Deciphering human-climate interactions in an ombrotrophic peat record: REE, Nd and Pb isotope signatures of dust supplies over the last 2500 years (Misten bog, Belgium)
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Abstract

A high-resolution peat record from Eastern Belgium reveals the chronology of dust deposition for the last 2500 years. REE and lithogenic elements in addition to Nd and Pb isotopes were measured in a 173 cm age-dated peat profile and provide a continuous chronology of dust source and intensity. Calculated dust flux show pronounced increases c. 300 BC, 600 AD, 1000 AD, 1200 AD and from 1700 AD, corresponding to local and regional human activities combined with climate change.

The Industrial Revolution samples (1700–1950 AD) are characterised by a significant enrichment in Sc-normalised REE abundance (sum REE/Sc > 25) due to intensive coal combustion. For the pre-Industrial Revolution samples, the Sc-normalised REE abundance (10 < Sum REE/Sc < 25) and the $\epsilon$Nd variability ($/C_0 < 9$) are interpreted by a mixing between dust particles from local soils and long-range transport of desert particles. Three periods characterised by dominant-distal sources (c. 320 AD, 1000 AD and 1700 AD) are consistent with local wetter-than-average intervals as indicated by a lower degree of peat humification. Local erosion prevails during the drier (higher humification) intervals (100 AD, 600 AD). On a global scale, more distal supplies are driven during colder periods, in particular during the Oort and Maunder minima, suggesting a potential link between dust deposition and global climate. Combining REE abundance, fractionation between Light REE and Heavy REE and Nd isotope data in ombrotrophic peat allows one to distinguish between dust flux changes related to human and climate forcings.

1. INTRODUCTION

Our knowledge of climate evolution is derived from the analysis of biological and geological archives, such as tree rings (e.g., Lieubeau et al., 2007), ice cores (e.g., Lambert et al., 2012), marine and lacustrine sediments (e.g., Bradley, 1999). Peatlands (i.e., soils accumulating partially decomposed plant remains with above 50% of organic matter and greater than 30 cm deep, Clymo, 1987) are continental archives of particular interest because they are easy to date, have a high temporal resolution (decadal) and contain multiple measurable parameters dependent on environmental conditions including temperature and/or humidity,
atmospheric circulation and wind strength (e.g., Chambers et al., 2012). In particular ombrotrophic bogs are commonly used to reconstruct Holocene climate variability (e.g., Dupont, 1986; Hong et al., 2000; Shotyk et al., 2002; Mauquoy et al., 2002; Chambers and Charman, 2004; Roos-Barraclough et al., 2004; Sapkota et al., 2007; Lamentowicz et al., 2008; Moschen et al., 2011; Kylander et al., 2013). Ombrotrophic environments are hydrologically isolated from the surrounding landscapes; they receive all of their water and nutrients from precipitation (rain, snow, fog) and wind, with no influence from streams (e.g. Chambers and Charman, 2004). Ombrotrophic peatland is often bog, dominated by Sphagnum mosses. In comparison with ice cores, they have two main advantages: (1) a widespread terrestrial global distribution, providing easy access and sampling, (2) the easy application of radioisotope dating techniques ($^{210}$Pb and $^{14}$C). Since ombrotrophic peat is almost exclusively constituted of organic matter, it yields high-resolution and low-uncertainty chronologies (Charman and Mäkilä, 2003).

In addition to pollen (e.g. Persch, 1950; Anshari et al., 2001; Davis et al., 2003; Finsinger et al., 2006), there are a variety of complementary potential indicators of past climate in peatland profiles. Moisture content of the Sphagnum mosses, water table depth, humification levels, macromains and testate amoebae are directly linked to climate, and more specifically to the balance between evaporation and precipitation (e.g. McCarthy et al., 1995; Mauquoy et al., 2002; Barber et al., 2003; Roos-Barraclough et al., 2004; Lamentowicz et al., 2008; Mitchell et al., 2008). The oxygen, carbon and deuterium stable isotope compositions of peat plant cellulose have been used to reconstruct air temperatures (Dupont, 1986; Hong et al., 2000; Moschen et al., 2011). Besides those classical biological proxies, the inorganic fraction of peat also provides information on the abundance and origin of atmospheric mineral dust affecting the Earth’s climate system (Goudie and Middleton, 2001; Harrison et al., 2001; Oppenheimer, 2003).

North African deserts currently represent the largest worldwide source of mineral dust (Moulin et al., 1997), supplying ~0.8 x 10$^9$ tons per year of material transported in suspension in the atmosphere (Goudie and Middleton, 2001; Laurent et al., 2008). According to Vanderstraeten et al. (2008), “the amount of airborne dust varies in accordance with the general and local meteorological situation, the complexity of relief forms, lithology and provenance (direction and distance from the source) of the dust”. Dust is first uplifted by local winds, transported by an increased vertical velocity to higher latitudes (Engelstaedter and Washington, 2007) and then transported over hundreds to thousands of kilometers along three main transport pathways (Goudie and Middleton, 2001) (see SM1). Most of the dust is carried westward over the North Atlantic Ocean by the trade winds (D’Almeida, 1986; Kellogg and Griffin, 2006; Scheuvens et al., 2013). However, due to peculiar meteorological conditions (e.g., low pressure systems, creation of easterly waves – White et al., 2012; Scheuvens et al., 2013), an eastward or a northward flow may punctually bring dust across the Mediterranean Sea to adjacent...
countries. Occasionally dust is even deposited north of the Alps, transported by anticyclonic cells and washed out by rain (see Stuut et al., 2009 for a review). White et al. (2012) have reported more than 500 dust-fall events across Europe since 1900. For instance, in Belgium calculated backward trajectories have allowed the determination of a Saharan origin for a dust event observed in March 2007 above Brussels (Vanderstraeten et al., 2008).

Previous work has used peat cores as dust archives (Shotyk et al., 1998, 2002; Björck and Clemmensen, 2004; Martini and Martinez-Cortizas, 2006; Sapkota et al., 2007; De Vleeschouwer et al., 2009; Le Roux et al., 2012; Kylander et al., 2013). For instance Shotyk et al. (1998) used the geochemical signature of peat to reconstruct the atmospheric particulate flux for the entire Holocene in a 6 m bog in the Swiss Jura. The changes in dust flux were further linked to major modification in atmospheric trajectories and therefore to climate reorganisation. Later Sapkota et al. (2007) published a record of 6000 years of atmospheric dust deposition in southern South America and Kylander et al. (2013) have reconstructed 8500 years of dust deposition in Sweden.

