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Tracing Material Cycle Using Stable Isotopes: Carbon Monoxide from Automobile

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ABSTRACT

We estimate up-to-date values of the average isotopic compositions of CO emitted from automobiles. In the estimation, we determined the isotopic compositions of CO in tail pipe exhaust for four gasoline automobiles and two diesel automobiles under varying conditions of both idling and running. While the dependence on the automobile manufacturer is little, each automobile equipped with functional catalytic converter exhibits a large temporal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variation. They tend to show ^{13}C - and ^{18}O -enrichment in accordance with the reduction of CO in exhaust, suggesting that the functional catalytic converter in engines enhances the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of CO from tail pipes through a kinetic isotope effect during CO destruction. Assuming that automobiles run a modeled driving cycle, we estimated the average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO to be $-23.8 \pm 0.8\text{‰}_{\text{PDB}}$ and $+25.3 \pm 1.0\text{‰}_{\text{SMOW}}$, respectively, for recent gasoline automobiles, and $-19.5 \pm 0.7\text{‰}_{\text{PDB}}$ and $+15.1 \pm 1.0\text{‰}_{\text{SMOW}}$, respectively, for recent diesel automobiles. While the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of recent gasoline automobiles coincide well with the isotopic compositions of source CO in present trunk road atmosphere estimated in this study, those are $+4$ to $+6\text{‰}$ ($\delta^{13}\text{C}$) and $+1$ to $+3\text{‰}$ ($\delta^{18}\text{O}$) higher than those reported previously and also those emitted from old, non-catalyst automobiles determined in this study. Recent improvements in functional catalytic converters have enhanced and will enhance the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of CO from automobiles.

Keywords: Gasoline automobile, Carbon monoxide, Exhaust, Isotope, Functional catalytic converter

INTRODUCTION

Stable Isotopes

All materials consist of elements. Representative elements of them on the earth surface are carbon, oxygen, hydrogen, and nitrogen. Our interests on natural histories in general are summarized as studying cycling and recycling processes of these elements in our present and/or paleo environments. These studies, however, are always difficult so that many scientific tracers have been developed by

scientists. In this paper, we introduce natural stable isotopic compositions as useful tracers to study material cycles on the earth.

Earth atmosphere consists of several components such as water vapor, carbon dioxide, methane, nitrous oxide, and carbon monoxide. Some of the atmospheric components in present atmosphere could be derived from anthropogenic sources, such as car exhaust or power plants. On the other hand, some of them could be derived from natural sources such as animals, plants, or soil. To distinguish the origin is

the important theme for us. One of the most useful tool to distinguish the origin is the natural stable isotopic compositions.

The above mentioned components have chemical formulae of H_2O , CO_2 , CH_4 , N_2O and CO , respectively, irrespective to their origin. Despite of the same chemical formula, each component may exhibit slightly different average weight per molecule according to its origin. The average weight depends on from what and how the components were produced. Rain in Sapporo, for example, is 0.0001% heavier than that in Antarctica. Carbon dioxide emitted from a person as breath, for example, is about 0.0006% lighter than that already existing in atmosphere.

These differences are due to the variations in ratios of isotopes that constitute each element. In case of carbon monoxide, for example, the share of $^{12}\text{C}^{16}\text{O}$ is 99% but heavier molecules such as $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ are also included. If we can determine the precise isotopic ratio in a component, we can use the ratio as tracers for studying its origin. The use of the natural isotopes as tracers began in 1950s but recent progress in analytical chemistry enlarged the fields of their application. In this paper, we introduce one of its applications to the studies: carbon monoxide (CO) from automobile exhaust [1].

Carbon Monoxide and Automobile Exhaust

Carbon monoxide (CO) is the major reaction partner in tropospheric hydroxyl radical reactions and hence strongly affects the oxidizing capacity of the atmosphere as well as the concentrations of other trace gases. Furthermore, atmospheric CO is a good indicator of the effects of human activity on atmosphere since fossil fuel combustion is one of its representative sources.

Stable isotopic compositions of CO have provided important information on the sources and fates of atmospheric CO [e.g. 2–3]. By way of the isotopic compositions, atmospheric CO can be traced to its source. In order to utilize isotopic information to assign sources, however, we must have accurate average isotopic compositions of the CO emitted from each representative CO source.

