MEASURING ^{14}C CONCENTRATION IN WINE TO MONITOR GLOBAL DISTRIBUTION OF ^{14}C

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ABSTRACT. Using liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS), radiocarbon concentrations were measured for wine from 8 wineries located in 7 countries in the Northern and Southern hemispheres. The ^{14}C concentrations of ethanol and residual materials in the wine were correlated (correlation coefficient 0.82). The $\Delta^{14}C$ measurements of wine samples from the mid-latitudes in the Northern Hemisphere were approximately 11‰ lower than the extrapolations from Schauinsland data, suggesting a local fossil fuel effect. $\Delta^{14}C$ measurements from the wine samples from the Southern Hemisphere were higher than those from the Northern Hemisphere. The offsets of the 4 wine $\Delta^{14}C$ measurements were significant, with values between approximately 8‰ and 15‰. Because the harvest years of the mixed grapes were estimated to be 7–12 yr older than their vintage years, this leads to a caveat when determining the ^{14}C concentrations of the year using the wine vintage.

INTRODUCTION

Samples of distilled ethanol and residual material were extracted from wine and their radiocarbon content was measured. Previously, an important profile of cosmogenic ^{14}C was measured using old wines from the period 1909–1952, indicating an 11-yr solar cycle modulated on the Suess effect (Burchuladze et al. 1980). It also is evident from measurements of the atomic bomb pulse profile after 1960 that wines are good indicators of the ^{14}C content in the atmosphere, and they are available for the age determination of a certain vintage (Burchuladze et al. 1989; Schönhofer 1992). Moreover, recently a valuable study used wine samples to investigate the fossil fuel emissions in Europe (Palstra et al. 2008). These studies have shown that wines, like tree rings, can be useful for monitoring ^{14}C concentrations in the atmosphere.

The time profiles from compiled data show that the bomb peak of atmospheric ^{14}C concentrations in the Southern Hemisphere appears to have a delay of about 3 yr when compared to that of the Northern Hemisphere, but the ^{14}C concentrations are similar in both hemispheres after 1970 (Hua and Barbetti 2004). This indicates that the air is well-mixed by atmospheric circulation on a global scale by way of air exchange between the stratosphere and troposphere (Nydal 1968; Nydal and Lovseth 1983). Also, the ^{14}C concentrations are exponentially decreasing with a time constant of 16 yr, indicating the air-sea exchange of global carbon circulation (Rakowski et al. 2008).

It is important to monitor contemporary ^{14}C concentrations on a global scale because the global density of ^{14}C provides information about a region's CO_2 emissions from fossil fuels (Rakowski et al. 2008) and the latest patterns of air exchange between the convective mixed layer, less than 3 km above the ground, and the free troposphere above that layer. Monitoring global data is also useful for

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tuning up the carbon cycle box models (Beer et al. 2012). Wines are appropriate samples for this purpose because obtaining samples from wineries that distribute around the world is easy and relatively inexpensive (except for older vintages) via commercial networks. Also, as wineries are typically located in green, suburban areas, they are not affected by the air pollution that can be present in a larger city.

Wine is fermented, typically without heat, using grapes harvested during the same year (which is a rule of vintage). Because the ethanol in wine is directly fermented from the glucose of grapes, contamination during the fermentation process could be lower compared to alcoholic beverages that are brewed with an additional step of glycosylation to glucose from starch. This is an advantage of using wine samples for ^{14}C measurements. However, "vintage" is loosely defined. Some wine contains a blend of previous years' grapes or juice in addition to those from the recent harvest. Therefore, it is necessary to check how well the ^{14}C concentrations in wine represent the ^{14}C levels in the ambient air during the vintage year as well as the previous blending years.

