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CHEMICAL ELEMENTS AND HEAVY METALS IN EUROPEAN LARCH TREE RINGS FROM REMOTE AND POLLUTED SITES IN THE EUROPEAN ALPS

ABSTRACT: LEONELLI G., BATTIPAGLIA G., CHERUBINI P., MORRA DI CELLA U. & PELFINI M., *Chemical elements and heavy metals in European larch tree rings from remote and polluted sites in the European Alps*. (IT ISSN 0391-9838, 2011).

Air pollution dispersal in the European Alps has been studied both for glacial and forest environments. In this study, chemical elements and heavy metals in the tree rings were analyzed for seven sites of European larch (*Larix decidua* Mill.) in the Italian European Alps. At three sites in the proximities of the Mont Blanc Tunnel (MBT) entrance the analyses were performed at the yearly scale on the periods 1950-1970 (comprising the MBT opening in 1965) and 1985-2008 (comprising the 3-yr MBT closure after the 1999 car accident) with the aim to check if trees recorded at the yearly scale variations in chemical elements and changes in heavy metals concentrations over time. At the regional scale, the analyses on heavy metals were conducted without annual resolution for most sites on the common periods 1950-1970 / 1985-1998 with the aim to detect possible ongoing trends and differences between some Alpine sites. Chemical elements concentrations at Entrèves (EN) sites varied significantly between heartwood and sapwood with generally higher concentrations in sapwood. At EN sites no clear patterns were found for heavy metals before and after the MBT opening and during its 3-yr closure. We found that the "high" site (ENH) was generally less polluted than the "close" (ENC) and the "far" (ENF) sites. At site ENC we found higher values of Cr, Ni and Cu, whereas at site ENF we found higher values for all the other elements analyzed. The analysis of heavy metals at the regional scale revealed generally no significant temporal changes in concentrations except for Cr and Cu, showing higher values in the recent period. On comparing the heavy metals concentration between the seven sites, the Palud site showed almost always the highest concentrations, except for Ni and Cu that were higher in two remote sites close to glacial environments in the Gressoney and Valtellina valleys. Dendrochemical analysis revealed that the temporal information in the tree rings is covered by too many signals and no environmental changes are recorded at the yearly scale by European larch. However tree rings may provide useful information on ongoing long-term trends and on the spatial definition of pollutant dispersal in the Alpine environment.

KEY WORDS: Tree ring, Chemical elements, Heavy metals, Air pollution, European larch, European Alps.

RIASSUNTO: LEONELLI G., BATTIPAGLIA G., CHERUBINI P., MORRA DI CELLA U. & PELFINI M., *Elementi chimici e metalli pesanti negli anelli di accrescimento di larice europeo da siti remoti e inquinati nelle Alpi*. (IT ISSN 0391-9838, 2011).

La dispersione degli inquinanti atmosferici nelle Alpi è stata studiata sia per gli ambienti glaciali sia per quelli forestali. In questo lavoro, sono stati analizzati elementi chimici e metalli pesanti negli anelli di accrescimento di esemplari di larice europeo (*Larix decidua*) provenienti da sette siti nelle Alpi italiane. In tre siti in prossimità dell'ingresso del Tunnel del Monte Bianco (TMB) sono state effettuate analisi a scala annuale sui periodi 1950-1970 (comprendente l'apertura del TMB nel 1965) e 1985-2008 (comprendente la chiusura di 3 anni dopo l'incidente d'auto avvenuto nel 1999) con lo scopo di verificare se gli alberi avessero registrato a scala annuale variazioni di concentrazione di elementi chimici e di metalli pesanti nel tempo. A scala regionale l'analisi sui metalli pesanti è stata effettuata senza risoluzione annuale per la maggior parte dei siti, sui periodi comuni 1950-1970 / 1985-1998 con lo scopo di determinare possibili trend in corso ed eventuali differenze tra alcuni siti Alpini. Gli elementi chimici analizzati ai siti di Entrèves (EN) sono risultati variare significativamente tra duramen e alburno, con concentrazioni generalmente maggiori nell'alburno. Ai siti EN non si sono trovate particolari variazioni per i metalli pesanti prima e dopo l'apertura del TMB e durante la sua chiusura di 3 anni. Il sito «alto» (ENH) è risultato generalmente meno inqui-

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nato dei siti «vicino» (ENC) e «lontano» (ENF). Al sito ENC sono stati osservati valori più alti per quanto riguarda Cr, Ni e Cu, mentre al sito ENE i valori risultano più alti per tutti gli altri elementi analizzati. Le analisi dei metalli pesanti a scala regionale non ha mostrato in generale alcuna variazione temporale significativa nelle concentrazioni eccetto che per Cr e Cu, elementi che mostrano valori più alti per il periodo recente. Comparando le concentrazioni dei metalli pesanti tra i sette siti, il sito Palud ha mostrato quasi sempre le concentrazioni più alte, eccetto che per Ni e Cu che sono risultati più elevati nei due siti remoti ubicati in ambienti glaciali nella Valle di Gressoney e in Valtellina. Le analisi dendrochimiche hanno mostrato come l'informazione temporale sia coperta da troppi segnali e come il larice europeo non abbia registrato le variazioni ambientali a scala annuale. Dall'analisi dei dati è possibile osservare come gli anelli di accrescimento degli alberi posoono fornire informazioni utili su trend in corso e sulla definizione spaziale della dispersione di inquinanti nell'ambiente Alpino.

TERMINI CHIAVE: Anelli di accrescimento degli alberi, Elementi chimici, Metalli pesanti, Inquinamento atmosferico, Larice europeo, Alpi Europee.

INTRODUCTION

Tree rings are widely used for reconstructing past climatic conditions and environmental events. The study of the chemical elements concentration in the tree rings has been developed for studying the physiological questions and nutrient distribution in trees, for example for establishing the limits between heartwood and sapwood (Wright & Will, 1958; Hart, 1968; Lambert & *alii*, 1983; Lövestam & *alii*, 1990), for assessing patterns of nutrient concentrations in the trees (for review: Meerts, 2002), or for tracing changes in nutrient availability in declining forests (Beauregard, 2010). Dendrochemistry has been applied in many studies, following the idea that trees can act as «environmental archives», for establishing the impact of air, water and soil pollution in the environment at different spatio-temporal scales (Baes & McLaughlin, 1984; Bondietti & *alii*, 1990; Peterson & Anderson, 1990; Lageard & *alii*, 2008). Recently, dendrochemical analyses have been applied also for the chronological reconstruction of past volcanic events (Unlu & *alii*, 2009), a field that is furthermore opening new perspective for dating e.g. the Thera eruption (Pearson & *alii*, 2009). Tree-ring width is influenced by a variety of limiting factors that may cover the damage induced by a single pollutant, and trees may not react or react very independently to pollution for heavy metals in the soil or along heavy highways (Schweingruber, 1996). According to Fischer (1993) even genetically identical trees can react differently to pollutants.

For past climate reconstructions, in literature it is rarely considered that natural proxies like the tree rings (that are frequently used for climate reconstructions at the yearly scale), may have been impacted in the past and recent times also by non-climatic factors like pollution. Therefore studies about climate change impacts on the Alpine environments should be supported also by studies on environmental changes occurred over time. In fact, pollution may alter the climatic signal in tree ring chronologies. In a recent study, Kern & *alii* (2009) found that during a period of exploitation of a sulphur mine, a nitrogen diffusion in the environment occurred and trees produced larger rings than the corresponding summer temperatures can explain, demonstrating that climatic signal in tree-ring chronologies may be altered by pollution.

Pollutant dispersal in the Alpine environment and the assessment of their trends over time is a topic of high interest because of the potential impact on the fragile high-altitude ecosystems and on the resident population. Several studies have been performed on the Alps analyzing ice cores and snow from the Mont Blanc area for reconstructing lead and heavy metals presence and trends, mostly finding increasing trends of pollutants of different origins over about 200 years of analysis (Van de Velde & *alii*, 1998; 2000; Rosman & *alii*, 2000; Burton & *alii*, 2006), and higher concentrations especially after 1950 (Van de Velde & *alii*, 1999). Based on an integrated approach and 3D aerial dispersal models, the aerial dispersion of vehicular traffic exhaust in the Mont Blanc Tunnel (MBT) area after 1999 has been studied, and the area close to the tunnel entrance resulted the most polluted (Nanni & *alii*, 2004).