The gasoline-fuelled automobile is one of the most representative sources for CO in the atmosphere, especially in the urban area. Stevens et al. [3] reported stable isotopic compositions of atmospheric CO in several large cities to estimate the average isotopic compositions of CO from automobile exhaust, assuming that the major CO source in the urban atmosphere is the gasoline automobile. However, more than thirty years have passed since their study

and the average CO concentration in an automobile exhaust has been reduced to <10% of the earlier value. Hence it is essential that we evaluate the average isotopic composition of CO from the present-day automobile fleet.

In recent years, much data has been reported on isotopic compositions of CO in the exhaust of gasoline automobiles by measuring samples taken directly from their tail pipes [4–6]. The samples, however, were limited to those emitted from idling automobiles, while, in fact, most of the CO stems from running automobiles. In addition, the number and the kinds of data in each study were limited. The number of data was less than five in each study, and the data were limited to $\delta^{18}\text{O}$ in the work of Brenninkmeijer and Röckmann [4] and Huff and Thiemens [5]. Furthermore, both results and interpretations are somewhat contradictory. While both Brenninkmeijer and Rockmann [4] and Huff and Thiemens [5] reported large $\delta^{18}\text{O}$ variations, Kato et al. [6] reported almost homogeneous $\delta^{18}\text{O}$ values in all their studied gasoline automobiles. While Huff and Thiemens [5] attribute the large $\delta^{18}\text{O}$ variation to the role of a catalytic converter in recent but not in older engines, Brenninkmeijer and Röckmann [4] found large $\delta^{18}\text{O}$ variations in a single, non-catalyst automobile.

To estimate the current average isotopic composition of CO from gasoline automobiles, Tsunogai et al. [1] determined the detailed temporal variation of concentrations of $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ of CO emitted from the tail pipes of several kinds of automobiles under varying idling/running conditions, such as cold/hot idling, driving speed and loading. The values will be useful for promoting future studies of atmospheric CO using stable isotopes as tracers. Recent developments in continuous-flow isotope ratio mass spectrometry (CF-IRMS) for CO allow such detailed studies by drastically reducing the sample size and time needed for analyses [7–9].

SAMPLING

We selected three recent gasoline automobiles for this study: 1999 Mazda Familia (No. 1), 1991 Nissan Primera (No. 2), and 2001 Honda Acty (No. 3). Some recently added features such as lean-burn, or direct fuel injections are not included in this work. All these vehicles were equipped with functional three-way catalytic converter to purify the exhaust. General Rh-loaded cerium oxide was employed as the catalyst. Besides the above models, we also measured an old, non-catalyst gasoline automobile

(1966 Volkswagen Type 1: No. 4) and two more recent diesel automobiles (1998 Nissan AD: No. 5, and 2000 Nissan Mistral: No. 6) for comparison. Detailed descriptions of the automobiles are presented in Table 1.

Automobile exhaust was sampled by using glass bottle (volume: 200 ml) fitted with in- and outlet stopcocks. The inlet is connected to tail pipes using Tygon tubing. After purging of exhaust gases through the bottle, we closed the two stopcocks. Ex-

Table 1 List and detailed descriptions of studied automobiles [1]

No.	type	manufacture	model	year	cylinder displacement	cleaning system
1	gasoline	Mazda	Familia	1999	1500 cc	TW ^{*1} (Pt/Rh)
2	gasoline	Nissan	Primera	1991	2000 cc	TW ^{*1} (Pt/Rh)
3	gasoline	Honda	Acty	2001	660 cc	TW ^{*1} (Pd/Rh)
4	gasoline	Volkswagen	Type1	1966	1300 cc	-----
5	diesel	Nissan	AD	1998	1700 cc	EGR ^{*2}
6	diesel	Nissan	Mistral	2000	2800 cc	EGR ^{*2}

^{*1} TW: Three way functional catalytic converter

^{*2} EGR: Exhaust Gas Re-circulation system

Table 2 Concentration and isotopic compositions of CO in exhaust emitted from gasoline automobiles [1].

