetation programme.

3.3. C elemental contents, C/N ratio and $\delta^{13}C$ signatures

With respect to C, the mean content in moss tissues across Europe was 44.05 %, ranging from 25.17 to 51.07 % (Table 3). According to its spatial pattern (Fig. 4A), the largest C concentrations were observed in the northernmost sampled countries (UK, Sweden and Finland), whereas mosses collected in central and southern Europe exhibited lower total C values.

Considering the correlation analyses, the data revealed a significant negative relationship between carbon (C) and nitrogen (N) concentrations in mosses ($r = -0.480, p < 0.01$), similar to the correlation with the percentage of agricultural soil per EMEP cell ($r = -0.310, p < 0.01$), and with the NHy/NOx ratio in wet deposition (r = −0.312, p < 0.01) (Table S1). These results were in line with those observed in $\delta^{15}N$ signatures and suggest detrimental effects of N-reduced compounds on C

Table 3
Summary statistics of total C concentration (%, dry weight) in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Country	Number of sites	Mean	Standard deviation	Minimum	Maximum
Austria	219	43.79	1.69	26.16	47.77
Belgium	27	42.43	3.54	29.38	47.82
Bulgaria	31	41.21	2.52	32.73	44.29
Croatia	90	43.58	0.94	38.62	45.23
Finland	150	45.51	0.81	42.34	50.31
France	166	42.87	1.88	31.24	45.10
Germany	17	43.49	1.15	40.02	44.70
Italy	20	45.18	0.89	43.35	46.78
Macedonia	72	43.33	0.93	39.98	45.08
Slovenia	–				
Spain	115	41.70	3.90	25.17	46.66
Sweden	100	45.93	0.90	43.91	47.68
Switzerland	10	43.96	0.59	42.65	44.66
Turkey	72	41.31	2.30	28.82	43.53
UK	169	47.13	1.52	35.02	51.07
Europe	**1258**	**44.05**	**2.60**	**25.17**	**51.07**

fixation. To further investigate this, the C/N ratio was examined, as changes in the tissue stoichiometry have been associated with the impacts of N pollution (Arróniz-Crespo et al., 2008; Du et al., 2014).

In order to counterbalance the toxic effects of NH_y compounds, plants have developed several mechanisms operating at different levels. However, when the foliar uptake of NH_y exceeds the assimilation capacity, N begins to accumulate in tissues, causing adverse effects (Bittsánszky et al., 2015; Krupa, 2003). One detoxification strategy involves storing nitrogen in organic compounds, such as amino acids (Krupa, 2003; Paulissen et al., 2005). This process, aimed at reducing NH_y cytosolic toxicity, relies on the availability of C skeletons (Koranda et al., 2007). However, when the photosynthetic machinery is affected, C fixation is disrupted, resulting in decreased C/N ratios and increased stress levels caused by nitrogen accumulation (Munzi et al., 2013).

The results of C/N ratios showed a mean for Europe of 38.13, with values ranging from 11.15 to 118.21 (Table 4). Spatially, the highest ratios were found in Sweden, Finland and UK (Fig. 4B), following a north-south gradient similar to that observed for tissue N concentrations (Fig. 2A). On the contrary, the lowest C/N values were recorded in central Europe, especially in Belgium, Croatia and France, as well as in specific areas in southern UK, southern Sweden and in the eastern countries (Fig. 4B). These patterns totally agreed with those found for EMEP modeled N deposition (Fig. S2). Statistical correlations and regression analyses corroborated these results, showing a significantly negative relationship of C/N ratios with EMEP modeled total N deposition ($r = -0.552, p < 0.01$) and with N contents in mosses ($r = -0.980$, $p < 0.01$) (Table S1 and Fig. S7).

These data indicated that in N-enriched areas, mosses fail to compensate for elevated N uptake with increased C assimilation rates, which suggests a N-induced deleterious effect on the photosynthetic machinery of the species growing in those regions. Regression analysis (Fig. S7) further support this, showing that mosses with tissue N contents exceeding 1.1–1.2 % may experience physiological alterations due to enhanced N deposition. Therefore, C/N ratios show a great potential to identify regions at risk from atmospheric N pollution across Europe.