In the present study, the main objective was to assess spatial and time distribution of air pollutants in the Alpine environment by means of a dendrochemical approach. We wanted to check if tree rings of European larch from some sites in the European Alps recorded yearly variations in chemical elements (e.g. macronutrients: P, K and Ca, Mg, S; micronutrients: B, Cu, Fe, Cl, Mn, Mo, Zn; and some other element like Na) and heavy metals, consistently with some air pollution changes occurred over time. In particular, we focussed on the Mont Blanc area where strong air pollution changes have happened at the opening of the MBT in 1965 and at its 3yr closure in the 1999-2002 period. At the regional scale we compared heavy metal concentrations at several sites with the aim to compare information from polluted and remote sites (with respect to air pollution), including also data previously collected in other works (Orlandi & *alii*, 2002, tab. 1).

METHODS OF ANALYSIS

Dendrochemical data from seven sites of European larch (*Larix decidua* Mill.) in the Italian European Alps (Valle d'Aosta and Lombardy regions; fig. 1) were collected from different studies performed over the last decade and recently (table 1). Tree rings were analysed with two methods (Atomic absorption spectroscopy, last decade data, and inductively coupled plasma mass spectrometry, recent data), with different pooling techniques and in two laboratories (table 1).

The present study was based on the yearly-resolved data of chemical element concentrations obtained from the Mont Blanc area (EN sites) and on the comparison of heavy metals concentrations in the tree rings of seven sites from the European Alps. The three EN sites, in the proximities of the Mont Blanc Tunnel (MBT) entrance, ENC - close to the highway: at 1370 m a.s.l., 2 m from the highway, ENH, at higher altitude: at 1410 m a.s.l., 30 m, and ENF, far from the highway: at 1410 m a.s.l., 300 m, were analysed on the periods 1950-1970 (comprising the MBT

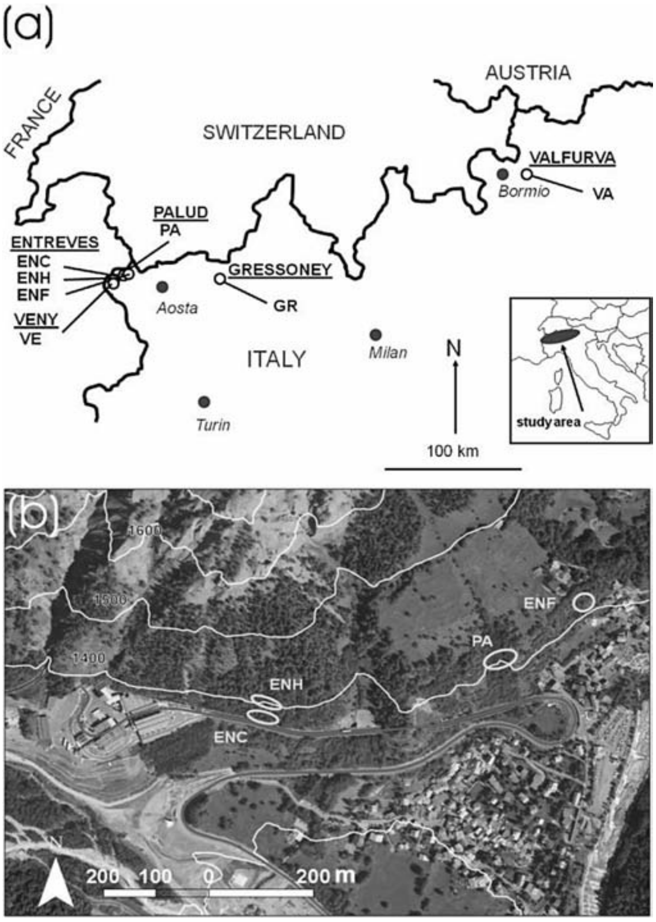

FIG. 1 - Study sites of European larch in the Mont Blanc Tunnel area and in the Italian European Alps selected for this study. For the ortophoto: © Regione Autonoma Valle d'Aosta, Assessorato Territorio, Ambiente e Opere Pubbliche, Ortophoto Edition 2006 - Aut. n. 1156 of 28.08.2007.

opening in 1965) and 1985-2008 (comprising the 3-yr MBT closure after the 1999 car accident occurred in the tunnel) aiming to check how trees recorded the air pollution changes occurred in the environment in the vicinity of the MBT highway. Air pollution changes over time have been quite strong in this area: the road traffic between Italy and France constantly increased since the MBT opening, passing from 602,000 vehicles per year (period 1965-1970) up to 1,935,000 per year (period 1993-1998), 373,000 in 1999, 0 in 2001-2002, and 1,671,000 per year (period 2003-2008) (data of TMB GEIE, 2009). At these sites, four cores per tree were taken from five trees and then prepared for yearly resolved analyses in the laboratory. At the regional scale, data of heavy metals in the tree rings were compared on the common periods 1950-1970 and 1985-1998 with the aim to detect possible ongoing trends over time and differences between polluted and remote Alpine sites (tab. 1).

Ring-width chronologies were constructed at all sites with the aim to correctly date all the tree rings in each core before splitting and milling them (different year- or tree-pooling techniques were used; table 1). Visual and statistical verification of the dating was performed by crossdating the growth series with trees from the same site as well as with different reference chronologies from the Alps.

Chemical analysis

– *EN sites.*

Samples were weighted and then digested by means of HNO_3 at 65% and HF at 1%, at a temperature of 230°C, pressure of 140bar. After cooling, the samples were then analyzed by means of ICP-MS, using both white and National Institute of Standards and Technology samples. At EN sites we analyzed B, Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba and Pb.

– *VE, VA sites.*

The wood samples were weighted and then mineralized by means of oxidation reactions with HNO_3 at 65%, at a temperature of 130°C for two hours in a silicon bath. After cooling, milli-Q water was added, the samples were filtered and the standard solutions containing the heavy metals were then prepared for Atomic Absorption Spectroscopy, using also white samples. At these sites the heavy metals Cr, Ni, Cu, Cd (only VA site) and Pb were analyzed (tab. 1).

– *PA, GR sites.*

The wood samples were weighted and then mineralized by means of oxidation reactions with HNO_3 at 65%, at a temperature of 350°C up to the complete consumption of the organic matter. After cooling, milli-Q water was added, the samples were filtered and the standard solutions containing the heavy metals were then prepared for Atomic Absorption Spectroscopy, using also white samples. At these sites heavy metals Cr, Ni, Cu, Cd and Pb were analyzed (Orlandi & *alii*, 2001, tab. 1).

DATA ANALYSIS

The concentrations in ppm from the chemical analyses were not normally distributed, presented highly variable variances between groups, presented different number of observations per group and had also a different annual resolution. Since ANOVA prerequisites were not met, we performed the analysis of mean rank differences by means of the Kruskal & Wallis (1952) test. The significance of the differences in mean ranks between the two time periods was assessed by the chi-squared statistics. In case of multiple comparisons between more than two groups, we assessed the significance of the mean rank differences at $p<0.05$ by applying the least significant difference (LSD) *post hoc* test with the Bonferroni correction for avoiding the inflation of alpha. At EN sites we performed the analyses considering only the common years presenting values of concentrations for maintaining the annual resolution of the comparisons between sites. At the other sites, the beginnings and the ends of the two periods of analysis sometimes include mean con-

TABLE 1 - Original dataset consistency and site characteristics. The analysis of the chemical elements were performed at EN sites on the periods 1950-1970 / 1985-2008, and the analysis of the heavy metals at all sites on the periods 1950-1970 / 1985-1998. Site codes as in fig. 1; MBT=Mont Blanc Tunnel; UNIMIB=Università di Milano-Bicocca; WSL= Swiss Federal Institute of Forest, Snow and Landscape Research; C.E.=Chemical elements; H.M.=Heavy metals; AAS=Atomic absorption spectroscopy; ICP-MS=Inductively coupled plasma mass spectrometry.