Sample ID	Car No.	Status	Load	Speed (km/h)	rpm	CO (ppm)	$\delta^{13}\text{C}$ (‰PDB)	$\delta^{18}\text{O}$ (‰SMOW)
FML-22b	1	Hot idling	-	0	1000	870	-24.1	+22.4
FML-19	1	Running	middle	10	1300	3.2×10^3	-26.2	+22.5
FML-3b	1	Running	middle	30	1500	2.6×10^3	-24.1	+25.6
FML-27b	1	Running	middle	50	1900	1.9×10^3	-20.4	+28.2
FML-13	1	Running	middle	10→30	1800	3.9×10^3	-24.2	+25.3
FML-50b	1	Hot idling	-	0	2000	32	-14.8	+32.0
FML-30b	1	Hot idling	-	0	4000	85	-10.2	+36.1
FML-N14	1	Hot idling	-	0	6000	244	-21.4	+25.6
PRI-11	2	Cold idling	-	0	800	2.9×10^4	-27.3	+19.6
PRI-12	2	Cold idling	-	0	800	2.7×10^4	-28.2	+23.7
PRI-6	2	Running	middle	10→40	1800	1.1×10^3	-21.4	+27.6
PRI-40	2	Running	middle	40→70	2600	3.2×10^3	-21.3	+28.2
PRI-100	2	Running	middle	70	2500	2.3×10^3	-23.8	+26.9
PRI-2	2	Running	middle	70→40	2600	5.9×10^3	-25.8	+24.1
PRI-1	2	Running	middle	40→10	1800	2.3×10^3	-22.3	+25.8
PRI-21	2	Running	high		1500	3.9×10^3	-25.3	+25.4
PRI-16	2	Running	low		1500	4.2×10^3	-25.5	+24.5
ACT-J2	3	Hot idling		0		1.9	-5.4	+27.3
ACT-J3	3	Hot idling		0		1.9	-5.3	+27.9
ACT-J5	3	Running	low	46	3300	53	-5.1	+28.2
ACT-J7	3	Running	middle	62	4600	92	-9.5	+28.7
ACT-J9	3	Running	high	46	3300	141	-18.6	+22.9
VWG-F1	4	Cold idling	-	0	1000	-	-27.2	+15.4
VWG-F2	4	Hot idling	-	0	3000	-	-25.9	+22.3
VWG-F3	4	Hot idling	-	0	1000	-	-26.7	+16.5
VWG-O1	4	Hot idling	-	0	1000	1.2×10^4	-29.2	+20.1
VWG-O2	4	Hot idling	-	0	1000	2.8×10^4	-27.4	+11.6
VWG-O3	4	Hot idling	-	0	1000	3.0×10^4	-26.8	+15.1
VW G-T1	4	Hot idling	-	0	2000	1.7×10^4	-28.1	+21.0
VW G-T2	4	Hot idling	-	0	2000	1.5×10^4	-28.6	+20.7
VW G-T3	4	Hot idling	-	0	2000	1.4×10^4	-29.3	+20.0
VW G-H1	4	Hot idling	-	0	3000	2.6×10^4	-27.5	+20.9
VW G-H2	4	Hot idling	-	0	3000	2.4×10^4	-29.2	+20.3
VW G-H3	4	Hot idling	-	0	3000	1.7×10^4	-29.1	+20.6

cept for the No. 3 automobile, the experiments were all conducted under the natural atmosphere on the campus of Hokkaido University where the background CO content is ca. 0.3 ppmv. For the sampling of idling automobiles, Tsunogai et al. [1] attached ca. 0.3 m Tygon tubing to their tail pipes to connect with the inlet of sampling bottles. For the sampling of running automobiles, Tsunogai et al. [1] used ca. 3 m Tygon tubing to introduce tail pipe exhaust to sampling bottles installed in the interior of automobile cabins. In the case of the non-catalyst automobile (No. 4), however, the CO content was too high (>1%) to introduce exhaust to the cabin and Tsunogai et al. [1] were forced to abandon both the sampling and measurements. As for the No. 3 automobile, the experiments were conducted within a laboratory, of Japan Automobile Research Institute, where a driving simulator system (chassis dynamometer) was available [10]. With this system, it was possible to inject a purified atmosphere (CO < 0.01 ppmv) to the air intake of the engine even when sampling from a running automobile. The sampling states are presented in Table 2 and 3, together with the analytical results.

In order to evaluate whether the estimated isotopic compositions are reasonable for the representatives of those of automobile CO to atmosphere or not, Tsunogai et al. [1] also sampled trunk road atmosphere to obtain the average isotopic compositions of CO from actually running automobiles. Pre-evacuated clean glass bottles (200 ml) were used for sampling. Atmospheric samples were collected at

two stations on Route No. 5, Japanese national trunk road, by opening a stopcock of a pre-evacuated bottle and allowing atmospheric pressure to be attained. The stations are located ca. 50 m apart in downtown Sapporo, a city with a population of 1.8 million. One is located on a sidewalk that faces toward a major intersection of the trunk road and the other is on a bridge crossing over the trunk road. The minimum distance from tail pipes to the sampling points was ca. 5 m in both stations. From November 3rd to 7th, 2000, atmospheric samples were collected every 8 hours at both stations. The average volumes of traffic on the trunk road were ca. 16,000 automobiles per day during the period.

