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Geochemical records of paleocontamination in late pleistocene lake sediments in West Flanders (Belgium)

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ABSTRACT

Concentrations of trace elements in Late Pleistocene lake sediments from two localities in West Flanders (Belgium) were studied using inductively coupled plasma-mass spectrometry. The studied sediments were deposited during the transition of the Allerød to the Younger Dryas. Trace elements enter lake environments from a variety of sources, but mostly from bedrock weathering in catchments and as wind-blown dust particles. These sources create a natural trace element background in lake sediment records. The concentration and distribution of trace elements across the studied lake sediment sequences display features consistent with inputs of materials other than those from soil or bedrock. Input from volcanic eruptions, biomass burning and meteorite impacts should be considered among the main sources of nonanthropogenic contamination of lake environments.

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KEYWORDS Trace elements; lake sediments; contamination

Introduction

Long, continuous high-resolution records of Quaternary environmental changes are scarce except for polar region ice cores. Lake sediments are important additional natural archives of environmental information. In particular, trace elements are important for such reconstructions. Trace elements enter pristine lake environments mostly as wind-blown dust particles, and by weathering of bedrock followed by transport through runoff creating natural trace element background in lake sediments. Recently, a lot of attention has been given to the pollution of the environment with byproducts of anthropogenic activity (see Grimm et al. 2008; Boyle et al. 2016 for references). However, in the past, pristine environmental conditions were also compromised by pollutants/contaminants, but resulting from natural events. Volcanoes are one of the most important natural sources of contaminants to the atmosphere (e.g. Nriagu 1989; Hinkley et al. 1999; Self et al. 2004; Raible et al. 2016), and another important source is biomass burning (Gaudichet et al. 1995; Krachler et al. 2003; Ofosu et al. 2013; Zennaro et al. 2014). Large meteorite impacts/explosions could also contribute to contamination (Morgan et al. 2013; Wittke et al. 2013; Andronikov et al. 2014). Signatures of volcanic eruptions, biomass burning and meteorite impacts/explosions can be present in geochemical records of lake sediments.

Volcanoes of continental Europe were active in the Pleistocene with two regions dominating volcanic activity: Eifel (Germany) and Massif Central (France). Although most volcanoes in the Eifel erupted before the latest Pleistocene, the Laacher See volcano erupted explosively *c*. 12 880 cal yr BP with >6 km³ of erupted material covering an area of ~1300 km² in lava and ash deposits (Wörner and Schmincke 1984; Ammann and Lotter 1989; van den Bogaard 1995; Schmincke et al. 1999; Litt et al. 2001; Lane et al. 2011; Riede 2016). Massif Central was active during the late Quaternary until *c*. 6000 cal yr BP (Downes 1987; Simkin and Siebert 1994). One of the eruptions of Le Puy de la Nugère (Chaîne des Puys) took place 12 950 ± 10 cal yr BP (tephra LAUT1; Vannière et al. 2004) and products of another eruption (Les Roches Tephra, 12 010 ± 150 ¹⁴C years BP or 13 549–15 349 cal yr BP; Vannière et al. 2004) extended as far as 30 km to the southeast of its source (Vernet and Raynal 2005). A very strong pyroclastic eruption of Puy de Dôme volcano is recorded for 10 700 ± 100 cal yr BP (Miallier et al. 2010). Further, the trachytic CF7 Tephra (from 9160 ± 40 cal yr BP to 6670 ± 50 cal yr BP; Vernet and Raynal 2008; Miallier et al. 2010) is known in several sedimentary sections located around Clermont-Ferrand.

In addition to the volcanoes of continental Europe, the Iceland hotspot has been active since >60 Ma (e.g. Lawver and Muller 1994), and the presence of Icelandic volcanic material is known in Pleistocene sediments across Europe (Lind et al. 2013, 2016 and references therein). One of the well-recognized occurrences of such material throughout northern Europe is the Vedde ash, produced by an eruption of the Katla volcano *c*. 12 100 cal yr BP (Birks et al. 1996; Lind et al. 2013, 2016). In addition to the Vedde ash, other Icelandic volcanic activity reflected in Late Pleistocene sediments in Europe is represented by Borrobol (14 400–12 700 cal yr BP), Borrobol-type (16 600–13 600 cal yr BP) and Panifeler (14 100–13 600 cal yr BP) tephras (Lind et al. 2013, 2016 and references therein).

Regional fires (i.e. biomass burning) occurred frequently in the Late Pleistocene (Daniau et al. 2010; van Hoesel 2014 and references therein) due to the forestation (producing abundant potential fuel) generated in response to the warming climate (Hoek and Bohncke 2002). Overall, biomass burning emissions have been found to contribute >90% of the measured concentrations of P, Cl, S, K, Cu and Zn in modern atmospheric aerosol particles (Gaudichet et al. 1995; Krachler et al. 2003; Ofosu et al. 2013).

Meteorite impacts are a well-known phenomenon throughout the Earth's history, but only very large impacts produce enough material for global contamination. Notably, a large bolide might have exploded over the North American Laurentide Ice Sheet in the Late Pleistocene (Firestone et al. 2007), and the Younger Dryas Impact Hypothesis proposes that this episode of multiple airbursts/impacts occurred at $12\ 800\ \pm\ 300\ cal\ yr$ BP (see Kennett et al. 2015 and references therein). Transportation of the impact/explosion-related microparticles by the dominating eastward movement of air masses (Isarin and Renssen 1999) could have resulted in distal fallout as far as in Europe (cf. Grousset and Biscaye 2005; Morgan et al. 2013). Some studies suggest that material related to meteorite/comet airburst impact events might be present in the Late Pleistocene sediments of Western Europe (e.g. Wittke et al. 2013 and references therein).