WINE SAMPLES AND ^{14}C MEASUREMENTS

Nine wine samples were chosen from the Northern and Southern hemispheres. The 8 wineries are located in 7 countries as shown in Table 1. The information regarding the longitude and latitude of each winery is solely derived from the bottle's label. All of the samples are red wine. The 2 wine samples from Japan are produced by 2 wineries located in the same area (20 km apart). The 2 Chilean wine samples are produced by the same winery for the 2 kinds of grape cultivars. Data in the "Grape cultivar" column in the table is taken from the wine bottle's label description. Except for the wine of AUS-cs, each grape cultivar was stated to be 100%. Also, the vintage of each wine sample is described according the bottle's label. Although the harvest year of grapes might involve an uncertainty, the year of wine production should be the vintage.

Table 1 Locations, grape cultivars, and vintages of the wine samples.

ID	Country	Latitude	Longitude	Grape cultivar	Vintage
Northern Hemisphere					
CAN-ml	Canada	49°50′N	119°36′W	Merlot (100%)	2004
ESP-tp	Spain	39°20′N	3°10′W	Tempranillo	2010/2011
	Spain	39°20′N	3°10′W	Tempranillo	2010/2011
JPN-mb	Japan	38°10′N	140°17′E	Muscat berry A (100%)	2010
	Japan	38°10′N	140°17′E	Muscat berry A (100%)	2010
	Japan	38°10′N	140°17′E	Muscat berry A (100%)	2010
	Japan	38°10′N	140°17′E	Muscat berry A (100%)	2010
JPN-cs	Japan	38°3′N	140°10′E	Cabernet Sauvignon (100%)	2009
Southern Hemisphere					
PER-cs	Peru	13°5′S	76°22′W	Cabernet Sauvignon (100%)	2009
ZAF-cs	South Africa	33°38′S	18°51′E	Cabernet Sauvignon (100%)	2006
CHL-cs	Chile	34°10′S	70°45′W	Cabernet Sauvignon	2010
	Chile	34°10′S	70°45′W	Cabernet Sauvignon	2010
	Chile	34°10′S	70°45′W	Cabernet Sauvignon	2010
	Chile	34°10′S	70°45′W	Cabernet Sauvignon	2010
CHL-ml	Chile	34°10′S	70°45′W	Merlot	2011
AUS-cs	Australia	34°32′S	138°57′E	Cabernet Sauvignon? Syrah (main constituent)	2010[a]

[a]Probably 2010.

Two kinds of ^{14}C measuring samples were extracted from the wine samples. One is distilled ethanol from the wine and the other is residual matter. The ethanol distilled twice was more refined, removing its water component using a molecular sieve. The ^{14}C concentrations of the ethanol samples were directly measured without benzene production using an ultra-low background liquid scintillation counting system (LSC) Quantulus™ (Takahashi et al. 2011). The typical error of ^{14}C measurements was 5‰.

The residual matter after the first distillation, which is a kind of wine sludge, was dried out and the graphite sample was produced from its burning. It is important to check whether or not both the ethanol and residual samples indicate the same ^{14}C concentrations, because the fermentation process might provide a kind of fractionation effect. The ^{14}C concentrations of residual samples were measured with an error less than 3‰ using the new Compact AMS at Yamagata University (Tokanai et al. 2011). In addition to the $\delta^{13}C$ measurements by AMS for pMC correction, the other $\delta^{13}C$ values were independently measured using the mass analyzer for stable isotopes IsoPrime™ to examine the $\delta^{13}C$ characteristics of the residual matter of wine samples.

To investigate the fluctuations in the distillation process, 4 samples were produced from the wines from Japan and Chile, respectively, replicating the process. Regarding replication, the relative standard deviations were 0.13% and 0.15% for ethanol samples of JPN-mb and CHL-cs, respectively. For residual matter samples, the values were 0.25% and 0.07%, respectively. These results indicate that the fluctuation of the distillation process is not significant over the ^{14}C measuring errors.