ANALYSIS

Mixing ratios and stable isotopic compositions of CO were measured using the method described by Tsunogai et al. [9]. In brief, the procedures were as follows. For each measurement, sample of appropriate volume (1 ml STP for a 20 ppmv exhaust gas, for example) was introduced into a vacuum line and gathered onto the head of a preconcentration column immersed in liquid nitrogen, packed with silica gel, and then Molecular sieve 5A. The preconcentration column was then gradually heated to room temperature while flushing with ultrapure helium. After discarding the rapidly eluted portions such as O₂, Ar, N₂, and CH₄, the subsequently eluted CO portion was gathered on the second trap, packed with Molecular sieve 5A and cooled with liquid nitrogen.

Table 3 Concentration and isotopic compositions of exhaust emitted from diesel automobiles [1].

Sample ID	Car No.	Status	Load	Speed (km/h)	rpm	CO (ppm)	$\delta^{13}\text{C}$ (‰PDB)	$\delta^{18}\text{O}$ (‰SMOW)
ADV-6z	5	Cold idling	-	0	1000	667	-21.0	+13.7
ADV-22z	5	Cold idling	-	0	1000	429	-20.9	+12.7
ADV-19z	5	Cold idling	-	0	1000	328	-20.8	+14.2
ADV-GOz	5	Hot idling	-	0	1000	145	-18.4	+14.4
ADV-50z	5	Running	middle	10	1300	185	-18.7	+14.4
ADV-30z	5	Running	middle	10→30	1800	185	-18.0	+15.2
ADV-27z	5	Running	middle	30	1500	192	-18.1	+15.5
ADV-14z	5	Running	middle	30→50	2500	173	-17.0	+17.0
ADV-10	5	Running	middle	50	1900	429	-18.0	+17.4
ADV-3z	5	Running	middle	50→30	2500	244	-25.8	+10.1
ADV-13z	5	Running	middle	30→10	1800	193	-24.0	+10.8
MST-I1	6	Hot idling	-	0	500	93	-18.9	+13.5
MST-I2	6	Hot idling	-	0	500	70	-19.5	+10.4
MST-O1	6	Hot idling	-	0	1000	183	-19.4	+10.4
MST-O2	6	Hot idling	-	0	1000	181	-19.2	+11.8
MST-T1	6	Hot idling	-	0	2000	416	-20.5	+9.8
MST-T2	6	Hot idling	-	0	2000	481	-21.0	+9.9

More than 99% of the moisture and CO_2 were retained in the first preconcentration column. Liquid nitrogen was then removed from the second trap, to allow the temperature to increase to ambient and to separate CO from residual N_2 , and CH_4 etc. in the fraction. Highly purified CO was then injected into the head of the Molsieve 5A PLOT capillary column while the column head was kept at -180°C , to concentrate the CO at the head of the separation column. The column head was then quickly heated to 80°C under a continuous helium flow rate of 0.3 ml/min. The column-separated CO was directly introduced to a mass spectrometer for content and carbon-isotope ratio measurements by simultaneous monitoring of the masses of ^{28}CO , ^{29}CO , and ^{30}CO . We also introduced CO_2 into the mass spectrometer just before and after the CO peak while simultaneously monitoring the masses of ^{28}CO , ^{29}CO , and ^{30}CO , so as to use the CO_2 -derived CO fragment ion in the mass spectrometer as a running standard for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ calculations. In addition to the samples, we measured a working-standard gas mixture containing CO of known concentration (245 ppm) and known $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions at least once a day in the same manner as the samples themselves.

The method for the delta calculations of samples is as follows. By using the peak area ratios of mass 28 vs. 29 and mass 28 vs. 30, the δ value between the sample and running standard (CO fragment ion from CO_2) during sample analysis was calculated. For normalization to an international standard, the following relation was used:

$$\delta_{\text{sa-std}} = \delta_{\text{sa-rs}} + \delta_{\text{rs-std}} + (\delta_{\text{sa-rs}} \times \delta_{\text{rs-std}})/1000 \quad (1)$$

where $\delta_{\text{rs-std}}$ is the δ value for the running standard CO fragment against the international standard, which is deduced from the measurement of the working-standard gas mixture that contains CO of known δ compositions ($\delta_{\text{ws-std}}$).