We compare the results of geochemical studies of the Late Pleistocene lake sediments from two localities in West Flanders, Belgium (Figure 1), and consider the results from the point of view of the presence of non-anthropogenic components that may support either the Younger Dryas Impact Hypothesis or another trigger for Younger Dryas cooling.

Materials and methods

Sites

Two sites in West Flanders, Snellegem Pond and Maldegem Meadow (Figure 1), were cored. Snellegem Pond (51.167325 N; 3.14446 E; 8 m a.s.l.), also known as St. Andries-Beisborek site in Verbruggen (1979), is situated in Eocene sands. The pond is located within the extent of a former Late-Glacial lake 10 km southwest from the city of Bruges, not far from the village of Zedelgem. The whole sediment sequence (230 cm) in Snellegem Pond consists of fine- to medium-grained sand, which becomes silty sand at a depth of ~188 cm (Verbruggen 1979; Denys et al. 1990).



Figure 1. A schematic map showing locations of the studied sites: (1) Snellegem Pond; (2) Maldegem Meadow. Directions and distances to the Laacher See volcano and to the Massif Central are shown.

At \sim 170 cm, a transition to carbonaceous lake marl occurs. The lithology changes into gyttja and peat at \sim 103 cm. In the lower part of the peat deposit (between 100 and 82 cm), several thin layers of eolian sand occur. From the level of 70 cm up, sediments consist of clayish peat containing rare small lenses of fine-grained sand. The late-glacial sediments are overlain by 30 cm of Holocene deposits.

Three age estimations for the Snellegem sequence are known. Two are from changes in pollen, and one is from radiocarbon dating. The first age estimation is given by a sharp decrease of the AP/NAP ratio at a depth of 170 cm that indicates a vegetation change from biozone 1b to biozone 1c (Verbruggen 1979; van der Putten, personal communication). This change took place at *c*. 14 100 cal yr BP (Hoek 2001), which is very close to the onset of Greenland Interstadial-1d (GI-1d) at 14 075 cal yr BP (Rasmussen et al. 2006). The second age determination is defined by a sudden rise of *Pinus* pollen at a depth of 130 cm (Verbruggen 1979; van der Putten, personal communication). In the Netherlands, the arrival of *Pinus sylvestris* from the southeast has been determined at 11 250 ¹⁴C years BP or 13 197 cal yr BP (Hoek 1997; 2001). The third age determination is a radio-carbon dating of 10 940 \pm 60 ¹⁴C years BP (12 807 cal yr BP) obtained from the depth of 99 cm by Verbruggen (1979). This age is close to 12 846 cal yr BP, which is the age proposed for the onset of Greenland Stadial-1 (GS-1; Lowe et al. 2008) and for the beginning of the Younger Dryas cooling.

Maldegem Meadow (51.19340 N; 3.42743 E; 9 m a.s.l), also known as Maldegem-Ede (Verbruggen 1979), is located in an agricultural field near the village of Maldegem, 15 km east of the city of Bruges. The field is within the area of a small Late Pleistocene lake and situated on Eocene clayish sand and sand. The Late Pleistocene sediment sequence here has a thickness of 190 cm, and pollen studies indicate that it covers the time interval from 15 500 cal yr BP to 6000 cal yr BP (i.e. from Late Glacial to Subboreal: biozones Ia to VIIIb; Verbruggen 1979; Verbruggen et al. 1996; cf. Hoek 2001; Bos et al. 2008). There are no absolute age determinations for the recovered part of the Maldegem sequence, but pollen data suggest that the sediments were deposited during the first half of the Younger Dryas (biozone III: Verbruggen 1979; cf. Hoek 2001).

Sampling, sample preparation and analytical techniques

During fieldwork at Snellegem Pond, coring was conducted in the deepest part of the basin where the most complete sequence is developed and where cores were previously obtained by Verbruggen (1979). Coring was conducted manually using a 1.5 m long probe gouge. Two cores (Snellegem-1 and 2) were recovered and stratigraphically correlated with the previous cores using two markers evident in the Snellegem-1 core. These markers are described in Verbruggen's (1979) stratigraphic scheme. The first marker is a sharp change in lithology from marl to gyttja and peat at ~ 103 cm, while the second marker is the lowest thin layer of the eolian sand, located at the depth of 100 cm. Material just above this layer (at 99 cm) has been dated to 10940 ± 60^{14} C years BP (12 807 cal yr BP) by Verbruggen (1979). The first core (Snellegem-1) was thus determined to have been recovered from the depth range of 116–88 cm and displayed two lithological units, the lower one consisting of yellowish lake marl, and the upper one consisting of interlayers of dark-brown peat and gyttja, while the second core (Snellegem-2) was determined to have been recovered from a depth of 100-76 cm and consisted of interlayers of dark-brown peat and gyttja. Each recovered Snellegem core was cut into individual samples in steps of 1-3 cm, resulting in 14 samples and 8 samples from the Snellegem-1 and -2 cores, respectively. For Maldegem Meadow, the same coring technique resulted in the recovery of one core from a depth range of 132-112 cm. The recovered part of the Maldegem sequence was represented by dark-brown peat with loam layers, sandy loam laminae and marl intercalations. The recovered Maldegem core was cut into five samples in steps of 4-5 cm.