Site code	Site	Site environment	Altitude m a.s.l.	Number of trees	Lab of analysis - Analysis of	First year of analysis	Last year of analysis	Tree pooling Y(nr.)/N	Year pooling Y(nr.)/N	Method of analysis	Latitude (N)	Longitude (E)	Author reference
VE	Veny	Along a forest road	1700 [1]	4	UNIMIB - H.M.	1804, variable	1998	N	Y (5yr)	AAS	45° 48' 26'' [1]	6° 55' 57'' [1]	Guidetti (1999)
ENC	Entrèves	Close to the MBT highway	1370	5	WSL - C.E.	1950; 1985	1970; 2008	Y (5)	N	ICP-MS	45° 49' 03''	6° 57' 23''	Leonelli (this work)
ENH	Entrèves	At higher altitude, in forest, MBT highway area	1410	5	WSL - C.E.	1950; 1985	1970; 2008	Y (5)	N	ICP-MS	45° 49' 04''	6° 57' 23''	Leonelli (this work)
ENF	Entrèves	Far from the MBT highway	1410	5	WSL - C.E.	1950; 1985	1970; 2008	Y (5)	N	ICP-MS	45° 49' 11''	6° 57' 51''	Leonelli (this work)
PA	Palud	Close to the MBT highway	1400 [1]	15	UNIMIB - H.M.	1940	2000	N	Y (10yr)	AAS	45° 49' 08'' [1]	6° 57' 47'' [1]	Apollonio (2000)
GR	Gressoney	Remote site close to Lys Glacier	2100 [1]	23	UNIMIB - H.M.	1900, variable	1999	N	Y (10yr)	AAS	45° 52' 17'' [1]	7° 48' 38'' [1]	Cozzi (2000); Orlandi & *alii* (2002)
VA	Valfurva	Remote site close to a glacier river	1750 [1]	8	UNIMIB - H.M.	1900	1999	N	Y (10yr)	AAS	46° 24' 28'' [1]	10° 30' 22'' [1]	Cafiero (2000)

[1] Approximate value.

centration values referring also to tree rings out of the considered time intervals because of the year pooling approach.

RESULTS

Tree-ring chronologies - EN sites

Ring-width chronologies at EN sites span from 1977 (ENC), 1910 (ENH), 1860 (ENF) to 2008. Tree rings resulted much wider at site ENC (4.3±1.3 mm) with trees 27±4 yr old, than at site ENH (1.8±0.8mm) with trees 82±15 yr old, and ENF (1.9±1.4 mm) with tress 134±8 yr old. The three mean chronologies are based only on five trees per site, however, two event years are visible in 1997 and 2007 at all sites (fig. 2).

Chemical elements - EN sites

The chronologies of the chemical elements B, Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba and Pb were constructed for sites ENC, ENH and ENF for the periods 1950-1970 and 1985-2008 (fig. 3a). At ENC and ENH sites, only few tree-ring samples revealed traces of the chemical elements B, Co, Mo, and Cd, thus they were not further analyzed.

– *Time Period Analysis*

At ENC site the first ring of sapwood ranged between 1998-1999 (about 11 yr of sapwood in the 20 cores of the site). At ENH site the first ring of sapwood ranged between 1985-1987 (about 23 yr of sapwood), at site ENF the first ring of sapwood ranged between 1973-1975 (about 35 yr of sapwood). Therefore, except for site ENC, the two time periods analyzed, separately comprised tree rings of heartwood (1950-1970) and of sapwood (1985-2008). At site ENC the 1985-2008 period had about half of the tree rings of heartwood and half of the tree rings of sapwood.

In general, we found that the concentrations of the chemical elements analyzed at ENH and ENF sites varied significantly over time (for most elements the variation is statistically significant at p<0.001) showing higher concentrations in the recent period of analysis (fig. 3a). Instead, the concentrations of Al, P (at ENF site), Fe (ENH), Ni, Pb (ENF) did not change significantly over the two periods of analysis. At site ENC, for Na, K, Mg and Ca we found a

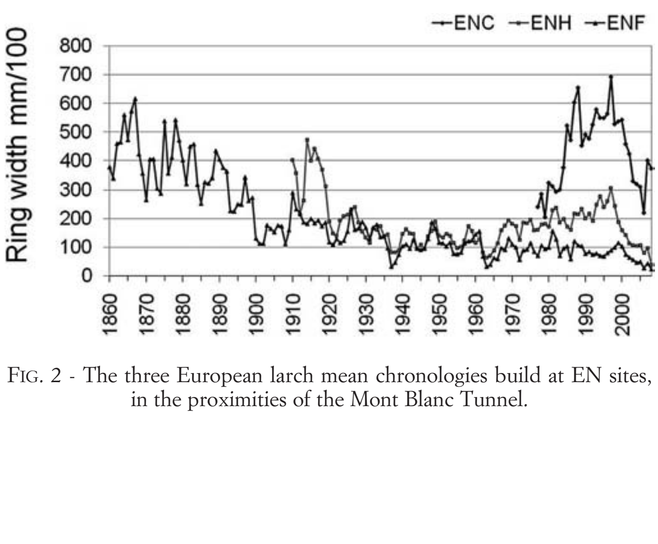

FIG. 2 - The three European larch mean chronologies build at EN sites, in the proximities of the Mont Blanc Tunnel.

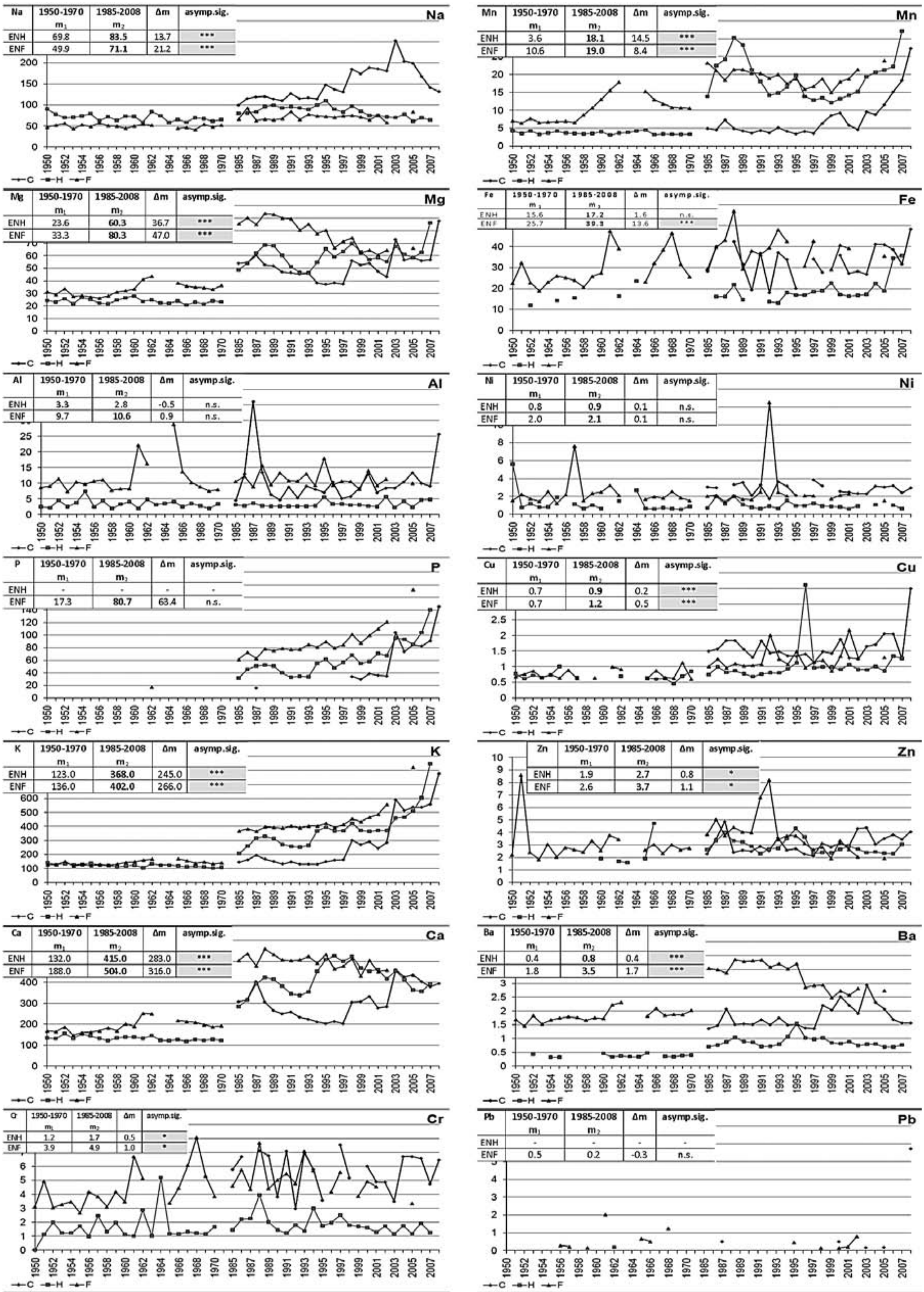

FIG. 3A - Chronologies of the chemical elements analyzed at the yearly scale at the EN sites, Mont Blanc area. Concentrations are in ppm. The tables within each graph report median values of heavy metals concentrations, and their difference, over the two periods of analysis. The differences in mean ranks between the two periods were assessed by means of the Kruskal-Wallis test; the statistical significance of these differences is reported (asymp.sig.= asymptote significance, chi-square test). Highest median values are in bold. ***= p<0.001; **=p<0.01; *=p<0.05.

positive concentration peak in the tree ring 1998, first year of sapwood (one year before the MBT closure) and generally higher values of concentrations in the following rings.