The CO content of a sample is calculated by comparing each ^{28}CO peak area with that of the working standard gas mixture. The precision of the mixing-ratio determinations was estimated to be $<5\%$. An analytical precision of 0.2‰ for ^{13}C and 0.4‰ for ^{18}O can be achieved for samples containing as little as 300 pmol CO within the forty minutes required for a single sample analysis. Analytical blanks associated with the method are less than 1 pmol. The extent of analytical error in $\delta^{13}\text{C}$ due to mass-independent fractionation of oxygen is estimated to be less than 0.1‰ for the samples in this study [5, 11].

RESULTS AND DISCUSSION

Tail Pipe $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ of Gasoline-fuelled Automobiles

Tsunogai et al. [1] found large variations in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO emitted from gasoline automobiles via their tail pipes (Table 2). The $\delta^{13}\text{C}_{\text{CO}}$ varies from -29.2 to $-5.1\text{‰}_{\text{PDB}}$ and $\delta^{18}\text{O}$ varies from $+11.6$ to $+36.1\text{‰}_{\text{SMOW}}$. The CO contents in exhaust are much higher than the ambient CO. Therefore, it can safely be assumed that all CO in exhaust is derived from the engine.

Brenninkmeijer and Röckmann [4] reported $\delta^{18}\text{O}$ values of $+6\text{‰}_{\text{SMOW}}$ and $+19.5\text{‰}_{\text{SMOW}}$ for a single gasoline automobile under idling conditions. Huff and Thiemens [5] reported $\delta^{18}\text{O}$ values from $+10\text{‰}$ to $+30\text{‰}_{\text{SMOW}}$ for five different idling gasoline engines. Kato et al. [6] reported almost uniform $\delta^{13}\text{C}$ values of $-29.9 \pm 0.3\text{‰}_{\text{PDB}}$ and uniform $\delta^{18}\text{O}$ values of $+22.3 \pm 0.3\text{‰}_{\text{SMOW}}$ for two different gasoline automobiles. Most of the data published before are within the range observed in their study.

One of the most striking features of our results is that each recent gasoline automobile (Nos. 1–3) shows linear correlations on the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot, while the old, non-catalyst automobile (No. 4) does not show any such correlation (Fig. 1). Besides, Nos. 1 and 2 exhibit almost the same trend on the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot. Based on the difference in the slopes of the correlations, Tsunogai et al. [1] classified the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations in the gasoline automobiles into three categories (Gasoline1, Gasoline2,

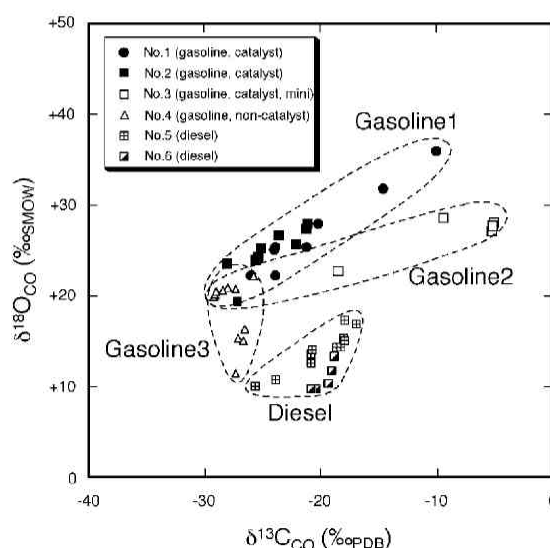


Fig. 1 Relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of tail pipe CO for all the automobiles [1]

and Gasoline3) for further interpretations (see Fig. 1). The category Gasoline1 comprised all the data from both the Nos. 1 and 2 automobiles. The category Gasoline2 comprises all the data from the No. 3 automobile. The category Gasoline3 included all the data of the old No. 4 automobile. In addition, we classified a part of the data of the No. 4 automobile - that located close to Gasoline1 and that located on the ^{13}C - and ^{18}O -depleted extension of the slope of Gasoline2 - as a cross over of the three categories (Fig. 1).