A few grams of material from each sample were dried and pulverized. Approximately 50 mg of the pulverized material was digested in a mixture of concentrated HNO₃ and HF in 15 mL Teflon beakers. The beakers were sealed and heated at 130°C for 48 h, during which time they were ultrasonicated twice. After cooling, the solution was dried and then re-dissolved in 5% HNO3. An analytical blank solution was prepared using the same procedure. Aliquots of the International Association of Geoanalysts SdAR-1 material (enhanced river sand; Webb et al. 2012) were used as additional reference materials. A Finnigan Element2 inductively coupled plasma-mass spectrometer (ICP-MS) was used for the analysis. Analyses were run in a low-resolution mode (M/ Δ M ~300) for all isotopes and additionally in a medium resolution mode (M/ Δ M ~4000) for Sc⁴⁵, Ti⁴⁷, V⁵¹, Cr⁵³, Co⁵⁹, Ni⁶⁰, Cu⁶³ and Zn⁶⁶ in order to separate isotopes from interfering molecular species. Solution standards consisted of known amounts of the analyzed elements and were prepared using multi-element solutions obtained from High-Purity Standards Company (Charleston, SC, USA). A standard-blank solution was prepared at the same time using successive dilutions of the 5% HNO₃ standard-carrier solution. Sample concentrations were determined by first subtracting blank signal intensities from those obtained from the sample and standard solutions. A calibration curve was then obtained by performing a linear least-squares regression for each element using the blank-subtracted counts and the known concentrations in each standard solution. In all cases, the R^2 coefficients were 0.998 or higher.

Results

Snellegem sequence

The lower (organic-poor) studied part of the Snellegem sequence is homogeneous (carbonaceous lake marl). Several geochemical features of interest were present. The most prominent was presented in sample SNG-3 (111-108 cm), which displayed markedly elevated concentrations of Ni, Cu and Zn, and slightly elevated concentrations of Ti, V, Cr, Co, Zr, Nb, Hf, Ta, Pb and U relative to other samples of this part of the sequence. Sample SNG-3 also showed lowered concentrations of Sr and Ba, and a higher Ni/Sc (16.6) ratio in comparison to the surrounding horizons (Table 1). The horizon above (108-106 cm; SNG-4) was characterized by markedly lowered concentrations of light (L) and some medium (M) rare earth elements (REE), lowered concentrations of Ti, Cr, Rb, Zr, Nb, Hf, Ta, Pb and Th, elevated concentrations of Sr and W, and high Ni/Sc (19.2), and Ni/Cr (3.0) ratios. The next horizon upwards (106-105 cm; SNG-5) was geochemically similar to SNG-4, except for concentrations of Sr and W, which were lower. Finally, the uppermost horizon in the organic-poor part (105-104 cm; SNG-6) displayed enrichment in elements such as Ti, V, Zn, Y, most REE, W, Pb and U relative to the underlying horizons. The characteristics of SNG-6 therefore appeared to be transitional between those displayed by the organic-poor part of the section below and the true 'transition zone' (i.e. between the organic-poor and organic-rich parts of the Snellegem sequence; see below) located above. The organic-poor part of the sequence was therefore in general characterized by deep troughs at Rb-Cs, Th-Pb, Nb, Zr-Hf, Ti, Sc-V and Cr, and peaks at W, U, Sr and Zn-Cu, on the normalized to the Average Continental Crust (ACC) trace element diagram (Figure 2a).

The transition zone between the organic-poor and organic-rich parts of the Snellegem sequence did not show any pronounced geochemical markers except for the horizon at 104–102 cm (SNG-7), which was characterized by the highest concentration of Sr when compared to any other sample (the Sr/Y ratio was 104). A trace element ACC-normalized diagram for samples from this transition zone (Figure 2a) displays features similar to those observed in samples from the lower part of the sequence, including marked peaks at Sr, but with overall much higher concentrations of most trace elements. The only notable difference was a less-pronounced Th–Pb trough in comparison to the organic-poor part of the sequence.

The organic-rich (upper) part of the Snellegem sequence did not display pronounced geochemical markers except for the lowered total concentration of trace elements and an elevated Sr/Y ratio (>32) for the horizon of 88–85 cm (ZGD-5) (Table 1). Additionally, a few geochemical markers of 'second rank' were identified. First, the horizon of 97–94 cm (ZGD-2) displayed enrichment in Co and Zn, whereas the horizon of 98–96 cm (SNG-10) displayed enrichment in Co only. Second, the horizon of 96–94 cm (SNG-11) was enriched in Cr and Ni, was slightly depleted in LREE and MREE and had an elevated Ni/Sc ratio (13.9). Third, similar characteristics to SNG-11 (enrichment in Cr and Ni, and slight depletion in LREE and MREE), but with additionally elevated concentrations of Co, were observed for the horizon of 97–94 cm (ZGD-2). Fourth, the horizons of 92–90 cm (SNG-13) and 91–88 cm (ZGD-4) were enriched in Ba. Finally, the horizon of 79–76 cm (ZGD-8) displayed detectable enrichment in Zr. Trace element ACC-normalized diagrams (Figure 2a,b) did nonetheless differentiate this part of the sequence from both lower and transition parts. First, in addition to overall higher concentrations of trace elements, the sediments displayed marked troughs for Sr, while sample SNG-11 displayed peaks at Ni and Cr. Second, a Th–Pb trough, which was typical for the lower and transition zones of the sequence, was absent.