No clear patterns were found both for element concentrations and for heavy metals before and after the opening of the Tunnel and during its 3-yr closure at all sites.

Despite some periods with few data available at some EN sites, many couples of elements show similar trends and patterns over time and for some of them we found very high correlation values. In particular, on the period 1950-1970 we found very high correlations (r≥0.9) for the couples Mg-Ca, Mg-Mn, Mn-K, Mn-Ca, Fe-Cr (all at site ENF), and Ni-Cr (at site ENH) (table 2a). On the period 1985-2008 very high correlations (r≥0.9) between P-K (at all sites), Mg-Ba (Site ENF) and Ni-Cr (site ENC) (table 2b) were found. From our analysis, at most sites the couples Mg-Ca, Mn-K, Fe-Cr, Ni-Cr, Mg-Ba (only at site ENF) were highly correlated in both periods.

– *Site Analysis*

On comparing the concentrations between the EN sites in the two periods of analysis, we found that ENH site was showing lower concentrations with respect to ENC or ENF for all elements (fig. 3b). Site ENC presented exceptionally higher values of Na with respect to the other two sites, higher values also for Cr and Ni (however for both elements, not

TABLE 2A - Pearson's correlation values between couples of elements compared only within each site on the period 1950-1970. Values of r≥0.9 are shaded in dark grey, r≥0.8 are shaded in grey, r≥0.7 are shaded in light grey. Values of r≥0.8 also in table 2b for the same elements are reported in bold and underlined.

Chem. elem.		Na			Mg			Al			P			K			Ca			Cr			Mn			Fe			Ni			Cu			Zn			Ba		
	Site	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF
Na	ENC	-																																						
	ENH		1																																					
	ENF			1																																				
Mg	ENC	-																																						
	ENH		0.37		-	1																																		
	ENF			-0.03			1																																	
Al	ENC	-			-			-																																
	ENH		0.41			0.36			1																															
	ENF			0			0.59			1																														
P	ENC	-			-			-			-																													
	ENH		-			-			-			-																												
	ENF			-			-			-			-																											
K	ENC	-			-			-			-			-																										
	ENH		0.78			0.31			0.55			-			1																									
	ENF			0.07			0.89			0.72			-			1																								
Ca	ENC	-			-			-			-			-			-																							
	ENH		0.45			0.78			0.43			-			0.59			1																						
	ENF			0.01			0.93			0.66			-			0.87			1																					
Cr	ENC	-			-			-			-			-			-			-																				
	ENH		-0.02			-0.08			0.31			-			0.27			-0.04			1																			
	ENF			0.13			0.45			0.12			-			0.32			0.54			1																		
Mn	ENC	-			-			-			-			-			-			-			-																	
	ENH		0.39			0.37			0.55			-			0.67			0.31			0.37			1																
	ENF			-0.13			0.93			0.63			-			0.9			0.92			0.43			1															
Fe	ENC	-			-			-			-			-			-			-			-			-														
	ENH		-			-			-			-			-			-			-			-															
	ENF			0.16			0.6			0.25			-			0.47			0.69			0.93			0.58			1												
Ni	ENC	-			-			-			-			-			-			-			-			-			-											
	ENH		0.55			0.02			0.07			-			0.6			0.07			**0.9**			0.54			-			1										
	ENF			0.21			-0.13			0.07			-			-0.11			0.1			0.14			-0.1			0.08			1									
Cu	ENC	-			-			-			-			-			-			-			-			-			-			-								
	ENH		0.37			0.56			0.63			-			0.44			0.44			0.27			0.43			-			0.38			1							
	ENF			0.36			0.3			0.13			-			0.27			0.33			0.26			0.31			0.34			-0.09			1						
Zn	ENC	-			-			-			-			-			-			-			-			-			-			-			-					
	ENH		-			-			-			-			-			-			-			-			-			-			-			-				
	ENF			0.23			0			0.03			-			0.03			0.04			0.28			-0.04			0.29			0.07			0.13			1			
Ba	ENC	-			-			-			-			-			-			-			-			-			-			-			-			-		
	ENH		-0.08			0.36			0.03			-			-0.02			0.04			-0.15			0.45			-			-0.39			-0.12			-			1	
	ENF			0.21			**0.82**			0.47			-			0.72			0.87			0.44			0.78			0.6			0.05			0.44			-0.17			1

TABLE 2B - Pearson's correlation values between couples of elements compared only within each site on the period 1985-2008. Values of r≥0.9 are shaded in dark grey, r≥0.8 are shaded in grey, r≥0.7 are shaded in light grey. Values of r≥0.8 also in table 2a for the same elements are reported in bold and underlined.

Chem. elem.		Na			Mg			Al			P			K			Ca			Cr			Mn			Fe			Ni			Cu			Zn			Ba		
	Site	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF	ENC	ENH	ENF
Na	ENC	1																																						
	ENH		1																																					
	ENF			1																																				
Mg	ENC	0.31			1																																			
	ENH		-0.14			1																																		
	ENF			0.08			1																																	
Al	ENC	-0.08			0.54			1																																
	ENH		-0.1			0.32			1																															
	ENF			-0.02			0.34			1																														
P	ENC	0.06			0.79			0.06			1																													
	ENH		-0.63			0.72			0.44			1																												
	ENF			0.19			-0.61			-0.05			1																											
K	ENC	0.59			0.79			0.3			0.99			1																										
	ENH		-0.54			0.74			0.46			0.96			1																									
	ENF			0.2			-0.32			-0.11			0.98			1																								
Ca	ENC	0.57			0.81			0.48			0.63			0.81			1																							
	ENH		0.27			0.44			0.15			0.17			0.19			1																						
	ENF			0.02			**0.81**			0.66			-0.53			-0.54			1																					
Cr	ENC	-0.21			0.06			0.37			0.17			0.02			0.08			1																				
	ENH		0.41			0.1			-0.01			-0.22			-0.19			0.19			1																			
	ENF			0.11			0.53			0.72			-0.37			-0.42			0.74			1																		
Mn	ENC	0.23			0.79			0.45			0.84			**0.89**			0.65			0.11			1																	
	ENH		-0.08			0.6			0.17			0.42			0.42			-0.26			0.26			1																
	ENF			0.11			0.44			0.22			0.28			0.38			0.29			0.1			1															
Fe	ENC	0.03			0.47			0.77			0.63			0.45			0.45			0.84			0.52			1														
	ENH		-0.44			0.64			0.46			0.81			0.87			-0.11			-0.03			0.45			1													
	ENF			0			0.28			0.66			-0.05			-0.1			0.48			**0.81**			0.06			1												
Ni	ENC	-0.22			-0.02			0.13			0.15			-0.08			-0.05			0.91			-0.02			0.66			1											
	ENH		0.22			0.06			-0.11			-0.12			-0.17			0.01			**0.88**			0.35			-0.1			1										
	ENF			-0.18			0.04			0			-0.11			-0.13			0.13			-0.01			-0.06			0.06			1									
Cu	ENC	0.05			0.79			0.62			0.67			0.63			0.53			0.32			0.76			0.66			0.16			1								
	ENH		0			0.12			0.17			0.09			0.19			0.42			0.04			-0.13			0.1			-0.03			1							
	ENF			0.07			-0.28			0.12			0.29			0.2			-0.05			-0.04			0.05			0.17			0.6			1						
Zn	ENC	0.39			0.6			0.64			0.19			0.55			0.67			-0.09			0.49			0.29			-0.18			0.41			1					
	ENH		0.48			0.15			0.25			-0.17			-0.12			0.21			0.39			0.34			-0.23			0.35			0.28			1				
	ENF			0.1			0.6			0.16			-0.5			-0.46			0.53			0.27			0.14			0.14			0.72			0.26			1			
Ba	ENC	0.87			0.41			0.14			-0.22			0.43			0.59			-0.2			0.14			0.01			-0.21			0.09			0.51			1		
	ENH		0.67			0.28			0.27			-0.11			-0.05			0.69			0.38			-0.01			-0.2			0.22			0.21			0.66			1	
	ENF			0.02			**0.94**			0.44			-0.57			-0.51			0.8			0.57			0.39			0.31			0.17			-0.16			0.66			1

Na 1950-1970	ENH
ENH **29.0**	-
ENF 10.0	*

Na 1985-2008	ENC	ENH
ENC **47.9**	-	
ENH 26.3	*	-
ENF 12.8	*	*

Mn 1950-1970	ENH
ENH 10.0	-
ENF **29.0**	*

Mn 1985-2008	ENC	ENH
ENC 10.0	-	
ENH 35.3	*	-
ENF **41.7**	*	n.s.