Tsunogai et al. [1] speculate that the lowest $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ values in the categories Gasoline1 and Gasoline2 represent the original values of $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ produced within engines and the relative ^{13}C - and ^{18}O -enrichment of the other CO in category Gasoline1 and Gasoline2 from the original values might arise from a kinetic isotope effect during CO destruction on their functional catalytic converter. Their reasons are as follows: (1) the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in Gasoline1 and Gasoline2 are almost the same with the source material: gasoline ($\delta^{13}\text{C} = -28\text{‰PDB}$; Widory, 1999 [22]; Recio et al., 2001 [21]) and atmospheric oxygen ($\delta^{18}\text{O} = +23.5\text{‰SMOW}$, [12–13]), (2) there is a large variation in the automobiles having a three way functional catalytic converter (Nos. 1–3), while the data of non-catalyst automobile (No. 4) show little variation and, when plotted, are distributed in the most ^{13}C -depleted end in the categories Gasoline1 and Gasoline2, (3) presence of a clear depletion of CO content in exhaust gas in relation to the $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ enhancement in all the measured automobiles (Figs. 2 and 3), and (4) the $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ enhancements show a linear trend with the logarithm of CO concentration, suggesting that the observed temporal variations in concentrations and isotopic compositions are mostly derived from the kinetic isotope effect and that the magnitude of the carbon kinetic isotope effect is comparable to that of CO destruction on metal surfaces as cited in some literature (detailed explanation will be provided later).

Reason (1) implies that the carbon and oxygen isotopic effect is low for the usual CO production within a gasoline engine, as was also pointed out by Stevens et al. [3]. The ^{13}C - and ^{18}O -enrichments seen in Gasoline1 and Gasoline2 might reflect the respective efficiency of CO destruction in the system.

A more detailed explanation for reason (4) is as follows. The magnitude of the kinetic isotope effect (KIE) during CO removal can be defined as:

$$\text{KIE}(\%) = (k_{\text{CO}}/k^*_{\text{CO}} - 1) \times 1000 \quad (2)$$

where k^*_{CO} is the rate constant for the reaction of ^{13}CO or C^{18}O during removal reaction and k_{CO} is the rate constant for the reaction of ^{12}CO or C^{16}O . The KIE values for carbon (KIE_{C}) and oxygen (KIE_{O}) in the reaction $\text{CO} + \text{OH}$, for example, have been determined in many past studies to be around $\text{KIE}_{\text{C}} = +7$ and $\text{KIE}_{\text{O}} = -10$ under 1 atm pressure [14–16]. By using such defined KIE_{C} and the initial $\delta^{13}\text{C}$ composition ($\delta^{13}\text{C}_i$), the change in the $\delta^{13}\text{C}$ of the remaining CO ($\delta^{13}\text{C}_t$) is described by the general Rayleigh equation

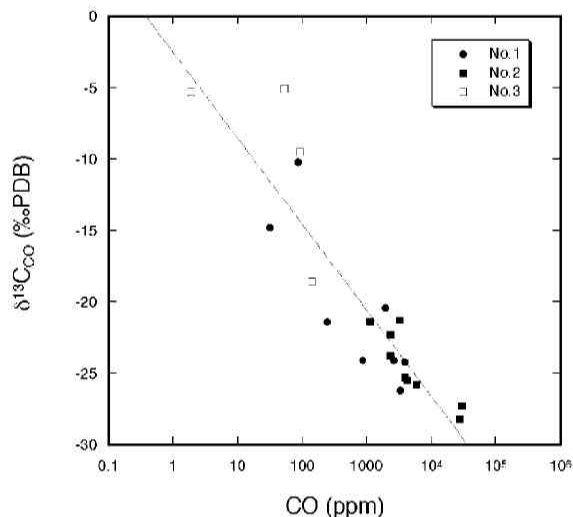


Fig. 2 Relationship between content and $\delta^{13}\text{C}$ of CO emitted from gasoline automobiles that have catalytic converter [1].

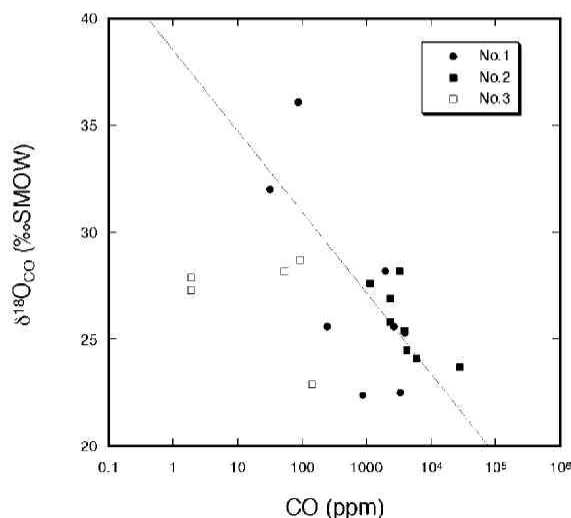


Fig. 3 Relationship between content and $\delta^{18}\text{O}$ of CO emitted from gasoline automobiles that have catalytic converter [1].