Maldegem sequence

The Maldegem sequence displayed only a few geochemical features of interest, possibly influenced by the lower sampling resolution as compared to the Snellegem sequence (see above). Notable features

		Snellegem-1									
Sample	SNG-1	SNG-2	SNG-3	SNG-4	SNG-5	SNG-6	SNG-7				
Interval	116–113 cm	113–111 cm	111–108 cm	108–106 cm	106–105 cm	105–104 cm	104–102 cm				
Sc	0.257	0.259	0.312	0.185	0.230	0.363	0.980				
Ti	97.33	90.63	109.2	49.09	56.76	95.08	278.9				
V	2.272	2.068	2.466	1.930	2.204	3.476	9.797				
Cr	1.900	2.108	2.396	1.185	1.595	2.433	7.138				
Co	1.096	0.966	1.301	1.119	1.332	1.807	4.192				
Ni	2.842	2.759	5.178	3.561	4.712	4.389	11.79				
Cu	1.393	1.324	4.429	1.812	3.682	2.295	6.945				
Zn	7.945	5.636	9.540	6.725	9.587	11.40	22.76				
Rb	1.958	2.054	2.367	1.041	1.238	1.985	5.598				
Sr	401.1	415.2	3/0.1	433./	395.4	354.2	501.9				
Y 7.	1.249	1.2/3	1.549	1.344	1.593	1.968	4.826				
Zr	4.098	4.210	4.952	2.842	2.475	3./8/	10.36				
	0.560	0.419	0.010	0.295	0.260	0.440	0.410				
Ra	60.83	57.42	53.07	59 31	62 20	66.05	108.8				
la	1 1 5 5	1 661	1 899	0 984	1 394	1 912	5 650				
Ce	2.355	3.202	3.559	1.813	2.571	3.692	11.13				
Pr	0.299	0.361	0.400	0.217	0.303	0.437	1.277				
Nd	1.154	1.377	1.563	0.953	1.313	1.821	5.078				
Sm	0.243	0.270	0.324	0.203	0.275	0.379	1.053				
Eu	0.087	0.089	0.095	0.081	0.098	0.124	0.289				
Gd	0.267	0.301	0.360	0.236	0.309	0.415	1.132				
Tb	0.041	0.044	0.052	0.037	0.048	0.064	0.171				
Dy	0.197	0.212	0.245	0.188	0.233	0.305	0.804				
Ho	0.041	0.044	0.050	0.040	0.048	0.062	0.163				
Er Tree	0.125	0.131	0.153	0.123	0.144	0.189	0.494				
1m Vh	0.015	0.015	0.018	0.015	0.017	0.023	0.062				
	0.114	0.110	0.132	0.107	0.121	0.104	0.422				
Hf	0.135	0.017	0.020	0.010	0.018	0.025	0.005				
Та	0.063	0.042	0.059	0.030	0.036	0.054	0.120				
W	0.079	0.104	0.074	0.108	0.083	0.223	0.269				
Pb	0.707	0.660	0.782	0.408	0.473	0.823	2.049				
Th	0.278	0.381	0.523	0.223	0.268	0.429	1.378				
U	0.115	0.130	0.123	0.122	0.140	0.179	0.562				
Ni/Sc	11.1	10.6	16.6	19.2	20.5	12.1	12.0				
Ni/Cr	1.50	1.31	2.16	3.01	2.95	1.80	1.65				
Sr/Y	321	326	239	323	248	180	104				
				Snellegem-1							
Sample	SNG-8	SNG-9	SNG-10	SNG-11	SNG-12	SNG-13	SNG-14				
Interval	102–100 cm	100–98 cm	98–96 cm	96–94 cm	94–92 cm	92–90 cm	90–88 cm				
Sc	1.538	1.909	4.109	4.086	4.657	4.066	5.012				
Ti	459.8	554.9	1179	1210	1218	1320	1298				
V	15.17	18.84	39.93	38.30	39.42	32.84	45.02				
Cr	13.79	13.05	29.18	96.88	31.55	32.60	37.06				
Со	6.018	5.142	11.26	8.546	7.592	5.979	9.331				
Ni	15.03	13.48	29.70	56.90	26.42	18.60	22.90				
Cu	7.884	6.683	13.61	14.25	14.08	11.18	12.93				
Zn	34.41	29.38	59.41	58./5	54.19	42.41	50.92				
nu Sr	0.0UD 371 0	10.42 272 1	23.13 104 5	23.91 135 2	24.39 150 0	24.82 171 0	52.00 122.0				
V	571.0	7 092	174.0	133.3	20.05	141.0 1710	152.0				
7r	16 56	18 40	40.96	41.85	20.03	17.12 <u>44</u> 01	20.42 ΔΛ 27				
Nb	1,938	2,339	4,990	5,030	5,144	5,175	5 403				
Cs	0.622	0.793	1.635	1.666	1.816	1.846	1.962				
Ba	108.4	93.37	161.6	159.0	162.5	228.2	191.0				
La	7.748	9.395	22.43	20.67	22.84	22.41	25.62				
Ce	15.68	19.26	45.56	41.71	45.60	43.65	54.72				

Tab	le	1.	Trace e	lement	composition	of La	te Pl	eistocene	sediments	from	Bel	gium	(ppm)).
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(Continued)

Table 1. Continued.