Mg 1950-1970	ENH
ENH 10.3	-
ENF **28.7**	*

Mg 1985-2008	ENC	ENH
ENC 13.1	-	
ENH 27.4	*	-
ENF **46.5**	*	*

Fe 1950-1970	ENH
ENH 2.5	-
ENF **6.5**	*

Fe 1985-2008	ENC	ENH
ENC 17.5	-	
ENH 5.9	*	-
ENF **23.1**	n.s.	*

Al 1950-1970	ENH
ENH 10.1	-
ENF **29.0**	*

Al 1985-2008	ENC	ENH
ENC 33.4	-	
ENH 10.4	*	-
ENF **43.2**	n.s.	*

Ni 1950-1970	ENH
ENH 10.6	-
ENF **24.4**	*

Ni 1985-2008	ENC	ENH
ENC **28.0**	-	
ENH 7.0	*	-
ENF 20.5	n.s.	*

P 1950-1970	ENH
ENH	-
ENF	-

P 1985-2008	ENC	ENH
ENC 5.0	-	
ENH 10.7	n.s.	-
ENF **17.3**	*	n.s.

Cu 1950-1970	ENH
ENH 13.4	-
ENF **15.6**	n.s.

Cu 1985-2008	ENC	ENH
ENC **43.7**	-	
ENH 13.6	*	-
ENF 29.7	*	*

K 1950-1970	ENH
ENH 13.2	-
ENF **27.8**	*

K 1985-2008	ENC	ENH
ENC 13.2	-	
ENH 29.3	*	-
ENF **44.6**	*	*

Zn 1950-1970	ENH
ENH 3.5	-
ENF **5.5**	n.s.

Zn 1985-2008	ENC	ENH
ENC 25.3	-	
ENH 26.0	n.s.	-
ENF **35.7**	n.s.	n.s

Ca 1950-1970	ENH
ENH 10.1	-
ENF **28.9**	*

Ca 1985-2008	ENC	ENH
ENC 11.5	-	
ENH 31.1	*	-
ENF **44.5**	*	*

Ba 1950-1970	ENH
ENH 6.0	-
ENF **17.0**	*

Ba 1985-2008	ENC	ENH
ENC 28.5	-	
ENH 10.5	*	-
ENF **47.9**	*	*

Cr 1950-1970	ENH
ENH 9.6	-
ENF **27.4**	*

Cr 1985-2008	ENC	ENH
ENC **28.9**	-	
ENH 7.2	*	-
ENF 23.9	n.s.	*

FIG. 3B - Mean ranks of heavy metals concentrations between all sites in the two periods of analysis. The differences in mean ranks between the two periods were assessed by means of the Kruskal-Wallis test; the statistical significance of these differences is reported (LSD test *=p<0.05). Highest mean rank values within each period are in bold.

significant differences with ENF), and Cu. Site ENF showed higher concentration with respect to the other two sites for most of the analyzed elements. In general if there were significant differences between ENH and ENF in the early period they also remained in the late period 1985-2008. This is true except for Mn (not significant differences in the 1985-2008 period; higher values also at ENH site) and Cu (significant differences in the 1985-2008 period; higher values at ENF site).

Heavy metals - all sites

The analysis of heavy metals at the regional scale comprised all seven sites and revealed generally no significant temporal changes over the periods 1950-1970 and 1985-1998 except for Cr and Cu at ENH, ENF and GR sites, showing significantly higher values in the late period 1985-1998 (table 3a). Significantly higher concentrations also of Ni and Pb in the late period were found at GR and VA sites.

Comparing the differences between sites in the two periods of analysis (table 3b), we found that PA site (close to the ENF site) showed always higher values than the other sites in both periods, except for Cu (higher values at VA site in 1985-1998) and Cd (higher values at VA site in both periods; missing values in PA).

Cr	1950-1970 m_1	1985-1998 m_2	_m	asymp.sig.
VE	1.3	1.3	0.0	n.s.
ENH	1.2	**1.9**	0.7	**
ENF	3.9	**5.3**	1.4	*
PA	9.8	**13.2**	3.4	n.s.
GR	6.0	**13.4**	7.4	*
VA	0.8	**3.3**	2.5	n.s.

Cu	1950-1970 m_1	1985-1998 m_2	_m	asymp.sig.
VE	**3.8**	3.2	-0.6	n.s.
ENH	0.7	**0.8**	0.1	***
ENF	0.7	**1.1**	0.4	***
PA	18.3	**20.0**	1.7	n.s.
GR	5.8	**12.0**	6.2	**
VA	15.9	**22.0**	6.1	n.s.

Pb	1950-1970 m_1	1985-1998 m_2	_m	asymp.sig.
VE	0.8	**0.9**	–	n.s.
ENH	–	–		–
ENF	–	–		–
PA	10.0	**10.5**	0.5	n.s.
GR	2.5	**4.0**	1.5	*
VA	13.4	**19.8**	6.4	*

Ni	1950-1970 m_1	1985-1998 m_2	_m	asymp.sig.
VE	0.1	**0.2**	0.1	n.s.
ENH	0.8	**1.0**	0.2	n.s.
ENF	2.0	**2.1**	0.1	n.s.
PA	30.2	**32.5**	2.3	n.s.
GR	6.2	**10.1**	3.9	*
VA	15.9	**30.8**	14.9	*

Cd	1950-1970 m_1	1985-1998 m_2	_m	asymp.sig.
VE	–	–		–
ENH	–	–		–
ENF	–	–		–
PA	**2.3**	1.1	-1.2	n.s.
GR	1.3	**1.6**	0.3	n.s.
VA	2.4	**3.1**	0.7	n.s.

TABLE 3A - Median values of heavy metals concentrations, and their difference, over the two periods of analysis. The differences in mean ranks between the two periods were assessed by means of the Kruskal-Wallis test; the statistical significance of these differences is reported (asymp.sig.= asymptote significance, chi-square test). Highest median values are in bold. ***= p<0.001; **=p<0.01; *=p<0.05.

Cr 1950-1970

		VE	ENH	ENF	PA	GR
VE	66.6	-				
ENH	57.8	*	-			
ENF	99.7	n.s.	n.s.	-		
PA	**121.6**	*	n.s.	n.s.	-	
GR	99.4	n.s.	n.s.	n.s.	n.s.	-
VA	63.1	n.s.	n.s.	n.s.	*	n.s.

Cr 1985-1998

		VE	ENC	ENH	ENF	PA	GR
VE	31.1	-					
ENC	69.6	n.s.	-				
ENH	33.2	n.s.	n.s.	-			
ENF	67.3	n.s.	n.s.	n.s.	-		
PA	**80.1**	*	n.s.	*	n.s.	-	
GR	74.9	*	n.s.	*	n.s.	n.s.	-
VA	52.6	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Ni 1950-1970

		VE	ENH	ENF	PA	GR
VE	9.0	-				
ENH	27.8	n.s.	-			
ENF	50.7	n.s.	n.s.	-		
PA	**150.4**	*	*	*	-	
GR	91.3	*	*	n.s.	*	-
VA	119.8	*	*	*	n.s.	n.s.

Ni 1985-1998

		VE	ENC	ENH	ENF	PA	GR
VE	11.0	-					
ENC	43.5	n.s.	-				
ENH	15.2	n.s.	n.s.	-			
ENF	35.2	n.s.	n.s.	n.s.	-		
PA	**104.1**	*	*	*	*	-	
GR	70.2	*	n.s.	*	n.s.	*	-
VA	100.3	*	*	*	*	n.s.	n.s.

Cu 1950-1970

		VE	ENH	ENF	PA	GR
VE	54.0	-				
ENH	17.0	n.s.	-			
ENF	20.6	n.s.	n.s.	-		
PA	**140.4**	*	*	*	-	
GR	85.7	n.s.	*	*	*	-
VA	133.1	*	*	*	n.s.	*

Cu 1985-1998

		VE	ENC	ENH	ENF	PA	GR
VE	45.4	-					
ENC	35.1	n.s.	-				
ENH	12.9	n.s.	n.s.	-			
ENF	23.6	n.s.	n.s.	n.s.	-		
PA	101.8	*	*	*	*	-	
GR	79.6	n.s.	*	*	*	n.s.	-
VA	**108.4**	*	*	*	*	n.s.	n.s.