RESULTS AND DISCUSSION

Figure 1 shows the correlation between the measured ^{14}C concentrations of the ethanol and the residual matter samples using LSC and AMS. The straight line indicates the linear least-squares fitted model, which has a correlation coefficient of 0.82.

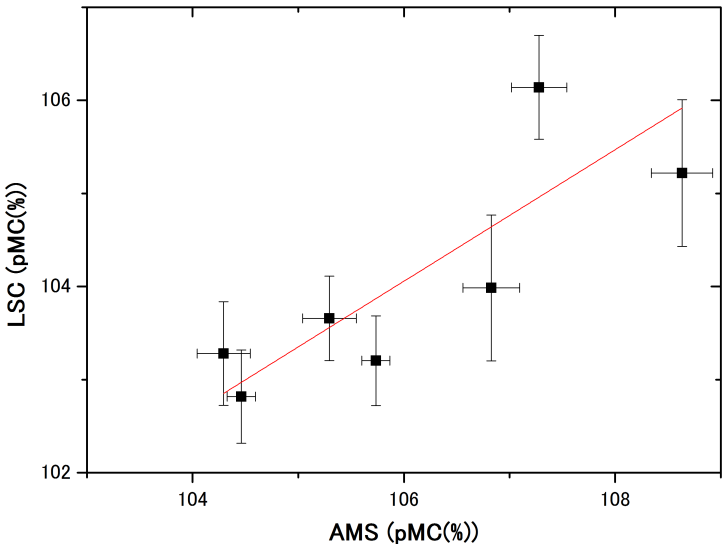

Figure 1 Correlation of ^{14}C concentrations between the distilled ethanol and the residual matter measured using LSC and AMS.

In Figure 2, ^{14}C concentrations are shown for the complete set of wine samples, from the higher latitudes in the Northern Hemisphere to the one in the Southern Hemisphere. The squares and circles indicate the wine samples of Merlot and Cabernet Sauvignon, respectively. The triangle and diamond indicate the wine samples of Tempranillo and Muscat berry A, respectively. The open symbols and solid symbols denote the wine samples produced in the Northern and Southern Hemispheres, respectively.

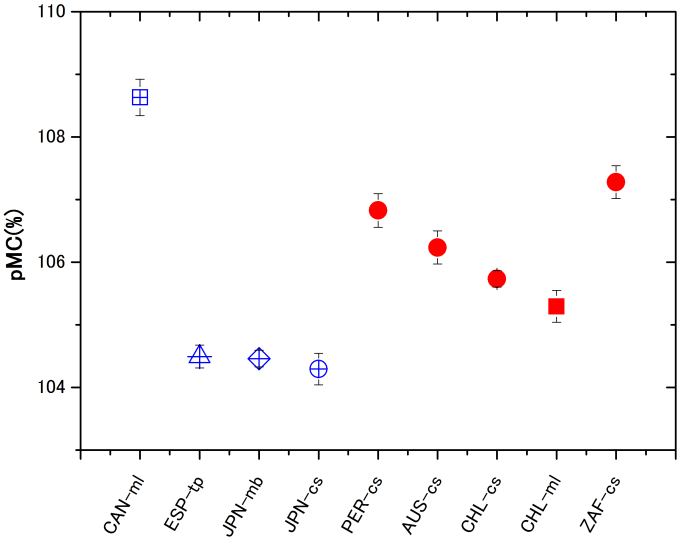

Figure 2 The ^{14}C concentrations for the wine samples from the higher latitude in the Northern Hemisphere to the one in the Southern Hemisphere. See the text above for an explanation of the symbols used.

In Figure 2, the ^{14}C concentrations of JPN-mb and JPN-cs are almost the same, although there were different grape cultivars in the different wineries. Also, the ^{14}C concentrations of CHL-cs and CHL-ml had similar values, although there were different grape cultivars in the same winery. Moreover, the CHL-cs concentration is evidently higher than the JPN-cs, although they used the same grape cultivar. Furthermore, as shown in Figure 3, the $\delta^{13}C$ values were normal for the wine samples between –27‰ and –28‰ from a C_3 plant except for JPN-mb, which may indicate some addition. Therefore, regardless of the $\delta^{13}C$ level, the Southern Hemisphere may have a higher ^{14}C contribution than the Northern Hemisphere for the same year.