				Snellegem-1						
Sample	SNG-1	SNG-2	SNG-3	SNG-4	SNG-5	SNG-6	SNG-7			
Interval	116–113 cm	113–111 cm	111–108 cm	108–106 cm	106–105 cm	105–104 cm	104–102 cm			
Pr	1.818	2.231	5.245	4,940	5.406	5.049	6.373			
Nd	7.215	8.921	20.82	20.32	22.50	20.67	26.78			
Sm	1.477	1.848	4.318	4.058	4.509	4.094	5.340			
Eu	0.386	0.459	1.015	0.914	1.047	1.002	1.244			
Gd	1.575	2.010	4.463	4.207	4.634	4.332	5.501			
Tb	0.235	0.298	0.683	0.654	0.714	0.712	0.821			
Dy	1.117	1.410	3.201	3.085	3.481	3.183	3.923			
HO Er	0.222	0.278	0.629	0.597	0.681	0.616	0.747			
EI Tm	0.076	0.044	0.240	0.226	2.007	1.0/1	2.204			
Yh	0.080	0.100	1 605	1 572	1 766	1 594	1 926			
lu	0.091	0.109	0.244	0.236	0.265	0.236	0.286			
Hf	0.512	0.567	1.247	1.266	1.313	1.406	1.419			
Та	0.165	0.195	0.394	0.416	0.416	0.464	0.557			
W	0.462	0.649	1.151	1.387	1.078	0.929	1.004			
Pb	3.404	4.227	9.254	10.27	10.76	11.20	12.99			
Th	1.933	2.540	5.582	6.415	6.263	5.535	6.735			
U	0.842	0.773	1.841	1.830	1.625	1.395	1.848			
NI/SC	9.78	7.06	7.23	13.92	5.67	4.57	4.57			
NI/Cr	1.09	1.03	1.02	0.59	0.84	0.57	0.62			
51/1	50.8	54.1	10.9	7.02	7.52	0.24	0.40			
	Snellegem-2									
Sample	ZGD-1	ZGD-2	ZGD-3	ZGD-4	ZGD-5	ZGD-6	ZGD-7			
Interval	100–97 cm	97–94 cm	94–91 cm	91–88 cm	88–85 cm	85–82 cm	82–79 cm			
Sc	2.111	4.070	4.470	4.474	2.116	3.862	4.450			
Ti	638.4	1166	1269	1330	905.2	1447	1440			
V	19.38	35.75	34.23	35.14	13.67	29.42	33.85			
Cr	17.80 5.601	41.33	34.05	3/.31	39.43	28.40	34.94			
Ni	17 37	37.41	30.90	21 54	9 250	20.75	8.554 24.03			
Cu	9.044	15.46	16.47	13.19	4.855	11.39	13.04			
Zn	26.86	105.9	43.65	36.67	14.38	38.64	51.86			
Rb	12.53	24.37	27.25	40.74	35.38	33.13	33.98			
Sr	108.1	158.4	133.2	155.0	207.5	162.0	87.02			
Y	9.703	19.12	19.43	17.26	6.363	15.21	18.06			
Zr	23.62	40.90	40.30	36.05	17.91	42.56	46.11			
Nb	2.585	4.807	5.342	5.155	2.678	5.626	5.362			
Cs Po	0.792	1.543	1./39	1.863	1.081	1./32	2.003			
Dd	00/0	142.5	107.2	250.0	7 700	194.0	100.0			
Ce	21 31	40.46	43 25	54 39	16 35	46 77	49.46			
Pr	2.584	4.160	5.150	6.296	1.935	5.072	5.787			
Nd	10.05	18.07	20.33	23.35	7.221	19.25	22.87			
Sm	2.155	4.022	4.401	4.568	1.539	3.980	4.817			
Eu	0.500	0.905	1.024	0.967	0.465	0.909	1.070			
Gd	2.307	4.203	4.817	5.186	1.742	4.441	5.237			
Tb	0.336	0.587	0.687	0.666	0.244	0.596	0.719			
Dy	1.648	3.015	3.313	3.0/3	1.189	2./33	3.308			
HO Er	0.327	0.555	0.656	0.605	0.229	0.533	0.637			
Tm	0.900	0.250	0.254	0.222	0.079	0.206	0.050 U 220			
Yb	0.878	1.578	1.612	1.463	0.582	1.347	1 511			
Lu	0.123	0.237	0.241	0.218	0.085	0.196	0.223			
Hf	0.618	1.070	1.081	2.330	0.526	1.175	1.275			
Та	0.178	0.325	0.356	0.358	0.213	0.400	0.381			
W	0.507	0.883	0.837	0.771	0.486	0.799	0.656			
Pb	6.645	9.272	9.802	11.01	7.292	10.43	10.41			
Th	2.346	4.560	4.633	6.622	1.954	4.791	5.224			

(Continued)