Cd 1950-1970

		VE	ENH	ENF	PA	GR
VE		-				
ENH		-	-			
ENF		-	-	-		
PA	70.4	-	-	-	-	
GR	51.9	-	-	-	*	-
VA	**73.5**	-	-	-	n.s.	n.s.

Cd 1985-1998

		VE	ENC	ENH	ENF	PA	GR
VE	-						
ENC	-	-					
ENH	-	-	-				
ENF	-	-	-	-			
PA	35.5	-	-	-	-	-	
GR	37.6	-	-	-	-	n.s.	-
VA	**49.9**	-	-	-	-	n.s.	n.s.

Pb 1950-1970

		VE	ENH	ENF	PA	GR
VE	24.3	-				
ENH		-	-			
ENF		-	-	-		
PA	**105.1**	*	-	-	-	
GR	59.3	n.s.	-	-	*	-
VA	118.4	*	-	-	n.s.	*

Pb 1985-1998

		VE	ENC	ENH	ENF	PA	GR
VE	7.6	-					
ENC	-	-					
ENH	-	-	-				
ENF	-	-	-	-			
PA	56.7	*	-	-	-	-	
GR	37.6	*	-	-	-	*	-
VA	**76.8**	*	-	-	-	n.s.	*

TABLE 3B - Mean ranks of heavy metals concentrations between all sites in the two periods of analysis. The differences in mean ranks between the two periods were assessed by means of the Kruskal-Wallis test; the statistical significance of these differences is reported (LSD test *=p<0.05). Highest mean rank values within each period are in bold.

DISCUSSION

In dendrochemistry, when comparing different studies it is always difficult to find comparable cases because of the heterogeneity of the findings. Most of the differences in the findings is due to the environmental complexity, to the species specific responses to pollutants, to the storage, redistribution and translocation of the different elements in the stems (related to the kind of element, to the tree physiological conditions, to the tissues chronological and physiological ages; Bruce & Guyettes, 1993; Berry, 1985), and to different sampling heights and analytical techniques (Myre & Camiré, 1994). However, many studies have found recurrent gradients in element concentrations passing from the heartwood to the sapwood (the physiologically active portion of the stem) (for review: Meerts, 2002). In particular, Myre & Camiré (1994) distinguish three general cases: i) increasing gradients with maximum values towards the external parts of the xylem (P and K); ii) decreasing gradients with maximum values towards the in inner portion of the xylem (Ca); iii) constant concentrations in all parts of the xylem (Zn, Al and Cu).

In accordance with what reported in literature for conifers (Myre & Camiré, 1994; Meerts 2002), we found marked increasing trends for the mobile nutrients P and K in the sapwood with highest values close to the cambium. Moreover, we found that the two elements resulted highly correlated at all sites ($r>0.9$). For immobile nutrients and nutrients of intermediate mobility (Ca, Mg and Mn) we still have generally higher values in the sapwood: this fact (especially for Ca) is not in accordance to what generally found in literature for conifers and for European larch (Okada & *alii*, 1993; Myre & Camiré, 1994). However, the high concentrations of Ca in the youngest wood of the trees have often be found in stressed environments (Peterson & Anderson 1990). The correlation between Ca, Mg and Mn was high over the two period analyzed (especially at site ENF), suggesting a common physiological use by the trees or coupled translocations related to the ion charges. Calcium is often regarded as an immobile element because it is fixed in xylem cell walls and incorporated into woody tissue, but a chemical analysis of the Atlantic white cedar showed that Ca concentration in the sapwood were higher than those in the immediately adjacent heartwood and this concentration pattern was explained as a process by which Ca is translocated to the youngest functional sapwood as heartwood is formed (Andrews & Siccama, 1995). Calcium in stems is related to the sapwood cross-sectional area and is regulated by transpiration and annual growth rates: a large sapwood area (and therefore a higher number of active vessels and a larger surface area of cell walls in the sapwood) may induce higher concentrations of Ca especially in slow-growing trees (Guyette & Cutter, 1995; McLaughlin & Wimmer, 1999). Calcium is a critical element in plants since it is involved in the cellular metabolism of the nucleus and mitochondria (Bidwell, 1974), it is an enzyme activator, it is involved in the nitrogen metabolism (Kramer and Kozlowski, 1979) and it is also important in the synthesis of pectin in the middle lamella of cell walls.

The change from heartwood to sapwood is generally abrupt for nutrient concentrations in the stems also in broadleaf species (Clément & Janin, 1976). This fast change in concentrations passing from heartwood to sapwood is visible at site ENC for Na, K, Mg and Ca (year 1998; fig. 3a). In our opinion this increase in element concentrations in the tree ring 1998 at site ENC is related to the passage from heartwood to sapwood and not related to the lack of air pollution started one year later, in 1999 (this, in fact, would also imply an improbable retroactive effect of pollution changes occurred in the environment).

The heavy metals uptake by trees follows three main pathways (Forget & Zayed, 1995; Jonsson & *alii*, 1997): i) uptake from the soil via the root system (the most important; Burton, 1985); ii) absorption by the leaves (with metals usually confined in the phloem; Bukovak & Wittwer, 1957); iii) deposition on the bark and subsequent absorption through it.

For heavy metals, we did not find particular trends over the two periods of analysis and among the years of the MBT closure. However, Fe, Cr, and Ni were highly correlated in the two periods of analysis, suggesting a coupled translocation of heavy metals in the stems at each site. Mobility of elements in the stem is a critical problem in dendrochemical analysis. Mobility of elements in the stems takes place for diffusion or for mass flow of the solution in the xylem. Another source of heavy metals in the xylem can be also the bark which may be always exposed to air pollutants and may allow the translocation of heavy metals from the outside environment (Lepp & Dollard, 1974; Watmough & Hutchinson, 2003), even though bark characteristics by species may impede any moisture and pollutant movement towards the xylem. In general, the concentrations of elements (Myre & Camirè, 1994) as well as of heavy metals (Hg; Sanjo & *alii*, 2004) in the bark may be higher than in the tree rings making it a valuable source of spatial information on air pollution dispersal. In fact, the bark may be constantly exposed to the air pollution sources and both elements and heavy metals may persist over time inside it, therefore allowing its possible use as a biomonitor (Santamarìa & Martìn, 1996; Pacheco & *alii*, 2001; Panichev & McCrindle, 2004).

The presence of an element in the solution depends on many factors (Cutter & Guyette, 1993): ion solubility, sap acidity and heartwood-sapwood equilibrium concentrations are among the most important. Moreover, Nabais & *alii* (1999) found seasonal changes in Pb concentrations in the tree rings with higher concentrations during the periods of slow growth. In another site, sampling the same tree after some years, they also found that Cd concentrations were related to the heartwood-sapwood boundary. Lead concentrations in the tree rings have been widely studied because of its relation to health and because of the low solubility of Pb. However, trees may not provide reliable information at the yearly scale on past variations in contaminated soils (Hagemayer & Weinad, 1996; Hagemayer, 2000) and a key role for absorption of elements is played also by soil acidity. For example, Pb is absorbed by trees mainly on acid soils and not on basic soils (Schweingruber, 1996).

No temporal information at the yearly scale on heavy metals concentrations in the tree rings is found also for Cd and Zn, being more related to physiological conditions of the trees and of the sapwood than to changes in soil pollution (Hagemeyer & Lohrie, 1995; Brackhage & *alii*, 1996). Despite these findings, some recent studies have shown that with dendrochemical analysis it is possible to date pollution events and therefore perform chronological reconstructions at different time scales (Burnett & *alii*, 2007; St-Laurent & *alii*, 2009) including a time gap between the emissions and the incorporation in the tree ring (15 years for Pb in black spruce; Aznar & *alii*, 2008).

Differences in element concentration between EN sites let us establish the spatial distribution of air pollutant in the Mont Blanc area. The ENH site resulted the less exposed to air pollution, whereas site ENF (also if being further away from the highway) showed the highest values for most of the elements. Site ENC, however, showed higher values of Na (probably linked to the dispersal of salts on the road), Cr and Ni (concentrations were statistically similar to those at site ENF). Similarly to Guyette & *alii*, (1991) that found no Pb in trees growing downwind from Pb smelters, we found only few years with measurable Pb in the tree rings, at all sites (and only one year at ENH site).