Recently Nd isotope data from the same Swiss Jura bog confirmed the importance of Sahara desert as a dust source over West Europe (Le Roux et al., 2012). In particular a sharp dust event at 8.4 kyr may suggest a role of atmospheric dust in the inception of the 8.2 kyr BP cold event. Moreover a long-term change in Sahara-dust supplies evidenced from 7 to 5 kyr B.P is consistent with the termination of the African humid period (Sahara aridification). Such studies underline the importance of high-resolution peat bog investigations for a better understanding of the role of dust in Holocene climate change. However ombrotrophic bogs record both natural and anthropogenic dust supplies. For instance, based on a high resolution study on the Misten peatland De Vleeschouwer et al. (2012) emphasized that variations in dust fluxes, derived from the elementary composition of the upper first meter of peat, could not be directly interpreted in term of climate changes for the late Holocene, and especially for the past millenium, where both influences are difficult to distinguish. Therefore before making any climate interpretations, the sources of dust must be identified. Radiogenic isotope signatures of sediments are often used as provenance proxies as they are not affected by erosion and transport (i.e., conservative behavior during the sedimentary cycle, Goldstein et al., 1984). Pb isotopes, particularly in petlands, have been often used as evidence of anthropogenic heavy metal pollution (e.g., Shotyk et al., 1998; Dunlap et al., 1999; Klaminder et al., 2005; Ferrat et al., 2012a,b). Another radiogenic isotope system, the Sm/Nd, is less sensitive to trace metal pollution, but Nd isotope data for peat samples are scarce, and have only been measured at a few sites (Blue Cypress in Florida; Kamenov et al., 2009; Etang de la Gruère in Switzerland, Le Roux et al., 2012). If their conservative behaviour can be demonstrated, both Nd and Pb isotopes may be used to discriminate between sources of dust in bogs.

In this study, we aim to measure REE content in peat samples to record the dust fluxes over the past 2500 years in western Europe. We use their Nd isotope signatures to decipher between local and distal dust supplies, while Pb isotopes are used to trace anthropogenic influences. We interpret the changes in dust sources with regard to local hydrological conditions derived from humification degree (dry/wet) and global climate conditions (cold/warm) from solar activities.

2. MATERIAL AND METHODS

The present study is focused on the upper section of an ombrotrophic bog located in a nationally protected peatland area, the Hautes-Fagnes Plateau in East Belgium (~3750 ha, Frankard et al., 1998). The Hautes-Fagnes Plateau is part of the Stavelot Massif, mainly composed of lower Paleozoic quartzites and pyllades (Verniers et al., 2001). The geological substratum is covered by post-Paleozoic sediments (clays of alteration, continental and marine sands, loess – Bourgignon, 1953) with some occasional outcrops of Early Cambrian (Revinian) quartzites. In the last 10 years, some geochemical work has been carried out on selected sites from the Hautes Fagnes Plateau (Gaida et al., 1993, 1997; Kempter, 1996; Renson et al., 2008) and in the Misten in particular (De Vleeschouwer et al., 2007, 2009, 2010, 2012; Allan et al., 2013a). The selected Misten bog is produced by an accumulation of 8 m (estimated by a radar surface prospecting – Wastiaux and Schumacker, 2003) of Holocene peat (De Vleeschouwer et al., 2007). For this study, cores were taken in February 2008: the upper meter was retrieved with a Ti-Wardenaar corer (Wardenaar, 1987) (core MIS-08-01W), whilst the next few meters were extracted with a Bielorussian corer (Belokopytov and Veresnevich, 1955) (core MIS-08-01b). The cores were stored at –40 °C, and frozen cores were cut at a 1.5 cm sampling interval by a stainless steel band saw at the University of Heidelberg (Givelet et al., 2004). The sample slices were sub-sampled into two. Half the sample slice was freeze-dried, then mechanically-ground, using an agate ball mill at the University of Liège, to measure the degree of humification, elemental concentrations and Nd and Pb isotope geochemistry. Remaining core samples were stored at –4 °C for further analyses, including dating. Peat densities were calculated by weighing a known volume of fresh peat extracted by a cylindrical stainless punch.

Here we focus on the upper 173 cm of peat, i.e., an ombrotrophic section (Allan et al., 2013c) that covers the past 2500 years (ages reported in Table 1). The Ca/Mg ratio and Sr concentrations were used to identify the ombrotrophic section as proposed by Shotyk et al. (2001). Note that such geochemical-derived limits are consistent with a biological limit (Payne, 2011), i.e., a sharp change in the testate amoebae assemblages (Master thesis T. Salpeteur, unpublished data).

The building of the age-depth model is described in Allan et al. (2013a). Briefly, it was established by merging cores MIS-08-01W and MIS-08-01b. The chronology was constrained by 210Pb activities measured on the upper 25 cm of peat by alpha spectrometry (Sikorski and Bluszcz, 2008) at the GADAM Centre (Gliwice, Poland)
The enrichment factor was calculated in regard with Upper Continental Crust (UCC) for selected REE (La, Nd, Eu and Yb) using Sc as a conservative element. Note density, humification level, age, accumulation rate and Ti content have been previously published in Allan et al. (2013b).
and ten \(^{14}\text{C}\) dates of extracted peat macromains by Acceleration Mass Spectrometer (AMS). The \(^{14}\text{C}\) samples have been prepared according to protocol by Piotrowska (2013) at the GADAM Centre. For the upper part, \(^{206}\text{Pb}\) age dates were derived using the CRS model (Appleby, 1978). To build the final age-depth model, \(^{206}\text{Pb}\) and \(^{14}\text{C}\) data were processed using Bacon software (Blaauw and Christen, 2011).