Figure 4 shows the $\Delta^{14}C$ of the wine samples as a function of vintage. In the figure, the dashed and dotted lines are an extrapolated estimation from the $^{14}CO_2$ data at Schauinsland for the 1976–2003 period (Levin and Kromer 2004), and a linear least-squares fitted line for $\Delta^{14}C$ values of the wine samples in the Southern Hemisphere, respectively. Compared to the extrapolated values, the $\Delta^{14}C$ of wine samples in Japan indicated approximately 11‰ lower values, similar to those from Spain, located in the mid-latitudes of the Northern Hemisphere. Assuming the dilution of ^{14}C concentrations due to local fossil fuel combustion, the fraction of CO_2 from fossil fuels is $1.05 \pm 0.1\%$, which is comparable to the fraction obtained from plant leaves from the same area in Japan (Sakurai et al., these proceedings). At the surface level in the mid-latitudes of the Northern Hemisphere, the ^{14}C concentrations are presumably influenced by the combustion of fossil fuels.

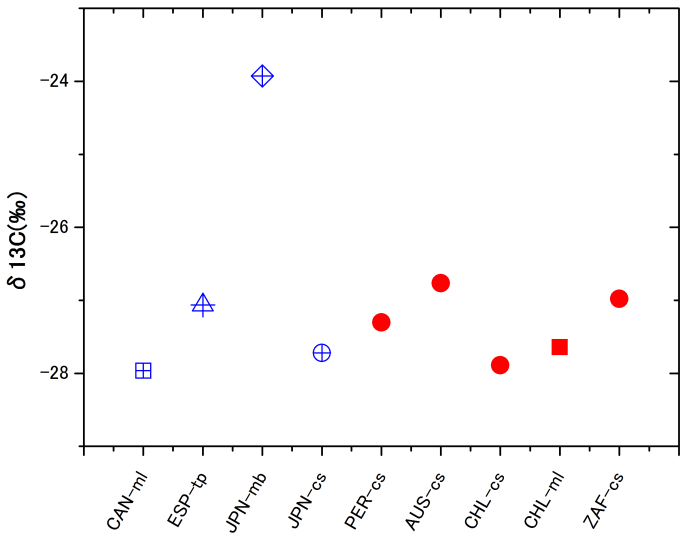

Figure 3 $\delta^{13}C$ values for the wine samples from higher latitudes in the Northern Hemisphere and the sample from the Southern Hemisphere. The symbols are the same as in Figure 2.

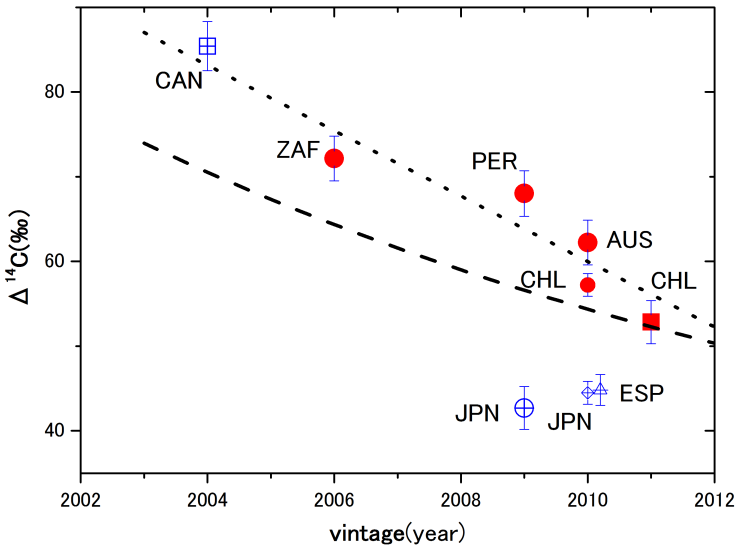

Figure 4 $\Delta^{14}C$ values of the wine samples as a function of vintage year. See the text for an explanation of the symbols.