Considering heavy metals concentrations at all sites we found always highest values at the PA site (that is located between the ENC and ENF sites), except for Cu and Cd that were higher in the trees growing at site VA, in a natural environment close to a glacier river, in a remote position with respect to air pollution sources. Significantly higher concentrations of Ni and Pb were detected for both the remote sites VA (close to a glacier river) and GR (close to a glacier), in the recent period of analysis (1985-1998; see also Orlandi & *alii*, 2002), underlining how changes in heavy metal concentrations may occur also at sites far from a direct source of atmospheric pollution. Atmospheric dispersal of pollutant as well as the accumulation of heavy metals into the glaciers and the subsequent release in the Alpine environment may explain these changes over time recorded in the trees for Ni and Pb, and also the meanly higher concentrations for Cu and Cr in the recent period. However, trees' physiological processes and the sapwood-heartwood transition may affect the element distributions within the stems (Hagemayer, 2000).

Pollutant dispersal in mountain environments is highly influenced by topography that can drive both aerial dispersal and deposition patterns (e.g. Nanni & *alii*, 2004), and by hydrography that influences the pollution dispersal downvalley and the deposition of pollutants along floodplains and river banks. A key role in evaluating the impact of anthropogenic depositions on high-altitude alpine forest is played also by soils whose chemistry may be highly altered according to the pollutant loads (Graber & *alii*, 1996). Coupling the analysis of soil types, lithology and soil chemical properties at each site investigated by means of dendrochemical approaches would surely help in better defining the mechanism regulating heavy metals bioavailability and plants uptake (e.g. Jung, 2008; Minkina & *alii*, 2001), and the soil pollutants adsorption or release under different climatic conditions (Dube & *alii*, 2000), thus helping in differentiating natural and anthropogenic signals of heavy metal concentration changes in the environment.

CONCLUSION

The dendrochemical analysis performed in this study using European larch tree rings in Central and Western European Alps revealed the following findings. i) The dendrochemical analysis at the yearly scale at the MBT area revealed either no particular interval-trend changes consistent to yearly air pollution changes occurred in the area and the difficulties to date at the yearly scale air pollution events, likely because of a soil buffer effect and because of the possible element translocations within the tree stems. ii) By analysing two separate time periods, for the recent period of analysis in the MBT area (samples of ENH and ENF sites constituted mainly of sapwood tree rings), we found significantly higher mean concentrations of some pollutants in the tree rings, namely Cr, Fe (highly correlated also with Ni), Mn, Cu, Zn and Ba. Ni and Pb had higher concentrations in the recent period also in the remote sites VA and GR. iii) At the regional scale the concentrations of heavy metals revealed significant differences between sites, underlining the possible use of European larch trees as biomonitors in the Alpine environment, also in remote sites. iv) Tree rings may be used as useful source of information on ongoing long-term trends and for obtaining precise spatial information for investigating air pollutant dispersal in the Alpine environment. v) A consequence of our findings is that tree rings may especially help in reconstructing the spatial dispersal of air pollutants at the site and the regional scales, potentially helping also in finding sites under low or no influence of air pollutants. Other possible complementary applications for the spatial definition of air pollution dispersal and its impact on the Alpine environment could also involve the analysis of bark chemistry and the analysis of soil type, lithology, and soil chemical properties at the study sites.

REFERENCES

ANDREWS J.A. & SICCAMA T.G. (1995) - *Retraslocation of calcium and magnesium at the heartwood-sapwood boundary of atlantic white cedar*. Ecology, 76, 659-663.

APOLLONIO P. (2000) - *Registrazione di un evento antropico nelle conifere alpine: l'esempio del Tunnel del Monte Bianco*. Master thesis A.A. 1999-2000, Università degli Studi di Milano-Bicocca.

AZNAR J.C., RICHER-LAFLECHE M., BEGIN C. & RODRIGUE R. (2008) - *Spatiotemporal reconstruction of lead contamination using tree rings and organic soil layer*s. Science of the Total Environment, 407, 233-241.

BAES III C.F. & MCLAUGHLIN S.B. (1984) - *Trace elements in tree rings: evidence of recent and historical air pollution.* Science, 4648, 494-497.

BEAUREGARD S.L., COTE B. & HOULE D. (2010) - *Application of compositional nutrient diagnosis (CND) to the dendrochemistry of three hardwoods in three geological regions of southern Quebec*. Dendrochronologia, 28, 23-36.

BERRY W.L. (1985) - *Plants factors influencing the use of plant analysis as a tool for biogeochemical prospecting*. In: Carlisle D., Berry W.L., Kaplan I.R. & Watterson J.R. (Eds), «Mineral exploration: biological systems and organic matter». Prentice-Hall, Englewood Cliffs, 14-32.

BONDIETTI E.A., MOMOSHIMA N., SHORTLE W.C. & SMITH K.T. (1990) - *A historical perspective on divalent cation trends in red spruce stemwood and the hypothetical relationship to acidic deposition*. Canadian Journal of Forest Research, 20, 1850-1858.

BIDWELL R.G.S. (1974) - *Plant physiology*. Macmilliam Publishing, New York.

BRACKHAGE C., HAGEMEYER J., BRECKLE S.W. & GRESZTA J. (1996) - *Radial distribution patterns of Cd and Zn in stems of Scots pine (Pinus sylvestris L.) trees analyzed 12 years after a contamination event*. Water, Air, & Soil Pollution, 90, 417-428.

BUKOVAK M.J. & WITTWER S.H. (1957) - *Absorption and mobility of foliar applied nutrients*. Plant Physiology, 32, 428-435.

BURNETT A., KURTZ A.C., BRABANDER D. & SHAILER M. (2007) - *Dendrochemical record of historical lead contamination sources, wells G&H superfund site, Woburn, Massachusetts.* Journal of Environmental Quality, 36, 1488-1494.

BURTON G.R., ROSMAN K.J.R., VAN DE VELDE K.P & BOUTRON C.F. (2006) - *A two century record of strontium isotopes from an ice core drilled at Mt Blanc, France*. Earth and Planetary Science Letters, 248, 217-226.

BURTON M.A.S. (1985) - *Tree rings*. In: «Historical Monitoring». Monitoring and Assessment Research Centre, report n. 31. University of London, 175-202.

CAFIERO L. (2000) - *Presenza di metalli pesanti e variazione strutturale della lignina nelle conifere delle Alpi: indagine dendrochimica nell'alta Valfurva*. Master thesis A.A. 1999-2000, Università degli Studi di Milano-Bicocca.

CLÉMENT A. & JANIN G. (1976) - *Étude comparée de la répartition des principaux cations et du phosphore dans une tige de peuplier «Fritzi-Pauley»*. Plant Soil, 45, 543-554.

CUTTER B.E. & GUYETTE R.P. (1993) - *Anatomical, Chemical, and Ecological Factors Affecting Tree Species Choice in Dendrochemistry Studies*. Journal of Environmental Quality, 22, 611-619.

COZZI M. (2000) - *Presenza di metalli pesanti e variazione strutturale della lignina nelle conifere delle Alpi: indagine dendrochimica nella Valle di Gressoney*. Master thesis A.A. 1999-2000, Università degli Studi di Milano-Bicocca.

DUBE A., ZBYTNIEWSKI R., KOWALKOWSKI T., CUKROWSKA E. & BUSZEWSKI B. (2000) - *Adsorption and migration of heavy metals in soil*. Polish Journal of Environmental Studies, 10, 1-10.

FORGET E. & ZAYED J. (1995) - *Tree-ring analysis for monitoring pollution by metals*. In: Lewis T.E. (Ed.), *Tree Rings as Indicators of Ecosystem Health*. CRC Press, Boca Raton, FL, 157-176.

GUYETTE R.P., CUTTER B.E. & HENDERSON G.S. (1991) - *Long-term correlations between mining activity and levels of lead and cadmium in tree-rings of Eastern red-cedar*. Journal of Environmental Quality, 20, 146-150.

GUYETTE R.P. & CUTTER B.E. (1995) - *Water-use efficiency as monitored by dendrochemistry*. In: Lewis T.E. (Ed.), «Tree rings as indicators of ecosystem health». CRC Press, Boca Raton, FL, 95-122.

GUIDETTI S. (1999) - *Variazione nel tempo delle concentrazioni di metalli pesanti e delle strutture del legno in alcune conifere delle Alpi Occidentali. Un esempio di indagine dendrochimica*. Master thesis A.A. 1998-1999, Università degli Studi di Milano-Bicocca.

GRABER W.K., SIEGWOLF R.T.W., NATER W. & LEONARDI S. (1996) - *Mapping the impact of anthropogenic depositions on high elevated alpine forests*. Environmental Software, 11, 59-64.