The humification degree (HD) was measured by a colorimetric method using an Aldrich spectrophotometer (Station Scientifique des Hautes Fagnes) on alkaline peat extracts, according to protocols given in Chambers et al. (2011). About 200 mg of dried and powdered peat samples were mixed with 100 ml of NaOH (8%), and the solution was boiled for 1 h. After cooling, the solution was brought to 200 ml with MQ distilled water, homogenized and filtered using Whatman (n\(^1\)) filter paper. Before measurement, 50 ml of solution was taken and diluted with 50 ml of MQ distilled water. A standard with a humification level of 100% (Humic acid technical, ALDRICH) was included in the measurement. The absorbance was measured at 540 nm. The humification percentage was derived from the ratio between the absorption values in peat samples and standard.

Elemental geochemical measurements were made on 200 mg of dried and powdered peat samples after digestion at high pressure (120 bars) and high temperature (240 \(^{\circ}\)C) in a microwave autoclave in Germany (Institute of Geochemistry Environmental, University of Heidelberg) following Krachler et al. (2002). Peat samples, blanks and vegetation standards were dissolved in 3 ml HNO\(_3\) (65%, analytical-reagent grade and further purified by sub-boiling distillation) and 0.1 ml HBF\(_4\) (50%, purum). The digestion of organic matter was improved by introducing H\(_2\)O\(_2\) vapours from the base cup of the device. After digestion, 3 ml of solution was transferred to a Falcon tube then filled up to 14 ml. In Toulouse, an aliquot of 500 \(\mu\)l was transferred into a new Falcon tube and diluted with 10 ml of HNO\(_3\) (2%, ultrapure) and 100 \(\mu\)g of an In-Re internal standard solution. Ti, Sc and Rare Earth Element (REE) contents were measured by a Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q-ICP-MS 7500 Agilent (Observatoire Midi-Pyrénées, Toulouse). The Agilent 7500 ce is equipped by a collision cell allowing to minimize interferences. Blank concentrations of diluted solutions are negligible, representing usually less than 0.1% of the digested diluted peat solutions. The limits of quantification were calculated from the intensity and standard deviation measurements of 6 blanks. They range between a few pg g\(^{-1}\) for La, one hundred pg g\(^{-1}\) for Nd, and a few ng g\(^{-1}\) for Pb and Ti. Such limits of detection are in the range or lower than published ICP-MS values: \(<\) a few tens of ng g\(^{-1}\) for the light REE La–Gd and \(<\) a few ng g\(^{-1}\) for the heavy REE Tb–Lu (Ferrat et al., 2012a, b). These are two orders of magnitude below the minimum concentrations measured for La, and in general one order of magnitude for Nd and Pb. The accuracy of the measurements, deduced from measurements of three certified plant standards (ICHTJ CTA-OTL-1 Oriental Tobacco Leaves, NIST/Tomato Leaves 1573 and JAEA Lichen 336), ranges within 80–98% for REE (i.e., 82–98% for La, 80–98% for Ce; 94% for Nd, 81–96% for Sm, 92–95% for Eu, 97% for Gd, 89% for Lu), and 92–97% for Pb. The reproducibility of the measurements is estimated by repeated measurements of 3 peat samples. The reproducibility averages 96% for La & Pb, and 98% for Ti. Corrections for isobaric interferences due to the formation of polyoxates (mainly Ce, La, Nd and Pr oxides) have been taken into account to obtain accurate trace element quantification and in particular for Eu and Gd (e.g., Meisel et al., 2002). For the Agilent 7500 ce, we correct for example the measurement for the three Gd isotopes (\(^{154}\text{Gd}, \(^{157}\text{Gd}\) and \(^{158}\text{Gd}\)) using well-known corrections for interferences (i.e., \(^{156}\text{Gd}\) for \(^{149}\text{Ce}\)/\(^{149}\text{O}\) and \(^{138}\text{La}\)/\(^{138}\text{O-H}\); \(^{157}\text{Gd}\) for \(^{141}\text{Pr}\)/\(^{140}\text{O}\) and \(^{140}\text{Ce}\)/\(^{140}\text{O-H}\); \(^{158}\text{Gd}\) for \(^{142}\text{Nd}\)/\(^{140}\text{O}\) & \(^{143}\text{Pr}\)/\(^{140}\text{O-H}\)).

Radiogenic isotope pretreatments were carried out in a class-100 clean laboratory at ULG. Between 0.1 and 1 g of dried peat were placed 6 h into an oven at 550 \(^{\circ}\)C to remove by combustion all organic matter (Chambers et al., 2011). After calcination, the samples were dissolved on a hot-plate (125 \(^{\circ}\)C) in 4 ml of HF (40%, 23 N) and 1 ml of HNO\(_3\) (65%, 14 N). The solution was evaporated to dryness and the residue was re-dissolved in 2 ml of HCl (6 N). All acids were of analytical reagent grade, further purified by sub-boiling distillation in PTFE vials. After evaporation, the sample was dissolved in 500 \(\mu\)l HBr 0.8 N and loaded on an HCl-preconditioned column with AG1-X8 (200–400 mesh) exchanging resin. Most cations, and REE in particular, were first eluted by 4 ml of HBr 0.8 N. Then Pb was eluted by 2 additional ml of HCl 6 N. The Pb-enriched solution was evaporated and kept in a Teflon vial until measurement. Nd was purified by a two-step column separation procedure. The REE-enriched solution was evaporated, dissolved in 500 \(\mu\)l HNO\(_3\) 2 N and then loaded onto a HNO\(_3\)-preconditioned column with TRU-spec 50–100 \(\mu\)m resin. After repeated column cleaning with HNO\(_3\) 2 N (7 \(\times\) 0.5 ml), the REE were collected by passing 2.5 ml of diluted HNO\(_3\) (0.05 N). This solution was directly loaded onto a preconditioned and precalibrated Ln-spec column following the modified scheme proposed by Mikova and Denkova (2007). The REE were sequentially eluted by HCl 0.25 N, Nd was collected after passing 2.75–3 ml. The Nd-enriched solution was evaporated and kept in a Teflon vial until measurement. The Nd and Pb isotope compositions were determined in static wet (Pb) or dynamic dry (Nd) mode on a Multi Collector-Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) Nu plasma at ULB in Brussels. The instrumental drift was controlled by standard bracketing using NBS981 standard data (Galer and Abouchami, 1998) for Pb and the Rennes standard data (Chauvel and Blchert-Toft, 2001) for Nd. Repeated standard measurements (for NBS981: \(^{208}\text{Pb}/^{204}\text{Pb}\) 36.7130 ± 0.0032, \(^{206}\text{Pb}/^{204}\text{Pb}\) 15.4958 ± 0.0012, \(^{208}\text{Pb}/^{204}\text{Pb}\) 16.9390 ± 0.0012, n = 41; for Rennes standard: \(^{143}\text{Nd}/^{144}\text{Nd}\) = 0.511957 ± 0.000033, n = 99) are consistent with the recommended values and are in agreement with the laboratory long term values (\(^{208}\text{Pb}/^{204}\text{Pb}\) 36.709 ± 0.021, \(^{206}\text{Pb}/^{204}\text{Pb}\) 15.4951 ± 0.0066, \(^{208}\text{Pb}/^{204}\text{Pb}\) 16.9392 ± 0.0006, n = 350; \(^{143}\text{Nd}/^{144}\text{Nd}\) = 0.511946, n = 750). Mass fractionation for Pb was corrected by using Ti as an
internal standard. Measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for mass fractionation using the $^{146}\text{Nd}/^{144}\text{Nd}$ values. The standardized and mass fractionation corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were expressed as $\varepsilon\text{Nd}$, as follows:

$$\varepsilon\text{Nd} = \left(\frac{^{143}\text{Nd}/^{144}\text{Nd} \text{corr.} - 0.512638}{0.512638}\right) \times 10000$$

with 0.512638 as the chondritic uniform reservoir (CHUR, data from Wasserburg et al., 1981) representing the bulk earth composition. For Nd, 2 duplicates give consistent results within 0.1–0.3 $\varepsilon\text{Nd}$; 4 replicates, analysed in wet mode, are consistent within 0.1–0.4 $\varepsilon\text{Nd}$ (Table 2a).

3. RESULTS

3.1. REE content

All REE display similar depth profiles. We report La and Nd as Light Rare Earth Elements (LREE), Eu as Middle Rare Earth Elements (MREE) and Yb as Heavy Rare Earth Elements (HREE) (Fig. 1, Table 1). The REE vary in parallel with the lithogenic elements such as Sc or Ti (e.g., coefficient correlation $R^2 = 0.83$ for Nd–Ti, 0.84 for La–Ti, 0.86 for Ce–Ti and 0.87 for Yb–Ti). Such trends demonstrate the conservative behavior of the REE in the peat sedimentary record, as previously demonstrated by Yliruokanen and Lehto (1995) and later by Krachler et al. (2003). For instance, the La content ranges between 0.19 and 3.7 $\mu$g g$^{-1}$. Similar range of composition was observed in the Black Forest peat record (0.26 < La < 3.4). The La content increases in the upper 50 cm, and the highest content is reached at 19 cm (1965 AD, Table 1a). The La content then decreases in the upper 10 cm (age younger than 1998 AD). At the surface, where there are living Sphagnum mosses, the value (0.19) is close to the preanthropogenic value (0.28 $\mu$g g$^{-1}$) measured at the base of the peat profile (753 cm, ca. 5500 BC, Allan et al., 2013c).

REE content has been normalized to the Upper Continental Crust (UCC – McLennan, 2001). All crustal-normalized REE patterns are flat, with a slight enrichment in Gd. For instance we report REE patterns (Fig. 2) for 3 peat samples characterized by different REE content: a REE-poor sample at the base of the studied peat section (169 cm, 400 BC, pre-Roman Period); an intermediate REE-rich sample (129 cm, 50 AD, Roman Period, Table 1b) and a REE-rich sample (21 cm, 1900 AD, Industrial Revolution). Note the REE pattern at the base of the peat record (i.e., mean of the samples analysed between 700 and 750 cm, minerotrophic peat, age < 5500 BC – Allan et al., 2013c) display a similar profile but with a lower LREE content.

3.2. Nd and Pb isotopic signatures

The Misten $\varepsilon\text{Nd}$ signatures vary between −13 and −10, the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios range between 1.15 and 1.19 (Table 2a and b, Fig. 3a). In spite of the narrow range of $\varepsilon\text{Nd}$ variation, some temporal trends are evident. The samples cluster in 4 groups according to their age interval: Iron Age and Roman Period (400 BC–300 AD, 173–108 cm); Middle Age (500–1300 AD, 87–40 cm); Industrial Revolution 1700–1950 AD, 29–20 cm); Contemporary period, here referred as “Modern Period”, (1973–2007 AD, upper 19 cm). In Fig. 3a the Middle Age samples are characterized by the highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (up to 1.19) and the most...
negative Nd signatures (down to −13). The more negative Nd excursion, confirmed by a replicate measurement, is observed for the 1000 AD sample. The Roman $^{206}\text{Pb}/^{207}\text{Pb}$ ratios range between 1.173 and 1.181, the εNd between −11 and −12. The $^{206}\text{Pb}/^{207}\text{Pb}$ signatures shift during the Industrial Revolution from 1.176 to 1.155. The Pb isotopic data for the Modern period remain within the same range of variation. The Nd peat signatures become less negative during the Industrial Revolution with values close to −11 since 1800 AD as well as during the Modern Period (with less negative signatures at 1998 and 2007 AD, with εNd = −10). The shift in the Pb isotopic data is linked with a significant enrichment in Pb content since the Industrial Revolution (Fig. 3b).

4. DISCUSSION

4.1. Misten REE deposition and comparison with other European peat records

Based on the sediment accumulation rate, the peat density and the sum of REE, we calculate the total accumulation rate (AR) of REE for each sample, as follows:

$$\text{AR}_X \text{ in mg m}^{-2} \text{ y}^{-1} = [X] \text{ in } \mu g \text{ g}^{-1} \times \text{peat density in g cm}^{-3} \times \text{peat growth rate in cm y}^{-1} \times 10$$

The AR ranges between 0.02 and 4.7 mg m$^{-2}$ yr$^{-1}$, remaining lower than 0.5 mg m$^{-2}$ yr$^{-1}$ for most of the peat record (Fig. 4). As an exception, we note a slight and brief increase during the Middle Ages (~560 AD, 83–85 cm, Table 1a) and a pronounced increase since the Industrial Revolution (<30 cm). The highest accumulation rate is reached at 15 cm (~1990 AD), then it decreases toward the peat surface and remains stable within the upper 10 cm (age younger than 1998 AD).