	Snellegem-1								
Sample	SNG-1	SNG-2	SNG-3	SNG-4	SNG-5	SNG-6	SNG-7		
Interval	116–113 cm	113–111 cm	111–108 cm	108–106 cm	106–105 cm	105–104 cm	104–102 cm		
U	0.716	1.577	2.025	1.205	0.592	0.998	1.223		
Ni/Sc	8.23	9.19	6.91	4.81	4.37	5.37	5.40		
Ni/Cr	0.97	0.91	0.91	0.58	0.23	0.73	0.69		
Sr/Y	11.1	8.28	6.85	8.98	32.6	10.6	4.81		
	Snell2			Maldegem					
Sample	ZGD-8	MLG-1	MLG-2	MLG-3	MLG-4	MLG-5			
Interval	79–76 cm	132–128 cm	128–124 cm	124–120 cm	120–116 cm	116–112 cm			
Sc	4.562	2.632	1.824	2.988	2.575	2.409			
Ti	1484	1533	916.4	1515	1499	1533			
V	38.60	21.24	11.15	21.52	18.96	19.05			
Cr	37.86	20.51	14.53	20.56	40.25	20.64			
Со	8.048	5.130	1.972	4.056	4.042	3.761			
Ni	21.38	13.07	7.037	13.70	13.34	9.941			
Cu	11.49	6.623	4.199	6.762	6.501	12.53			
Zn	42.77	33.26	13.47	23.10	24.49	17.05			
Rb	35.50	51.50	58.85	53.93	52.15	44.93			
Sr	72.53	93.52	147.8	118.5	128.6	137.1			
Y	18.70	12.22	6.112	11.42	10.80	9.331			
Zr	58.10	46.23	22.74	51.27	38.53	47.71			
Nb	5.330	4.894	2.697	4.338	4.726	4.185			
Cs	2.022	1.447	1.514	1.459	1.433	1.113			
Ba	184.2	292.9	324.4	301.6	277.6	264.7			
La	22.61	12.70	7.298	13.80	16.63	13.27			
Ce	53.08	26.13	14.73	29.46	33.63	27.62			
Pr	6.227	3.135	1.743	3.555	3.950	3.278			
Nd	24.62	11.89	6.485	13.19	14.41	12.01			
Sm	5.225	2.511	1.352	2.710	2.818	2.442			
Eu	1.211	0.693	0.490	0.713	0.661	0.600			
Gd	5.905	2.794	1.476	2.874	3.107	2.642			
Tb	0.765	0.401	0.217	0.416	0.422	0.365			
Dy	3.475	1.997	1.113	2.056	1.982	1.729			
Но	0.669	0.411	0.223	0.409	0.389	0.343			
Er	2.000	1.251	0.675	1.263	1.182	1.066			
Tm	0.255	0.168	0.094	0.168	0.152	0.140			
Yb	1.608	1.069	0.594	1.093	1.000	0.910			
Lu	0.229	0.165	0.088	0.164	0.149	0.135			
Ht	1.626	1.311	0.652	1.432	1.096	1.334			
Та	0.383	0.369	0.247	0.342	0.410	0.337			
W	3.012	0.698	0.660	0.667	0.638	4.253			
Pb	25.95	9.873	9.803	10.63	10.12	8.558			
lh 	5.152	3.208	1.899	3.231	4.112	3.434			
U	1.201	1.751	0.682	1./20	2.078	1.518			
NI/SC	4.69	4.96	3.86	4.59	5.18	4.13			
NI/Cr	0.56	0.64	0.48	0.67	0.33	0.48			
Sr/Y	3.88	/.65	24.2	10.4	11.9	14.7			

Table 1. Continued.

Note: The following isotopes were monitored during the analytical runs: Sc⁴⁵, Ti⁴⁷, V⁵¹, Cr⁵³, Co⁵⁹, Ni⁶⁰, Cu⁶³, Zn⁶⁶, R^{b85}, Sr⁸⁷, Y⁸⁹, Zr⁹⁰, Nb⁹³, Cs¹³³, Ba¹³⁷, La¹³⁹, Ce¹⁴⁰, Pr¹⁴¹, Nd¹⁴³, Sm¹⁴⁷, Eu¹⁵³, Gd¹⁵⁷, Tb¹⁵⁹, Dy¹⁶³, Ho¹⁶⁵, Er¹⁶⁶, Tm¹⁶⁹, Yb¹⁷², Lu¹⁷⁵, Hf¹⁷⁸, Ta¹⁸¹, W¹⁸², Pb²⁰⁶, Th²³² and U²³⁸.

were the horizon of 132–128 cm (MLG-1), which displayed elevated concentrations of Zn, and the horizon of 128–124 cm (MLG-2), which had a markedly lowered total concentration of trace elements. This latter horizon also showed an elevated Sr/Y ratio (>24) similar to that displayed by sample ZGD-5 from the Snellegem sequence. Further, the horizon of 124–120 cm (MLG-3) displayed detectable enrichment in Zr; the horizon of 120–116 cm (MLG-4) was slightly enriched in



Rb Cs W Ba Th Pb U Nb Ta La Ce Pr Sr Nd Zr Hf Sm Eu Ti Gd Tb Dy Ho Er Tm Y Yb Lu Zn Cu Sc V Co Ni Cr

Figure 2. ACC-normalized trace element diagram for lake sediments. (a) Snellegem-1 core (SNG-samples); (b), Snellegem-2 core (ZDG-samples); (c), Maldegem core (MLG-samples). The three types of trace element distributions correspond to three lithological parts of the sequence (see Figure 3a). ACC-normalizing values are after Wedepohl (1995).



Rb Cs W Ba Th Pb U Nb Ta La Ce Pr Sr Nd Zr Hf Sm Eu Ti Gd Tb Dy Ho Er Tm Y Yb Lu Zn Cu Sc V Co Ni Cr

Figure 2. Continued.

Cr; and the horizon of 116–112 cm (MLG-5) showed elevated concentrations of Cu. The trace element ACC-normalized diagram (Figure 2c) looked very similar to that for the upper part of Snellegem sequence (Figure 2a,b). The exception was sample MLG-5, which displayed strong peaks at W and Cu.

Chemostratigraphic correlation

Comparison of the two cores from Snellegem Pond showed that samples ZGD-7 and ZGD-8 (Snellegem-2 core) displayed very deep troughs for Sr (Figure 2b), a feature that was observed only for Snellegem-1 (SNG) samples collected from the organic-rich part of the sequence. Further, samples ZGD-4 and SNG-13 from the depths of 91–88 cm and 92–90 cm, respectively, displayed sharp increases in concentration of Ba that were distinct from samples from the lower (organic-poor) horizons, whilst the trace element patterns for these two samples appeared almost identical (Figure 2a, b). The described geochemical features thus allowed us to correlate the two cores recovered from sediments in Snellegem Pond.