HAGEMEYER J. (2000). *Trace metals in tree rings: what do they tell us?* In: Markert B. & Friese K. (Eds). «Trace elements. Their distribution and effects in the environment». Elsevier Science, 375-385.

HAGEMEYER J. & WEINAND T. (1996) - *Radial distributions of Pb in stems of young Norway spruce trees grown in Pb-contaminated soil*. Tree Physiology, 16, 591-594.

HAGEMEYER J. & LOHRIE K. (1995) - *Distribution of Cd and Zn in Hagemeyer J. & Lohrie, Kannual xylem rings of young spruce trees [Picea abies (L.) Karst.] grown in contaminated soil*. Trees - Structure and Function, 9, 195-199.

HART J.H. (1968) - *Morphological and chemical differences between sapwood, discolored sapwood, and heartwood in black locust and osage orange*. Forest Science, 24, 334-338.

JONSSON A., EKLUND M. & HAKANSSON K. (1997) - *Heavy metals of the 20th century recorded in oak tree rings*. Journal of Environmental Quality, 26, 1638-1643.

JUNG M.C. (2008) - *Heavy metal concentrations in soils and factors affecting metal uptake by plants in the vicinity of a Korean Cu-W mine*. Sensors, 8, 2413-2423.

KERN Z., POPA I., VARGA Z. & SZÉLES E. (2009) - *Degraded temperature sensitivity of a stone pine chronology explained by dendrochemical evidences*. Dendrochronologia, 27, 121-128.

KRAMER P.J. & KOZLOWSKI T.J. (1979) - *Physiology of wood plants*. Academic Press, Orlando FL, 811 pp.

KRUSKAL W.H. & WALLIS W.A. (1952) - *Use of ranks in one criterion variance analysis*. Journal of the American Statistics Association, 47, 583-621.

LAGEARD J.G.A., HOWELL J.A., ROTHWELL J.J. & DREW I.B. (2008) - *The utility of Pinus sylvestris L. in dendrochemical investigations: pollution impact of lead mining and smelting in Darley Dale, Derbyshire, UK*. Environmental Pollution, 153, 284-294.

LAMBERT M.J., TURNER J. & KELLY J. (1983) - *Nutrient relationships of tree species in a New South Wales subtropical rain forest*. Australian Forest Research, 13, 91-102.

LEPP N. & DOLLARD G. (1974) - *Studies on lateral movement of ^{210}Pb in woody stems-patterns observed in dormant and non-dormant stems*. Oecologia, 16, 179-184.

LÖVESTAM G., JOHANSSON E.M. & PALLON J. (1990) - *Elemental micro patterns in tree rings - a feasibility study using scanning proton microprobe analysis*. Ambio, 19, 87-93.

MCLAUGHLIN S.B. & WIMMER R. (1999) - *Calcium physiology and terrestrial ecosystem processes*. New Phytologist, 142, 373-417.

MEERTS P. (2002) - *Mineral nutrient concentrations in sapwood and heartwood: a literature review*. Annals of Forest Science, 59, 713-722.

MINKINA T.M., SAMOKHIN A.P. & NAZARENKO O.G. (2001) - *Translocation of heavy metals in soil-plant system*. In: Horst W.J & *alii* (Eds.), «Plant nutrition - Food and sustainability of agro-ecosystems». Kluwer Academic Publishers, 360-361.

MYRE R. & CAMIRÉ C. (1994) - *Distribution de P, K, Ca, Mg, Mn et Zn dans la tige des mélèzes européen et laricin*. Annals of Forest Science, 51, 121-134.

NABAIS C., FREITAS H. & HAGEMEYER J. (1999) - *Dendroanalysis: a tool for biomonitoring environmental pollution?* The Science of the Total Environment, 232, 33-37.

NANNI A., BRUSASCA G., CALORI G., FINARDI S., TINARELLI G., ZUBLENA M., AGNESOD G. & PESSION G. (2004) - *Integrated assessment of traffic impact in an Alpine region.* Science of the Total Environment, 334-335, 465-471.

OKADA N., KATAYAMA Y., NOBUCHI T., ISHIMARU Y. & AOKI A. (1993) - *Trace elements in the stems of trees V. Comparisons of radial distributions among softwood stems*. Mokuzai Gakkaishi, 39, 1111-1118.

ORLANDI M., PELFINI M., PAVAN M., SANTILLI M. & COLOMBINI M.P. (2002) - *Heavy metals variations in some conifers in Valle d'Aosta (Western Italian Alps) from 1930 to 2000.* Microchemical Journal, 73, 237-244.

PEARSON C.L., DALE D.S., BREWER P.W., KUNIHOLM P.I., LIPTON J. & MANNING S.W. (2009) - *Dendrochemical analysis of a tree-ring growth anomaly associated with the Late Bronze Age eruption of Thera*. Journal of Archaeological Science, 36, 1206-1214.

PETERSON D.L. & ANDERSON D.R. (1990) - *Content of Chemical Elements in Tree Rings of Lodgepole Pine and Whitebark Pine from a Subalpine Sierra Nevada Forest*. Research Paper PSW-20. Berkeley, CA: Pacific Southwest Research Station, Forest Service, U.S. Department of Agriculture; 9 pp.

PACHECO A.M.G., FREITAS M.C., BARROS L.I.C. & FIGUEIRA R. (2001) - *Investigating tree bark as an air-pollution biomonitor by means of neutron activation analysis*. Journal of Radioanalytical and Nuclear Chemistry, 249, 327-331.

PANICHEV N. & MCCRINDLE R.I. (2004) - *The application of bio-indicators for the assessment of air pollution*. Journal of Environmental Monitoring, 6, 121-123.

ROSMAN K.J.R., LY C., VAN DE VELDE K. & BOUTRON C.F. (2000) - *A two century record of lead isotopes in high altitude Alpine snow and ice*. Earth Planetary Science Letters, 176, 413-424.

ST-LAURENT J., SAINT-LAURENT D., DUPLESSIS P., HAHNI M. & BEGIN C. (2009) - *Application of Dendrochronological and Dendrochemical Methods for Dating Contamination Events of the Saint-Francois and Massawippi Riverbanks (Quebec, Canada).* Soil & Sediment Contamination, 18, 642-668.

SCHWEINGRUBER F.H. (1996) - *Tree rings and environment: dendroecology*. Haupt, Berne, 609 pp.

SANJO H., KENICHI S., WANG Y. & MASUNAGA S. (2004) - *Evaluation of outer bark and inner bark of Ginkgo biloba Linn. as indicators for mercury pollution*. Materials and Geoenvironment, 51, 1358-1361.

SANTAMARÌA J.M. & MARTÌN A. (1996) - *Tree bark as a bioindicator of air pollution in Navarra, Spain*. Water, Air, and Soil Pollution, 98, 381-387.

TMB GEIE (2009) - Data available at *http://www.tunnelmb.net*.

UNLU K., PEARSON C., HAUCK D.K. & KUNIHOLM P.I. (2009) - *Dating volcanic eruptions with tree-ring chemistry.* IEEE Potentials, 28, 36-44.

VAN DE VELDE K., BOUTRON C., FERRARI C., BELLOMI T., BARBANTE C., RUDNEV S. & BOLSHOV M. (1998) - *Seasonal variations of heavy metals in the 1960s Alpine ice: sources versus meteorological factors*, Earth Planetary Science Letters, 164, 521-533.

VAN DE VELDE K., FERRARI C., BARBANTE C., MORET I., BELLOMI T., HONG S. & BOUTRON C. (1999) - *A 200 year record of atmospheric Cobalt, Chromium, Molybdenum, and Antimony in high altitude alpine firn and ice*. Environmental Science & Technology, 33(20), 3495-3501.

VAN DE VELDE K., BARBANTE C., COZZI G., MORET I., BELLOMI T., FERRARI C. & BOUTRON C. (2000) - *Changes in the occurrence of silver, gold, platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century*. Atmospheric Environment, 34, 3117-3127.

WATMOUGH S.A. & HUTCHINSON T.C. (2003) - *Uptake of* ^{207}*Pb and* ^{111}*Cd through bark of mature sugar maple, white ash and white pine: a field experiment*. Environmental Pollution, 121, 39-48.

WRIGHT T.W. & WILL G.M. (1958) - *The nutrient content of Scots and Corsian pines growing on sand dunes*. Forestry, 31, 13-25.

YANOSKY T.M. & VROBLESKY D.A. (1995) - *Element analysis of tree rings in ground-water contamination studies*. In: Lewis T.E. (Ed.), «Tree rings as indicators of ecosystem health». CRC Press, Boca Raton, FL, 177-205.

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