Comparisons between our record with previously published peat data recorded from Europe and shown in Fig. 2. All REE patterns from peat samples are marked by relatively flat UCC-normalized patterns without any significant fractionation between LREE and HREE. It is notable that data from the Black Forest in Germany (BF – Aubert et al., 2006) display the largest range of variation. The range of variation is narrow in the Swiss samples from Etang de la Gruère (ETG, Krachler et al., 2003) but its REE-richest sample is consistent with the two other European records.

![Fig. 3a. εNd vs $^{206}\text{Pb}/^{207}\text{Pb}$](image)

Dots: Misten peat samples (data in Tables 2a and b). Colors according to age interval: blue, Roman and Late Roman Period (400BC–300AD, 173–108 cm); green, Middle Ages (500–1300AD, 87–40 cm); red, Industrial Revolution 1700–1950AD, 29–20 cm; dark blue, Modern Period (1973–2007AD, upper 19 cm). Grey dots: replicate and duplicate analyses (see Table 1). The vertical bars indicate the 2 sigma error bars on the Nd isotope measurement. Isotope Pb data for the Industrial Revolution and Modern period are from Allan et al. (2013a). Natural and anthropogenic dust sources are also reported. Squares: Isotope signature of potential local (Early Cambrian shales = −11.3, André et al., 1986; mean Paleozoic shales = −12.2, Linnemann et al., 2012), regional (European loess from Belgium, France and England – Gallet et al., 1998; European soils, geochemical atlas – http://www.gtk.fi/publ/foregsatlas/) or global natural dust sources (Saharan airbornes, Grousset et al., 1988a,b; Goldstein et al., 1984; Colin, 1993; Henry et al., 1994). Note the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for the natural dust sources is fixed at 1.20, if no Pb isotope available data. The lower panel reports the Misten peat data (dots) with regard to the signature of the main anthropogenic sources (triangles): Steel plant dust (Geagea et al., 2007); diesel and gasoline soot (Geagea et al., 2006a); urban airbornes (Geagea et al., 2006a); urban tree bark (Geagea et al., 2007, 2006a, 2008b) and regional Belgian and German Pb–Zn ores (Dejonghe, 1998; Durali-Mueller et al., 2007). All data, except for urban tree bark, are reported in Table 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Since all REE display similar trends, we compared the La accumulation rates of the Misten with the two European peat records. The pre-industrial values calculated for Black Forest (\(0.02 \text{ mg m}^{-2} \text{ yr}^{-1}\), Aubert et al., 2006) or for EGR (\(0.08 \text{ mg m}^{-2} \text{ yr}^{-1}\), Krachler et al., 2003) at 1800 AD are consistent with the lowest value measured at the base of the Misten record (0.02 mg m\(^{-2}\) yr\(^{-1}\) at 5500 BC, age from Allan et al., 2013c). In the three records, a significant increase is observed during the Industrial Revolution. At 1950 AD the three records are supplied by a similar range of accumulation rates of La, estimated from 0.20 to 0.30 mg m\(^{-2}\) yr\(^{-1}\). Then the La accumulation rate remains stable (EGR) or it slightly decreases (BF). The next (1990s) increase is not recorded in BF or EGR but the

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**Fig. 3b.** Binary diagram 1/Pb content and \(^{206}\text{Pb}/^{207}\text{Pb}.** Same color code than for Fig. 3a. Data from Table 2b. A Pb-enrichment is observed in the Industrial Revolution and Modern samples. This enrichment is associated with a significant shift in the Pb isotopic ratios, underlining the major human influence in the trace metal dust supplies to the Misten bog over the last 300 years.

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**Fig. 4.** Estimated accumulation rate (AR) of REE and evolution through the last 2500 years. Total (i.e., natural + anthropogenic) and anthropogenic AR for La, Nd and sum REE are reported versus age model. Accumulation rates are calculated from peat density, accumulation rate and elementary content (data in Table 1). The grey interval corresponds to the acrotelm peat section. The pre-anthropic REE AR measured at the base of the Misten peat accumulation (753 cm, ?7500BP) is reported for reference. La AR for Germany (BF, Aubert et al., 2006) and Switzerland (EGR, Krachler et al., 2003) are reported in comparison with Misten data EGR in the upper panel.
4.2. Natural versus anthropogenic contribution in REE deposition

In the Misten record the REE deposition displays significant changes over time (Fig. 4). Such changes could be the result of natural (e.g., large increase in long-range dust fluxes) and/or anthropogenic dust contribution. To estimate any excess in the REE deposition in the Misten peat record, we calculate a REE enrichment factor (EF) relative to the signature of the Upper Continental Crust (McLennan, 2001) as follows: EF = \((\text{REE/Sc})_{\text{sample}} / (\text{REE/Sc})_{\text{UCC}}\). All REE display similar EF profiles (Table 1, see also Supplementary data SM2). Individual REE EF >2 are observed between 125 and 130 cm (10 BC–50 AD, Roman Period, Table 1b), from 45 cm (1174 AD, Middle Ages, Table 1a) to 10 cm (1998 AD). The highest EF (9) is reached at 19 cm (1954 AD, Table 1a). The upper section EF then decreases to values lower than the preanthropogenic signature (EF 1.3 at 753 cm, see upper panel in SM2). Note the pre-anthropogenic EF values are close to those in American (Cypress Blue, Florida – Kamenov et al., 2009) and European peat records (EGR, Switzerland – Krachler et al., 2003; Black Forest, Germany – Aubert et al., 2006). However the EF of La does not exceed 2.5 even in the Modern period (see upper panel in SM2).

Using the UCC as a natural reference we calculated the detrital fraction of REE in equilibrium with the Sc content in our samples as follows: \(\text{Detrital REE} = \left(\frac{\text{sum REE}}{\text{Sc}}\right)_{\text{UCC}} / \left[\text{Sc}\right]_{\text{sample}}\). This detrital component is removed from the measured \([\text{REE}]_{\text{samples}}\) to estimate the excess, mainly anthropogenic, REE contribution. Some anthropogenic contribution is detected since the Roman Period, but the enrichment in all REE is only obvious since the Industrial Revolution. Fig. 4 shows for instance, the total (i.e., natural + anthropogenic) and anthropogenic fluxes for La, Nd and sum REE. The relationship between Pb content and Pb isotopic data (Fig. 3b) confirms the significant human influence in the Misten trace metal record over the last 3 centuries.