The results for tissue C results revealed a spatial distribution pattern (Fig. 4A) coincident with the distribution of topsoil organic C contents in Europe (de Brogniez et al., 2015; Jones et al., 2005), suggesting that the substrate may influence moss tissue chemistry. Although mosses obtain most of their nutrients from the atmosphere, some authors have reported that they are able to uptake carbon from the humus layer (Rousk et al., 2013). Additionally, several investigations have demonstrated that the bryosphere, located within the boundary layer next to the ground, captures an estimated 10–36 % of total forest floor CO_2 efflux arising from decomposition and heterotrophic soil respiration (Botting and Fredeen, 2006; Lindo and Gonzalez, 2010; Swanson and Flanagan,

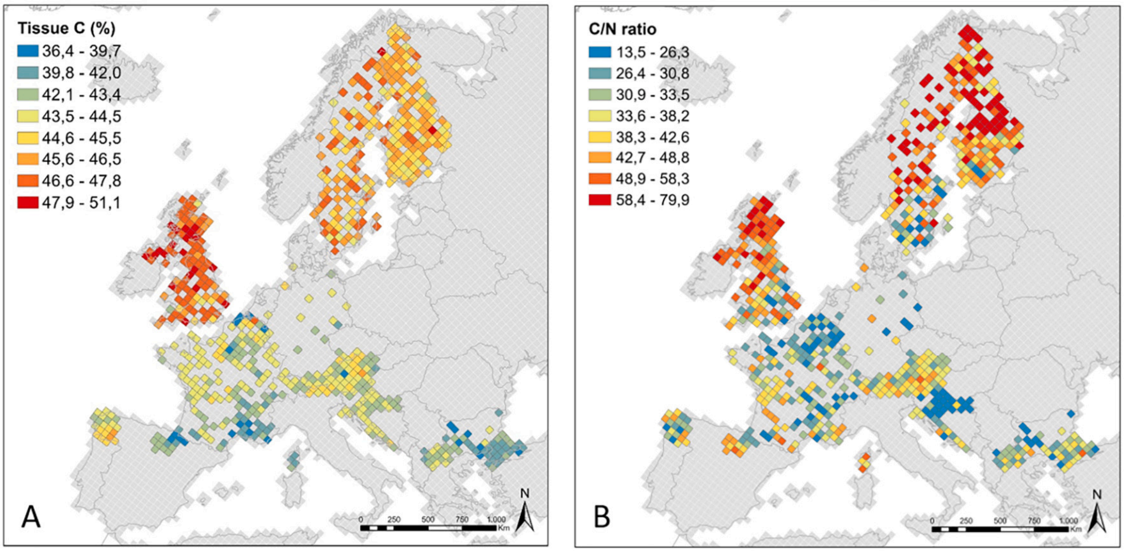

Fig. 4. Mean concentration of C (A) and mean C/N ratios (B) per EMEP grid cell in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Table 4
Summary statistics of C/N ratios in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Country	Number of sites	Mean	Standard deviation	Minimum	Maximum
Austria	219	37.79	8.14	21.15	58.85
Belgium	27	27.28	7.34	15.81	46.34
Bulgaria	31	32.10	7.28	17.66	49.74
Croatia	90	25.29	8.48	11.15	44.81
Finland	150	55.70	15.85	25.51	88.10
France	166	33.15	7.49	21.20	55.34
Germany	17	33.82	8.53	22.94	47.91
Italy	20	39.70	6.17	30.21	57.96
Macedonia	72	33.59	7.96	18.71	53.43
Slovenia	–				
Spain	115	34.29	9.22	17.42	57.95
Sweden	100	52.37	20.24	19.10	118.21
Switzerland	10	38.76	13.51	20.30	69.79
Turkey	72	34.26	7.47	17.46	53.85
UK	169	47.96	11.13	15.80	69.78
Europe	**1258**	**38.13**	**14.41**	**11.15**	**118.21**

Table 5
Summary statistics of $\delta^{13}C$ isotopic signatures (‰, dry weight) in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