Chemostratigraphic correlations could also be made between the Snellegem and Maldegem sequences. Notably, a markedly lowered total concentration of trace elements was detected for the horizon of 128–124 cm in the Maldegem sequence (MLG-2) and for the horizon of 88–85 cm in the Snellegem-2 sequence (ZGD-5) (Figures 2 and 3). Additionally, a peak at Pb was observed for these two samples (MLG-2 and ZGD-5), with all other samples displaying lowered concentrations of Pb on the ACC-normalized diagrams (Figure 2b,c). We therefore suggest that samples ZGD-5 and MLG-2 are correlated and reflect the same event. High concentrations of Ba detected in the Maldegem MLG-2 sample and in the Snellegem-2 ZGD-4 sample provide further support for this

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Figure 3. Distribution of the selected trace elements in sedimentary sequences from West Flanders; (a) Snellegem-1 core; (b), Snellegem-2 core; (c), Maldegem sequence core. T.Z., a transition zone between the organic-poor and organic-reach parts of the sequence; G.P., gyttja and peat. A thin layer at ~100 cm depth for the Snellegem-1 section is eolian sand within the organic-reach part of the sequence. Dashed lines in (b,c) show zones with low total trace element concentrations (see text for details). Trace element concentrations are given in ppm. Trace element concentrations in all samples have been normalized to a total of 1000 ppm. The age of 12 807 cal yr BP was determined by Verbruggen (1979) for the depth of 99 cm of Snellegem sequence (marked with a star). Stratigraphic positions of the collected samples are indicated by the gray bars adjacent to the lithological description.



Figure 3. Continued.

suggestion (the lower sampling resolution for the Maldegem sequence means sample MLG-2 likely combined features typical of both samples SNG-4 and SNG-5).

Discussion

The vertical distribution of trace element concentrations in the cores may serve as records of incorporation of 'anomalous' materials to sediments and therefore may provide information on timing and extent (and thus source) of contaminants-producing events (Figure 3). In particular, geochemical features of lake sediments from West Flanders point to the possible presence of materials originating from sources other than local soil or bedrock erosion.

Our results have identified three sequential geochemical markers in the organic-poor (lower) part of the Snellegem sequence, represented by samples SNG-3 (111–108 cm), SNG-4 (108–106 cm) and SNG-6 (105–104 cm). The identified geochemical markers allow us to make some suggestions about the origin of such markers.

First, geochemical features displayed by the sample SNG-3 may indicate the presence of material (s) significantly enriched in Co, Ni and Zn, and to a lesser extent, in Ti, V, Cr, Co, Zr, Nb, Hf, Ta, Pb and U. According to the suggested age-depth model, such material might have been added to sediments at *c*. 12 900 cal yr BP. Taking into account the Younger Dryas Impact Hypothesis (e.g. Firestone et al. 2007), some of the observed geochemical features could be explained by the presence of a meteoritic component. Meteorites are enriched in siderophile elements (in particular, in Ni and Co) and to a lesser extent in some other elements (e.g. V and Cr) when compared to most terrestrial materials (e.g. Anders and Grevesse 1989; Wedepohl 1995). These characteristics are consistent with the observed geochemical features of sample SNG-3 (elevated concentrations of Ni, Co, V, Cr), but are not unequivocal evidence of a meteoritic component. Instead, elevated concentrations of Ti, Zr, Nb, Hf, Ta, Pb and U could be consistent with the presence of volcanic material (e.g. Wastegård et al. 2000; Kuznetsov and Subetto 2004). Notably, the age of *c*. 12 900 cal yr BP suggested for

sediments represented by sample SNG-3 is very close to is the time of the Laacher See volcano eruption (*c*. 12 880 cal yr BP; see Schminke et al. 1999; Riede et al. 2011; Riede 2016). Although Belgium was not the main area for deposition of the Laacher See tephra, this tephra has been detected in Late Pleistocene sediments of Hautes Fagnes Plateau in East Belgium (Pissart 2003) and even in sediments from Sluggan Bog in Northern Ireland (Lowe et al. 2004).

Second, chemical characteristics displayed by sample SNG-4 are more difficult to interpret but again suggest an external influence. These characteristics – namely lowered concentrations of LREE and some MREE, Ti, Cr, Rb, Zr, Nb, Hf, Ta, Pb and Th accompanied by elevated concentrations of Sr and W – are different from those displayed by both underlying and overlying sediments of the Snellegem sequence. It is considered unlikely that they have anything to do with contamination, and could instead reflect a change in local or regional conditions of sedimentation arising from the still unknown event.

Third, chemical characteristics displayed by sample SNG-6 (the uppermost part of the organicpoor zone) are, in general, between those of the organic-poor part of the section and the transition zone (between the organic-poor and organic-rich parts) of the Snellegem sequence. Nonetheless, key geochemical signals from the lower (organic-poor) part of the sequence prevail in sample SNG-6. This indicates that material typical for the upper Snellegem sequence horizons (organic-rich) had just started to appear at the core-level represented by sample SNG-6, suggesting a transition to organic-enriched sediments typical of the Younger Dryas beginning *c*. 12 860 cal yr BP (the age suggested for sediments represented by sample SNG-6 according to the age-depth model). This evidently extended transition between the organic-poor part of the Snellegem sequence to the organicrich part suggests that the onset of the Younger Dryas cooling here was not abrupt, but took some time.