4.3. Source of dust

REE abundance and LREE/HREE fractionation are used to discriminate the sources of dust (Fig. 5). We report...
for each Misten peat samples their REE content (i.e., sum REE normalized to Sc to take into account any dilution effect) and their LREE/HREE fractionation (i.e., La/Nb/Sc). Two trends are obvious in Fig. 5: the peat samples are either enriched in REE (high sum REE/Sc) or displayed a fractionation between LREE and HREE (high LREE/HREE ratio). Moreover the distribution is controlled by the age of the samples. We will discuss the scattering of the peat Misten data successively for the samples of the pre-Industrial Revolution samples (1), the Industrial Revolution (2) and, the Modern Period (3).

(1) For most of the pre-Industrial Revolution samples, the ratios of the sum REE/Sc range between 10 and 25, with no LREE/HREE fractionation (1 < EF < 1.5 – Fig. 5). A similar range of Sc-normalised REE content is observed between the European soils (data from European soil geochemical atlas – http://www.gtk.fi/publ/foregsatlas/) and the Saharan airbornes (Moreno et al., 2006): it therefore characterizes the range for natural, regional and distal dust sources.

(2) During the Industrial Revolution, the Misten samples are enriched in REE (Fig. 2), even when normalized to Sc (Fig. 5). All Industrial Revolution samples (except one) present a sum REE/Sc ratio higher than 25, with no fractionation between La and Yb (Fig. 5). Those samples show a progressive increase in REE, reaching a maximum sum REE/Sc ratio (~100) in the sample found at 1937 AD, at the end of the Industrial Revolution interval (Table 1a). Such REE enrichment is explained by intensive coal combustion over this time interval, coals being characterized by a global REE enrichment (e.g., American coals – Vouk and Piver, 1983). Indeed the Misten samples point towards the average ratio of three main Belgian coal ores (mean sum REE/Sc = 120). When comparing the REE pattern of the

\begin{table}
\centering
\begin{tabular}{cccccc}
\hline
Depth cm & 143Nd/144Nd & ±2se & eNd & Mode & Run  \\
\hline
2.2 & 0.512123 & 0.000015 & -10.1 & Dry & 30 10 2009 \\
10.1 & 0.512119 & 0.000018 & -10.1 & Dry & 30 10 2009 \\
11.9 & 0.512048 & 0.000012 & -11.5 & Dry & 30 10 2009 \\
13.7 & 0.512046 & 0.000009 & -11.6 & Dry & 30 10 2009 \\
13.7R & 0.512047 & 0.000017 & -11.5 & Wet & 03 11 2009 \\
17.3 & 0.512018 & 0.000010 & -12.1 & Dry & 30 10 2009 \\
17.3R & 0.512039 & 0.000018 & -11.7 & Wet & 03 11 2009 \\
19.1 & 0.512058 & 0.000010 & -11.3 & Dry & 30 10 2009 \\
19.1R & 0.512086 & 0.000016 & -10.8 & Wet & 03 11 2009 \\
22.7 & 0.512073 & 0.000008 & -11.0 & Dry & 30 10 2009 \\
23.6 & 0.512066 & 0.000018 & -11.2 & Dry & 30 10 2009 \\
25.6 & 0.512009 & 0.000013 & -12.3 & Dry & 30 10 2009 \\
28.6 & 0.511988 & 0.000017 & -12.7 & Dry & 30 10 2009 \\
30.6 & 0.512019 & 0.000016 & -12.1 & Dry & 30 10 2009 \\
30.6R & 0.512003 & 0.000026 & -12.4 & Wet & 03 11 2009 \\
32.6 & 0.511995 & 0.000011 & -12.5 & Dry & 30 10 2009 \\
32.6D & 0.511984 & 0.003 & -12.8 & Dry & 30 10 2009 \\
40.6 & 0.512034 & 0.000012 & -11.8 & Dry & 30 10 2009 \\
50.6 & 0.511993 & 0.000015 & -12.6 & Dry & 30 10 2009 \\
52.6 & 0.512020 & 0.000013 & -12.1 & Dry & 30 10 2009 \\
56.7 & 0.511972 & 0.000009 & -13.0 & Dry & 30 10 2009 \\
56.7D & 0.511964 & 0.002 & -13.1 & Dry & 30 10 2009 \\
61.1 & 0.512002 & 0.000008 & -12.4 & Dry & 30 10 2009 \\
65.5 & 0.512039 & 0.000010 & -11.7 & Dry & 30 10 2009 \\
69.9 & 0.512039 & 0.000012 & -11.7 & Dry & 30 10 2009 \\
76.5 & 0.512055 & 0.000030 & -11.4 & Dry & 30 10 2009 \\
78.7 & 0.512049 & 0.000020 & -11.5 & Dry & 30 10 2009 \\
83.1 & 0.512033 & 0.000012 & -11.8 & Dry & 30 10 2009 \\
87.5 & 0.512016 & 0.000011 & -12.1 & Dry & 30 10 2009 \\
108.2 & 0.511997 & 0.000010 & -12.5 & Dry & 30 10 2009 \\
109.7 & 0.512020 & 0.000012 & -12.1 & Dry & 30 10 2009 \\
120.3 & 0.512042 & 0.000013 & -11.6 & Dry & 30 10 2009 \\
130.9 & 0.512044 & 0.000014 & -11.6 & Dry & 30 10 2009 \\
134 & 0.512067 & 0.000009 & -11.1 & Dry & 30 10 2009 \\
135 & 0.512046 & 0.000020 & -11.5 & Dry & 30 10 2009 \\
138 & 0.512110 & 0.000032 & -10.3 & Dry & 30 10 2009 \\
145.6 & 0.512061 & 0.000020 & -11.3 & Dry & 30 10 2009 \\
169.9 & 0.512063 & 0.000021 & -11.2 & Dry & 30 10 2009 \\
\hline
\end{tabular}
\caption{Nd isotopic data and eNd.}
\end{table}

Samples have been analysed in dry mode, replicate (in italics) in wet mode. Underlined values correspond to duplicates.