Country	Number of sites	Mean	Standard deviation	Minimum	Maximum
Austria	219	−30.47	1.41	−34.44	−26.62
Belgium	27	−30.86	0.94	−32.53	−28.61
Bulgaria	31	−29.43	1.13	−31.56	−26.89
Croatia	90	−30.65	1.80	−35.60	−27.16
Finland	150	−31.19	0.76	−33.46	−29.36
France	166	−30.05	0.68	−32.34	−28.02
Germany	17	−33.72	1.29	−35.19	−30.21
Italy	20	−28.90	1.32	−32.07	−26.76
Macedonia	72	−29.57	0.88	−32.38	−28.01
Slovenia	–				
Spain	115	−29.56	1.71	−39.31	−26.29
Sweden	100	−31.60	1.26	−34.22	−26.99
Switzerland	10	−29.60	1.07	−31.39	−28.22
Turkey	72	−29.09	0.83	−32.22	−26.84
UK	169	−30.01	0.91	−33.04	−27.24
Europe	**1258**	**−30.32**	**1.43**	**−39.31**	**−26.29**

2001). In consequence, both processes may act synergistically to increase the content of C in moss tissues, providing a supplemental C input in addition to atmospheric sources.

In addition to elemental measurements and similarly to $\delta^{15}N$ signatures, carbon stable isotopes may play a key role in the attribution of C sources and the identification of the main environmental factors influencing C fixation in mosses. The $^{13}C/^{12}C$ isotopic ratio of atmospheric CO_2, known to vary depending on its origin, has been effectively employed to trace potential CO_2 emission sources in pollution surveys (Lopez et al., 2013; Popa et al., 2014; Townsend-Small et al., 2012). However, relatively few studies have explored $\delta^{13}C$ signatures in plants as potential bioindicators of pollution emission sources in monitoring surveys (Díaz-Álvarez and Barrera, 2020; Liu et al., 2010, 2008b; Norra et al., 2005; Zambrano Garcia et al., 2009). This limited application may be due to the numerous environmental factors affecting the $\delta^{13}C$ signature in plant tissues, including temperature, water availability or altitude (Alewell et al., 2011; Deane-Coe et al., 2015; Menot and Burns, 2001; Skrzypek et al., 2007).

The $\delta^{13}C$ analyses of European mosses showed a mean value of −30.32 ‰, ranging from −39.31 to −26.29 ‰ (Table 5). Spatial trends (Fig. 5) indicated that the lowest $\delta^{13}C$ levels were observed in the northernmost countries (Finland and Sweden) and in central Europe (Germany, Belgium, Austria and Croatia, and locally in some areas of the south-east of UK). On the contrary, the highest values were registered in the southernmost sampling regions (Italy, Turkey, Bulgaria and Spain).

The spatial distribution of $\delta^{13}C$ in central and eastern Europe (Fig. 5) was coincident with the highest NO_x deposition loads modeled by EMEP (Fig. S2) in a such manner that the lowest $\delta^{13}C$ values were registered in those areas receiving the most elevated fluxes of oxidized compounds. Moreover, correlation analyses revealed a positive association between $\delta^{13}C$ signatures and the atmospheric wet NH_y/NO_x deposition ratios ($r = 0.315$, $p < 0.01$, Table S1). Since NO_x atmospheric emissions are typically associated with other gaseous pollutants, it can be expected that increased anthropogenic CO_2 concentrations in these areas contribute to the more negative $\delta^{13}C$ values in mosses. These findings are in line with previous studies by Liu et al. (2010, 2008b) and Lichtfouse et al. (2003), who observed lower $\delta^{13}C$ signatures in mosses from urban compared to rural locations. Similarly, Pataki et al. (2007) demonstrated a decreasing trend in $\delta^{13}C$ signatures of atmospheric CO_2 along a rural-to-urban gradient. On the other hand, $\delta^{13}C$ values in urban areas of China typically ranged from −29.5 to −31 ‰ (Liu et al., 2010,