$$\delta^{13}C_t = \delta^{13}C_i - KIE_c \times \ln[M_t/M_i] \quad (3)$$

where M_i and M_t stand for the initial and temporal amounts of CO. The linear variations of isotopic compositions in accordance with logarithm of CO content in exhaust suggest the variation must be due to kinetic isotope effect [e.g. 17]. The observed KIE_c and KIE_o are estimated to be +2.6 and +1.6, respectively, from the slopes in Figs. 2 and 3. The KIE_c during catalytic oxidation of CO over a metal surface has been reported to be +6.1 for Pd/Al₂O₃ at 323 K [18]. Although the precise chemical composition of the catalyst and the reaction temperature might be different, the KIE_c is of the same order of magnitude as our values estimated from the gas exhaust in Fig. 2. While no data is available for the KIE_o during catalytic oxidation of CO over a metal surface, the normal KIE_o ($KIE_o > 0$) might be also reasonable because the CO oxidation by microbial metabolism at soil surfaces also exhibits normal KIE_o of a similar magnitude [9]. In conclusion, it is not unreasonable to expect that fractionation occurs with such KIEs.

The category Gasoline2 is basically composed of the data taken from the No. 3 automobile. As for Gasoline2, the trend between $\delta^{13}C$ and $\delta^{18}O$ seems to be different from Gasoline1. This implies that the ratio between KIE_c and KIE_o during CO destruction at the functional catalytic converter of the No. 3 automobile is somewhat different from those of the other automobiles having functional catalytic converters. As we can see in Figs. 2 and 3, the main difference may arise from the KIE_o . At present, it is difficult to deduce the factors that determine KIE_o at catalytic metal surface. It must be reasonable, however, to conclude that only the No. 3 has a catalytic surface different from the other usual automobiles having functional catalytic converters, because the No. 3 is the only mini-car within the three automobiles (Table 1).

The reason for the $\delta^{18}O$ trend in Gasoline3 is also unclear at present. Some of the data show significant ^{18}O -depletion compared to the original $\delta^{18}O$ values found in the engines investigated above. We can recognize this trend, however, only in the oldest, and the only non-catalyst automobile (No. 4). Most of the low $\delta^{18}O$ is observed just after engine ignition, during idling. Besides, the low $\delta^{18}O$ values are mostly characterized by higher CO content in exhaust gas (Table 2). Brenninkmeijer and Röckmann [4] also reported similar ^{18}O -depletion in exhaust CO from a cold started, old, non-catalyst engine. Because the variation is mostly limited to $\delta^{18}O$, it must

originate during the CO generation stage within the engine.

During laboratory studies on the combustion of plants, Kato et al. [19] reported ^{18}O -depletion of CO produced during the smoldering stage of burning compared with the active flaming stage. The smoldering stage can be characterized by both lower temperature and more O₂-depleted combustion compared with the usual burning (flaming) stage, so that low temperature combustion and/or O₂-depleted combustion in an engine may result in the emission of ^{18}O -depleted CO. During the combustion of gasoline in an engine, most of carbon monoxide might be formed through the reactions of gasoline with atmospheric oxygen. The combustion under O₂-depleted conditions in engine may cause the generation of ^{18}O -depleted CO during reaction of gasoline with atmospheric O₂, by enhancing the KIE_o during the O₂ destruction stage. The wide isotopic variation depending on the engine state could be a useful indicator for studying the complex mechanisms of CO production within combustion systems.

Estimation of Average $\delta^{13}C_{CO}$ and $\delta^{18}O_{CO}$ from Tail Pipes

Tsunogai et al. [1] applied the exhaust gas data of the Nos. 1 and 2 to the so-called Japanese 10-15 driving cycle to estimate the average isotopic composition of CO from automobiles. The Japanese 10-15 driving cycle is a supposed average driving cycle model for automobiles established by the Japanese Ministry of Land, Infrastructure and Transport. The actual temporal variation of automobile velocity under the driving cycle is presented in Fig. 4, together with the variation of adopted concentration and isotopic composition for each driving state. The estimated average content, $\delta^{13}C_{CO}$ and $\delta^{18}O_{CO}$ were 2,250 ppm, $-23.8 \pm 0.8\text{‰PDB}$, and $+25.3 \pm 1.0\text{‰SMOW}$, respectively.