Table 2a Nd isotopic data and eNd.
Misten samples with the available REE signature of some of the important pollution sources in Europe, the samples characterized by the highest REE content and EF were close to the mean signatures of Belgian coals (Fig. 2).

(3) In contrast, the Modern Period samples are characterized by a shift in their La/Yb ratios (up to 2.5) without marked enrichment in REE (Fig. 5). The distribution of the Modern Period peat samples rather suggest another anthropogenic REE source. For instance, steel plant dust collected from an urban European area (close to the France–Germany border, Geagea et al., 2007) exhibits a marked enrichment in La (La/Yb = 3.7, Table 1a, Fig. 5) but only a slight enrichment in REE (Fig. 2). Steel plant dust could be a potential candidate to explain the observed REE fractionation in the Misten samples over the Modern Period.

For the Industrial Revolution and the Modern period, our REE data confirm the shift in Pb isotope ratios already observed by Allan et al. (2013a) in the upper Misten peat record (Fig. 3a and b). Based on trace metal elements and Pb isotope data they concluded that coal and metallurgy, in particular the exploitation of regional Pb–Zn ores, were the main pollutant activities over the past 300 years. In Belgium, anthropogenic dust was mainly derived from pre-1945 non-ferrous mining and refining (Schmitz; 1979; Dejonghe, 1998). The high dust contamination by coal combustion at AD 1937 is in agreement with the maximum Belgian coal production (1927–1955 AD in Rutledge, 2011) and with the historical pollution record in North European bogs (1930–1970 in Shotyk et al., 2003). It is likely that the presence of anthropogenic derived-REE in the environment (which strongly increased between 1950 and 2000) is due to their use in industry, medicine, and agriculture (Geagea et al., 2007).

Although we record an REE enrichment in the upper peat layers, no obvious influence of anthropogenic activities is observed in the Nd isotope Misten dataset for both the Roman period and the Middle Ages, the range of Nd isotope ratios being similar with the scattering of the natural dust sources (Fig. 3a and b, Table 3). We conclude therefore, that at least before the Industrial Revolution, the Nd isotope variations are mainly due to changes in relative proportion of regional and distal sources. In contrast, an influence of gasoline and then diesel soot may explain the shift towards less negative εNd values (from ~12 to
–10) observed for the Modern period samples. In the further climate-related interpretation of the Nd isotope signal we will not discuss the changes over the past 50 years and we will be cautious for the changes observed during the Industrial Revolution.

4.4. Climate-related dust record in Misten peat bog over the historical period

We propose here to integrate elemental and isotopic geochemical data to track potential climatic influences on
the ombrotrophic peatland. In order to decipher the climate signal in the dust deposition in the Misten bog we first utilise major and trace elements to derive the total dust deposition. Second, for each dust-rich identified interval we compare the Nd isotope composition with the local, regional or distal sources to identify the dominant natural atmospheric supplies. Third, we interpret the changes of sources in terms of local or global environmental changes.

Recently, the combination of elemental and isotopic Nd geochemical data has been successfully applied in Holocene ombrotrophic peat profile from Switzerland to quantify the dust deposition, to identify the sources of dust and to provide evidence of climate–dust interactions (Le Roux et al., 2012). Here the approach is applied but focused in on the historical period, an interval characterised by significant environmental perturbations due to human industrial activities.

The dust flux was calculated according to Shotyk et al. (1998) but we use either the sum of REE or the Ti content as the conservative element to calculate the Ti or the REE accumulation rate (AR) over the past 2500 years:

\[
\text{Dust fluxes calculated from element } X, \text{ expressed in g m}^{-2} \text{y}^{-1} = \frac{\text{AR}_X}{[X]_{\text{UCC}}}
\]

where \( X = \text{Ti or sum REE}, \ UCC = \text{Upper Continental Crust} \) (Ti = 4100 ppm; sum REE = 146.4 µg g\(^{-1}\) – data from McLennan, 2001).

Both elements give similar dust flux profiles, confirming the conservative behaviour of REE (Fig. 6). The Ti-calculated fluxes range between 0.5 and 5 g m\(^{-2}\) y\(^{-1}\) for more than 2000 years then increase up to 10 g m\(^{-2}\) y\(^{-1}\) at the beginning of the Industrial Revolution period (sample at 25 cm, 1788 AD). A second significant increase is observed over the past 50 years, the Ti-derived dust flux being multiplied by a factor of two between 1953 AD (7.4 g m\(^{-2}\) y\(^{-1}\) at 20 cm) and 1990 AD (17 g m\(^{-2}\) y\(^{-1}\) at 15 cm). This recent trend records the dominant anthropogenic source of dust deposition (including REE) in the upper 20 cm of the Misten bog.

A close-up view shows evidence of the existence of five intervals. The first interval covers most of the Roman period: it is characterised by a low dust flux, except for an increase around 300 BC. The following four intervals (600 AD, 1000 AD, 1200 AD and from 1700 AD) are characterized by an increase in dust fluxes, recording either the influence of human activities related to land use change (regional erosion due to forest clearance and soil cultivation activities) or to local or regional climate changes (humidity, temperature, wind strength). Recent studies performed on

![Fig. 6. Evolution of Ti-dust flux, sum REE-dust flux, abundance of arbustive (tree and shrub) pollen, changes in macrofossil assemblages (expressed as Dupont index, Dupont, 1986), peat humification degree and Nd isotope composition (expressed as εNd) measured in the Misten bog over the past 2500 years. Pollen and macrofossil data are from Stree et al. (2014) and De Vleeschouwer et al. (2010), respectively. The changes of radiocarbon cosmonuclide production (data from Reimer et al., 2009) represent the global climate conditions, with more radiocarbon production during colder intervals. The grand minimas of solar activity are reported from Usoskin et al. (2007). The dash boxes underline the distal-rich intervals corresponding to cold event. The arrows indicate intervals characterised by dominant local sources. See text for explanation.](image-url)
the upper 1 m of several Misten peat cores emphasize the last millennium changes in vegetation, organic and/or inorganic geochemistry mainly recorded human perturbations (De Vleeschouwer et al., 2009, 2012; Allan et al., 2013a,b).