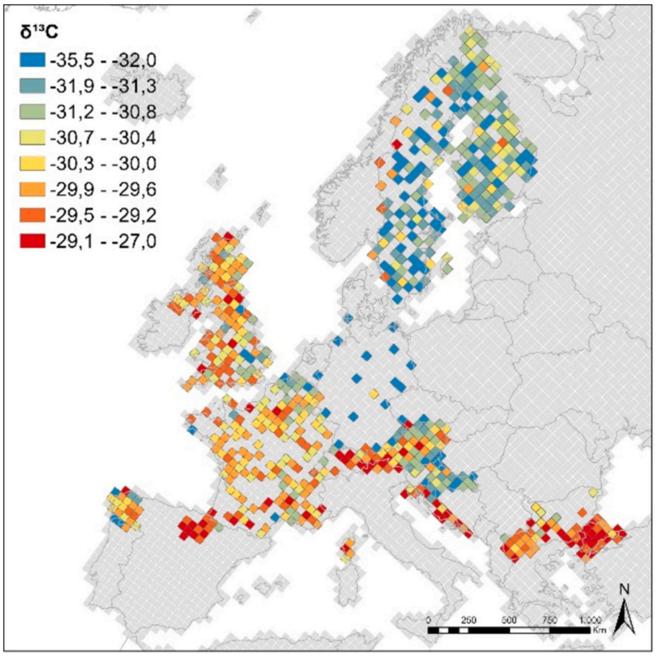

Fig. 5. Mean values of $\delta^{13}C$ per EMEP grid cell in selected moss samples collected across 15 European countries during the 2005/2006 ICP-Vegetation moss survey.

2008b), higher than those recorded in parts of Germany and Croatia, where mosses reached values below −32 ‰ (Table 5 and Fig. 5), in line with the results found by Lichtfouse et al. (2003) in grasses collected in Paris. These lower $\delta^{13}C$ values in the European sites might be explained by a greater proportion of CO_2 coming from the combustion of natural gas, a source known to produce ^{13}C depleted CO_2 (up to −41 ‰; (Pang et al., 2016; Widory, 2006)). Supporting this, studies by Zondervan and Meijer (1996) in the Netherlands and Lopez et al. (2013) in Paris determined that natural gas combustion accounted for >50 % of total fossil fuel CO_2 emissions in these regions. Consequently, C stable isotopes can be considered as effective markers of anthropogenic CO_2 in polluted areas. However, caution is advised due to the sensitivity of $\delta^{13}C$ to regional temperature gradients, as highlighted by a weak but significant positive correlation between these variables ($r = 0.331$, $p < 0.01$) (Table S1 and Fig. S8). Despite this, this relationship shows considerable variability (Fig. S8), likely influenced by factors such as anthropogenic emissions, altitude (with some of the least negative $\delta^{13}C$ values recorded at high altitudes in the Alps), and other environmental factors, which are discussed further below.

Following the above assumptions, the less negative $\delta^{13}C$ values found in the rest of central European countries and the UK would correspond to lower anthropogenic CO_2 sequestration by mosses, which is in accordance to the lower NO_x deposition loads recorded in these areas (Fig. S2). Furthermore, the '*Moss Survey Protocol*' (https://icpvegetation.ceh.ac.uk/moss-survey-protocol) specifies that samples are collected at locations away from the influence of pollution sources. Therefore, $\delta^{13}C$ values ranging between approximately −29.5 and −30.5 ‰ in this survey may be indicative of background conditions. In this respect, our results align with those reported by Lichtfouse et al. (2003), who determined $\delta^{13}C$ signatures in grasses from rural areas in France. Similarly, a more recent study conducted in northern Spain showed similar values of $\delta^{13}C$ isotopic ratios in a background area (−29.4 ± 0.41 ‰; Izquieta-Rojano et al. (2018)).