Observed geochemical features suggest that sediments from the lower (organic-poor) part of Snellegem sequence might also have experienced the addition of compositionally anomalous material during two short events *c*. 12 900 cal yr BP, i.e. shortly before or during the beginning of the Younger Dryas. One geochemical marker could be related to the Laacher See eruption via the possible presence of the volcanic material in sediments. However, a further geochemical marker could indicate the presence of siderophile element-enriched components indicative of a meteoritic contribution at a similar time to that of the Laacher See eruption (and thus temporally indistinguishable). Unfortunately, these observed features remain too subtle to serve as reliable confirmation of the presence of an extraterrestrial component, which would require confirmation by such data as Re–Os and/ or Cr isotope systematics.

The sediments from the horizons of 96–94 cm (SNG-11) and 97–94 cm (ZGD-2) in the organicrich (upper) part of the Snellegem sequence displayed elevated concentrations of Ni and Cr accompanied by lowered concentrations of LREE and MREE (Figures 2 and 3). It is notable that similar features are displayed by sample SNG-3 from the lower part of the Snellegem sequence. We have suggested that such features could be due to the presence of a meteoritic component. But even if a marker at the lower part of the Snellegem sequence is due to the incorporation of the meteorite-related material *c*. 12 900 cal yr BP (cf. Firestone et al. 2007), it is unlikely (although not impossible) that in just 100–150 years, a second meteorite impact affected the same region. It is instead possible that material resulting from a *c*. 12 900 cal yr BP event (or a series of events) was indirectly delivered to the lake sediments, for example, by glacial deposition of material deposited onto the Scandinavian Ice Sheet or later remobilization of the same material following its deposition by the ice sheet.

Another recognizable geochemical marker is represented by layers with a lowered total amount of trace elements in both the upper part of Snellegem sequence and in Maldegem sequence. These layers also displayed peaks at Sr on the ACC-normalized trace element diagram (Figure 2b,c) that can be explained by the presence of carbonate, a phase that is rich in Sr (Sr/Y ratios were 24–32; Table 1). Trace element characteristics of these two layers were very similar to the overall characteristics of sediments from the lower part of the Snellegem sequence, indicating a return to a

sedimentation regime similar to that represented by the lower part of the Snellegem sequence for a relatively short time (\sim 20–30 years) after *c*. 12 700 cal yr BP. We therefore suggest that mostly anoxic conditions in water bodies that existed after *c*. 12 900 cal yr BP (due to inputs of organic material and peat) were briefly and abruptly changed to oxic conditions after *c*. 12 700 cal yr BP, most likely as a result of a fresh water flush. This is evident in both Snellegem Pond and Maldegem Meadow sequences (a distance of \sim 20 km; Figure 1), and the lowland location of both sites near to many rivers (Yser, Leie, Schelde, Dandre and others) indicates that flooding of the area is a plausible explanation.

The information available so far is insufficient to judge whether or not the Snellegem and Maldegem sequences contain products of intensive biomass burning. However, biomass burning contributes to contamination of lakes today (Whitlock and Anderson 2003), and likely did so during the Late Glacial as well. Although the typical method for studying fire history is to systematically analyze lake sediments for charcoal particles, Andronikov and Andronikova (2016) have shown that biomass burning may also leave a geochemical fingerprint in sediments in the form of simultaneous troughs at Ta-Nb and Zr-Hf in ACC-normalized trace element diagrams. Such features are evident on ACC-normalized diagrams in this study (Figure 2), but surprisingly we found that such features are displayed by almost all samples in this study regardless of their stratigraphic position. This indicates that either the products of biomass burning are present throughout the sediments, or the sources of sediments were themselves characterized by simultaneously lowered concentrations of Zr, Hf, Ta and Nb. The former suggestion is supported by the study region being far from the edge of the Scandinavian Ice Sheet (Svendsen et al. 2004) where the climate was relatively warm and where vegetation containing highly flammable oils (pines, spruce and fir, the boreal type of forest at that time) was likely present. In contrast to previous studies that have found peaks in biomass burning products in general correspond to warming events (e.g. the Allerød interstadial; Daniau et al. 2010), our findings could suggest the significant presence of biomass burning in this region throughout the Allerød interstadial and the earlier episodes of the Younger Dryas stadial.

Conclusions

The concentration and distribution of trace elements within Late Pleistocene lake sediment sequences in West Flanders display features consistent with the addition of materials other than those from expected sources for lake sediments (i.e. they show evidence of contamination). Notably, the environment of Central Europe was significantly affected by eruptions of volcanoes of the Massif Central, and this study has additionally identified the possible presence of the Laacher See volcanic material (*c.* 12 900 cal yr BP) in these sediments.

Biomass burning is another contamination source that contributes to contamination of lakes today, and likely did so during the Late Glacial as well. Depending on the frequency of burning, this process could have provided an almost continuous source of contamination, in contrast to the discrete events that reflect volcanic eruptions. A contribution to contamination by biomass burning is only possible where there is enough fuel available, and this is considered likely in the study region due to its distance from the southern edge of the Scandinavian Ice Sheet.

Finally, contamination from meteorite impacts cannot be ruled out. Some geochemical markers were identified in the sediments studied, notably elevated concentrations of Ni and Cr accompanied by lowered concentrations of LREE and MREE, which are consistent with the presence of a meteoritic component. The presence of such a component may provide support for the Younger Dryas Meteorite Impact Hypotheses (Firestone et al. 2007). However, further analyses will be required to unambiguously confirm the presence of such a component in these sediments, and to constrain the exact timing of this component's appearance.

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