The climate interpretation of major and trace elements in ombrotrophic peat thus requires an additional proxy, here the Nd isotope signature, to distinguish between higher dust fluxes related to enhanced local erosion (mainly anthropogenic influence related to land use change) and higher dust fluxes related to enhanced distal supplies (mainly climatic influence). We use the Nd isotope signature of peat to decipher between local and distal sources (such as in Le Roux et al., 2012). The observed $\varepsilon$Nd variability (−13 to −9) in Misten peat samples is interpreted as a mixing between dust sources (Table 3) from local (Early Cambrian shales = −11.3, André et al., 1986; Early Cambrian phyllades = −10.8 and mean Paleozoic shales = −12.2, Linemann et al., 2012), regional soils (mean European crust = −10.8, Michard et al., 1985; mean European loess = −11.6, data from Gallet et al., 1998) and desert particles (mean Saharan airborne = −12.9 – data from Goldstein et al., 1984; Groussset et al., 1988a,b; Colin, 1993; Henry et al., 1994; Rognon et al., 1996). The $\varepsilon$Nd variability is further compared with the humification degree to evaluate the local relative humidity conditions (Fig. 6). The sum REE/Sc ratio is used as a complementary proxy to confirm the origin, (local/regional or distal) of the dust (see SM3).

(1) For most of the Roman period the $\varepsilon$Nd values (mean $-11.2$, the dust flux (0.9 g m$^{-2}$ y$^{-1}$ calculated from the sum REE) and the humification degree (HD $\sim$40%) remain stable. The range of $\varepsilon$Nd values is consistent with the signature of local soils (mean European crust = −10.8, mean European loess = −11.6). Note the local origin of the dust is also supported by the relatively low sum REE/Sc ratios ($<23$) for most of the Roman period (see SM3). For most of this first interval the relatively dry conditions (high HD) promote the erosion of local soils. The end of the Roman period is then characterized by a change in dust supplies. We observe a decrease of the $\varepsilon$Nd to −12.2 around 300 AD and an increase of the sum REE/Sc ratio $\geq$ 25 around 120 AD (see SM3). Those changes are not related to any significant increase in dust, so they may be explained by relatively greater supplies from distal sources (i.e., Saharan airborne), with local conditions being slightly wetter.

(2) The transition between the Roman period and the Middle Ages (400–600 AD) is marked by less negative $\varepsilon$Nd values and low sum REE/Sc ratios. The higher dust flux reflects more local erosion partly related to drier conditions; the degree of humification reaches its highest value (50%) within this interval. This interval is also marked by a slight decrease in arboreal pollen abundance. The low abundance of pollen indicative of agricultural (e.g., cereal pollen remain below 2% – Streel et al., 2014) suggests that the changes in dust supplies are driven by climate changes.

(3) The $\varepsilon$Nd data then shift again to more negative values (−13 at 1015 AD). The sum REE/Sc ratio also displays relatively high values (20–21 – see SM3). The higher dust flux records more distal supplies, the local erosion being reduced by the wetter soil conditions, as underlined by a short decrease of the degree of humification plus a change in the plant macroremain assemblages (De Vleeschouwer et al., 2010). We observe that the less negative $\varepsilon$Nd values, the highest dust flux and the low humification values occur within the Oort solar minima event (Fig. 6). For the Misten bog, a similar relationship between solar activity and dust flux was already suggested by De Vleeschouwer et al. (2012). The potential link between enhanced distal supplies and cold climate requires further investigation as little is known about the influence of a global colder climate event on Saharan airborne particle production and transport.

(4) The following increase in dust flux (at 45–47 cm, 1200–1174 AD) occurs during the Medieval Warm Period before the next cold event (Wolf solar minimum). More local erosion may be partly explained by drier conditions as evidenced by a brief increase in the degree of humification. Note that this change in local soil conditions is also sustained by drier plant macrofossil assemblages (De Vleeschouwer et al., 2010). The sharp increase in dust is probably also influenced by a major change in vegetation cover. Indeed this interval is marked by a sharp decrease in arboreal pollen abundance since 1150 AD (Fig. 6), most likely due to human-induced forest clearance for agriculture purposes (Streel et al., 2014). It coincides with a significant increase in cerealia and Plantago pollen, two pollen types that are directly related to farming activity. Since such land-use change enhances local erosion, the higher dust flux is therefore explained by both drier local conditions and human-controlled change in vegetal cover.

(5) The $\varepsilon$Nd return again to more negative values (−13) at the end of the Renaissance period (1691 AD at 30 cm). This shift coincides with high sum REE/Sc ratio (i.e., 25 around 1600 AD). The humification degree is variable during this interval, with on average wetter conditions. The enhanced distal-dust flux would reflect the global colder climate during the Maunder solar minimum (similar to point 3).

After the Maunder minimum the $\varepsilon$Nd becomes less negative, recording again more local dust supplies. Even this shift occurs during the post-Little Ice Age warming, the climate forcing is not obvious as coal combustion delivers a significant REE contribution during the Industrial Revolution (Fig. 5). Such anthropogenic sources bring no peculiar Nd isotope signature as the coal-derived dusts have a crustal fingerprint similar (see reported REE patterns at Fig. 3) with the local sources.
5. CONCLUSION

Our results provide evidence that climate forcing may be detected in ombrotrophic peat, even for the historical period that is characterised by a mixed climate-human control. The Mistent geochemical dataset emphasizes a significant anthropogenic REE contribution, first by coal combustion during the Industrial Revolution and then by industrial activities for the Modern Period. Before the Industrial Revolution, the REE abundance (10 < sumREE/Sc < 25) and δNd variability (−13 to −9) in peat is interpreted by a mixing between dust sources from local soils and distal desert particles. Dominant local dust supplies (at ca. 100 AD, 600 AD and 1200 AD) systematically occur during drier (higher humification) intervals, the erosion of surrounding soils being promoted by the local environmental conditions. In contrast, the three periods characterised by dominantly-distal sources (at ca. 320 AD, 1000 AD and 1700 AD) are consistent with local wetter intervals as indicated by their lower degree of humification. Since local erosion is reduced, the site is more sensitive to distal supplies. On a global scale, two of those distal-rich intervals (ca. 1000 AD and 1700 AD) occur during cold events, in particular during the Oort and Maunder minima. Such observations may suggest that cold climate would favour distal desert supplies, a hypothesis requiring further validation in other settings.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2014.03.014.

REFERENCE