The Nordic countries also exhibited low $\delta^{13}C$ signatures values (Fig. 5), although their atmospheric emissions circumstances differ significantly from those of central and eastern Europe (Fig. S2). This suggests that $\delta^{13}C$ values in these regions may be more strongly influenced by the lower temperatures (Figs. S8 and S9), as previously discussed. However, the observed $^{13}C/^{12}C$ ratios likely also reflect site-specific conditions rather than solely atmospheric pollution or temperature dependence, as indicated by the high dispersion observed in the spatial distribution of $\delta^{13}C$ within these countries (Fig. 5). In boreal and sub-boreal forests, where feather mosses, sphagnum and pleurocarpous carpet-forming species are widespread, these mosses play a key role in CO_2 and water-exchange processes between the terrestrial biosphere and the atmosphere (Williams and Flanagan, 1996). Notably, previous studies have demonstrated that understory moss layers in such ecosystems can assimilate a significant portion of the soil-respired CO_2, as explained before (Botting and Fredeen, 2006; Swanson and Flanagan, 2001). As a result, the $\delta^{13}C$ values in these regions may also reflect soil-moss interactions. In this regard, Flanagan et al. (1999) found a progressive enrichment of ^{13}C with depth in a moss-soil profile, with green mosses at the surface being the most ^{13}C depleted (−31 ‰). Similarly, Clymo and Bryant (2008) observed that dissolved gases such as CO_2 and CH_4 near the soil surface were more ^{13}C depleted than those at deeper levels, with difference exceeding 20 ‰. This depletion pattern is likely drive by the preferential release of ^{12}C during aerobic mineralization of soil organic matter, a process more pronounced in the upper part of the soil profile and favored by the lower decomposition rates in cooler temperatures (Alewell et al., 2011; Bowling et al., 2008; Egli et al., 2016). Additionally, root and microbial respiration can also modify $\delta^{13}C$ signatures of total soil CO_2 effux (Ehleringer et al., 2000; Werth and Kuzyakov, 2010). On the other hand, Scartazza et al. (2004) studied different ecosystem compartments, from soil to leaves from the upper layer, and found that while soil $\delta^{13}C$ was the most ^{13}C enriched, both buds and leaves from the bottom layer were the most ^{13}C depleted. Based on these findings, it is plausible that low $\delta^{13}C$ signatures in mosses from Finland and Sweden also reflect contributions from ^{13}C-depleted gaseous fluxes from the soil.

In any case, the considerably lower $\delta^{13}C$ signatures observed in the present survey in certain areas of the northern countries compared to other values from boreal forests (e.g. −31 ‰; (Flanagan et al., 1999)) suggest that a more ^{13}C-depleted source may also be influencing the C isotopic signatures of mosses in those locations. Although forested areas constitute the predominant land use in these latitudes, wetlands and peat bogs also accounts for a significant proportion, with the highest percentage of wetlands and peat bogs in Europe found in the Nordic countries ("CLC," 2006). These ecosystems are among the most remarkable natural sources of CH_4 in the atmosphere (Clymo and Bryant, 2008; Schaefer et al., 2016). In this context, mosses growing in peatlands have shown the ability to utilize CH_4 as a supplementary C source (Raghoebarsing et al., 2005), which is known to have a $\delta^{13}C$ signature much more negative than that of atmospheric CO_2 ($\delta^{13}C_{CH4}$ ∼−60 to −70 ‰; (Chasar et al., 2000; Sriskantharajah et al., 2012)). Thus, the more ^{13}C-depleted signatures in these areas may be a sign of CH_4 assimilation by mosses in such environments.

At the other end, the highest $\delta^{13}C$ signatures in mosses were found in the southernmost areas. Although N deposition was as low in these regions as in the Nordic countries, climatic conditions differed greatly, becoming warmer and drier towards the south (Jones, 2004). Several studies have investigated the influence of environmental factors on the $\delta^{13}C$ signatures in different ecological compartments (Bramley-Alves et al., 2015; Skrzypek et al., 2007; Toet et al., 2006; Werth and Kuzyakov, 2010), concluding that water availability and temperature are crucial factors in determining C isotopic partitioning. Specifically, it has been shown that plants growing in dry habitats under hydric stress tend to be more enriched in the heavier isotope (^{13}C enriched) (Pinto et al., 2012). In line with these findings, the higher $\delta^{13}C$ values observed in southern Europe in this survey may reflect conditions of lower water availability and higher temperature. Moreover, in dry and harsh environments like those found in the Mediterranean region, it has been proved that wind-blown soil dust can contribute to the elemental composition of mosses (Bargagli et al., 1995; Izquieta-Rojano et al., 2016). In this regard, soil C isotopic signatures are typically ^{13}C enriched (Guo et al., 2016; Scartazza et al., 2004). Thus, the higher $\delta^{13}C$ values observed in these areas might partly be due to the influence of soil particles deposited on the surface of mosses.