On the contrary, most of the $\Delta^{14}C$ values from wine samples in the Southern Hemisphere are higher than the extrapolated estimations, except the $\Delta^{14}C$ values of Chilean wine samples from 2010 and 2011. As shown in Table 2, the offsets from the extrapolated $\Delta^{14}C$ values are from 7.9‰ to 14.9‰ for the wine from 4 locations, compared with lower offsets for tropical plant material (Ehleringer et al. 2011). The vintage year is normally based on the harvest year of 75% of the fermented grapes, and hence there is a possibility that grapes older than the vintage year were mixed in during the fer-

mentation process, or older wines were blended. Assuming that 25% of the mixed grapes are older, and the $\Delta^{14}C$ of the vintages are the extrapolated values, the harvest years of the mixed grapes are estimated to be 7–12 yr older than the vintage years. It would not be reasonable to use such old grapes, because it would affect the profit of the wine producer. At present, it is difficult to clarify the $\Delta^{14}C$ values of the wine samples under the $^{14}CO_2$ level at Schauinsland.

Table 2 $\Delta^{14}C$ offsets of the wine samples from the extrapolations of Schauinsland data.

Year	Extrapolated $\Delta^{14}C$ (‰) from Schauinsland data	Wine ID	$\Delta^{14}C$ (‰)	Error (‰)	Offset from extrapolations (‰)
2003	74.0	—	—	—	—
2004	70.5	CAN-ml	85.4	2.9	14.9
2005	67.3	—	—	—	—
2006	64.3	ZAF-cs	72.2	2.6	7.9
2007	61.6	—	—	—	—
2008	59.0	—	—	—	—
2009	56.6	JPN-cs	42.7	2.5	–13.9
?	56.6	PER-cs	68.0	2.7	11.4
2010	54.4	ESP-tp	44.5	1.3	–9.9
?	54.4	JPN-mb	44.8	1.8	–9.6
?	54.4	CHL-cs	57.2	1.3	2.8
?	54.4	AUS-cs	62.2	2.7	7.8
2011	52.3	CHL-ml	52.8	2.5	0.5

CONCLUSION

Using LSC and AMS methods, ^{14}C concentrations were measured for ethanol and residual materials in wine from 8 wineries operating in 7 countries in the Northern and Southern hemispheres. The ^{14}C concentrations from both materials correlated well. From the investigation of ^{14}C concentrations and $\delta^{13}C$ values for the 9 wine samples, we confirmed that the ^{14}C concentrations from wine samples of the same vintage year depend on their growing location, not the grape cultivars or wineries, and hence not on the traditional fermentation process. Therefore, it is confirmed that wine samples can be used to investigate atmospheric ^{14}C concentrations on a global scale, although some wine mixtures cause a miscalculation of this interpretation by as much as 25%.

The $\Delta^{14}C$ of wine samples in Japan indicate approximately 11‰ lower values, as do those from Spain, located at the mid-latitudes of the Northern Hemisphere. At the surface level in the mid-latitude of the Northern Hemisphere, the ^{14}C concentrations are presumably influenced by fossil fuel combustion.

Except for Chilean wine from 2010 and 2011, which are comparable to the extrapolated values from Schauinsland data, the offsets from the extrapolations are significant, from 8‰ to 15‰. Assuming that 25% of the mixed grapes were older than the vintage year, the harvest years of the mixed grapes were estimated to be 7–12 yr older than the vintages. Therefore, it is necessary to be cautious when determining the ^{14}C concentrations using wine vintage.

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