4. Conclusions

According to our findings, the analysis of stable $\delta^{13}C$ and $\delta^{15}N$ signatures in mosses provides additional information to complement the analysis of C and N content in moss tissues obtained from European moss surveys. These isotopic signatures offer qualitative and quantitative valuable insights into the likely pollution sources of these elements. Moreover, the combined analysis of $\delta^{13}C$ and $\delta^{15}N$ was found to be highly effective in identifying key ecological processes and assessing the influence of various environmental factors on regional distribution patterns.

Results from total N concentrations aligned with previous surveys conducted under the ICP-Vegetation programme, confirming that Central and Eastern Europe are the most affected regions because of N deposition. Additionally, an association between ^{15}N depletion in moss tissues and the dominance of reduced N species in deposition was observed, whereas ^{15}N enrichment in mosses was linked to higher NO_x loads. This relationship was quantitatively confirmed using the MixSIAR model, which showed that NH_4^+ from wet deposition and NO_x from combustion sources accounted for 5 to 42 % and 27 to 55 % of the total N contributions, respectively. These sources were identified as the most significant N pools for mosses across Europe. This finding provides a framework for assessing historical changes in nitrogen deposition sources across Europe based on the isotopic approach presented in this study.

Combined results from total C and N contents underscored the significant influence of increasing N deposition loads on tissue stoichiometry. These findings highlight the great potential of using C/N ratios as a tool to identify N-related ecological impacts at a regional scale. However, while the analysis of $\delta^{13}C$ signatures suggested that more negative values in polluted areas might indicate anthropogenic CO_2 uptake by mosses, site-specific and environmental factors appear to significantly influence their spatial distribution. This underscores the need for caution when using $\delta^{13}C$ isotopic signatures for air quality biomonitoring, as their interpretation should be tailored to each study area. We recommend focusing regional-scale applications on identifying areas where pollution, environmental conditions, or ecological processes predominantly influence the distribution patterns.

CRediT authorship contribution statement

Sheila Izquieta-Rojano: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yasser Morera-Gómez:** Writing – review & editing, Visualization, Software, Methodology, Formal analysis, Data curation, Conceptualization. **David Elustondo:** Writing – review & editing, Writing – original draft, Supervision, Resources, Investigation, Conceptualization. **Esther Lasheras:** Writing – review & editing, Resources, Data curation. **Carolina Santamaría:** Writing – review & editing, Resources, Data curation. **Julen Torrens-Baile:** Writing – review & editing, Visualization, Software. **Renate Alber:** Writing – review & editing, Resources. **Lambe Barandovski:** Writing – review & editing, Resources. **Mahmut Coşkun:** Writing – review & editing, Resources. **Munevver Coskun:** Writing – review & editing, Resources. **Helena Danielsson:** Writing – review & editing, Resources. **Ludwig De Temmerman:** Writing – review & editing, Resources. **Harry Harmens:** Writing – review & editing, Resources. **Zvonka Jeran:** Writing – review & editing, Resources. **Sébastien Leblond:** Writing – review & editing, Resources. **Javier Martínez-Abaigar:** Writing – review & editing, Resources. **Encarnación Núñez-Olivera:** Writing – review & editing, Resources. **Roland Pesch:** Writing – review & editing, Software. **Gunilla Pihl karlsson:** Writing – review & editing, Resources. **Juha Piispanen:** Writing – review & editing, Resources. **Gerhard Soja:** Writing – review & editing, Resources. **Zdravko Spiric:** Writing – review & editing, Resources. **Trajče Stafilov:** Writing – review & editing, Resources. **Lotti Thöni:** Writing – review & editing, Resources. **Jesús Miguel Santamaría:** Writing – review & editing, Writing – original draft, Supervision, Resources, Investigation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.178043.

Data availability

Data will be made available on request.

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