The estimated isotopic compositions are presented in Table 4 together with their concentrations. The estimated average isotopic composition is enriched in ^{13}C and ^{18}O compared to the other previous estimates (Table 5) of Stevens et al. [3] for ca. 30 years ago, and Kato et al. [6] for 1997, based on old automobiles. We must adopt new estimates for the present automobile fleet. Besides, we must upgrade the values in the near future, since the enrichments in ^{13}C and ^{18}O will continue due to the improvements in catalytic converters.

Chanton et al. [20] determined $\delta^{13}C$ of methane in exhaust for 16 automobiles and found that recent models of automobiles tend to exhibit lower mixing

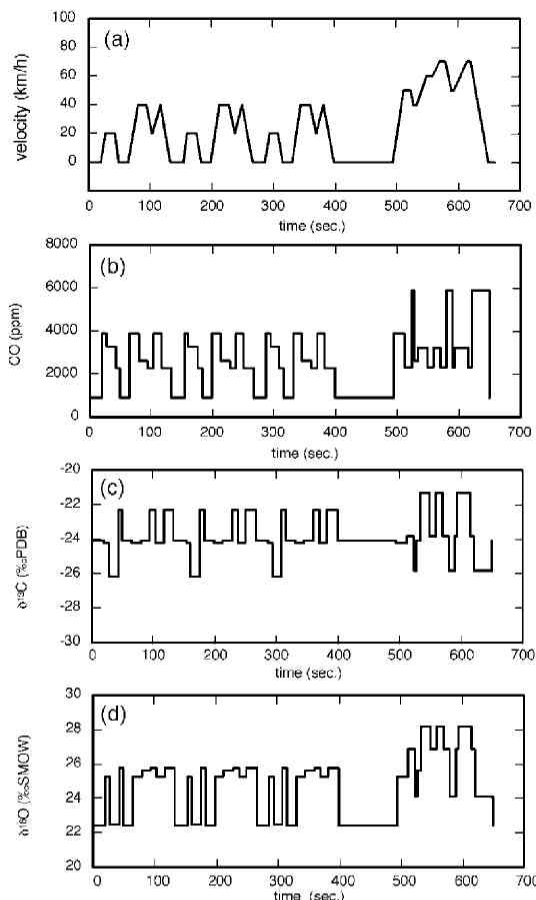


Fig. 4 The driving cycle model adopted in this study (Japanese 10·15 driving cycle) (a) for the estimation of average CO emission from gasoline automobiles, together with the adopted CO content (b), $\delta^{13}\text{C}$ (c), and $\delta^{18}\text{O}$ value (d) for each driving state. Each data set of (b), (c), and (d) is chosen from actually determined data sets of car No. 1 or 2 in Table 2, which is under the corresponding driving condition with (a) [1].

ratio of methane accompanying higher $\delta^{13}\text{C}$ values. The trend can also reasonably be accountable by KIE during destruction of methane at functional catalytic converters. Recent popularization and improvements of catalytic converters in engine enhance not only $\delta^{13}\text{C}_{\text{CO}}$ but also $\delta^{13}\text{C}_{\text{CH}_4}$ in exhaust.

Tsunogai et al. [1] did not include the data from the No. 3 automobile in the calculation because of the low CO contents. Besides, the number of such mini automobiles (660 cc) is so limited that their contributions may be neglected. These aspects together with the actual data of trunk road atmosphere are elaborated later.

Tail Pipe CO of Diesel Automobiles

As shown in Table 3, diesel automobiles in general (Nos. 5 and 6) are characterized by lower CO concentrations than those of gasoline automobiles that have similar volumes of cylinder displacement (Nos. 1 and 2). Even in the low CO diesel automobiles, the CO contents in exhaust are much higher than the ambient CO. Therefore, it can safely be assumed that all the CO in exhaust is derived from the engine. The results for two diesel automobiles (Nos. 5 and 6) coincide well with each other. Both of them show variations in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO. The $\delta^{13}\text{C}$ of CO varies from -25.8 to -17.0 ‰PDB whereas $\delta^{18}\text{O}$ varies from $+9.8$ to $+17.4$ ‰SMOW. Kato et al. [6] reported almost uniform values of -22.2 ± 1.1 ‰PDB for $\delta^{13}\text{C}$ and $+10.9 \pm 0.8$ ‰SMOW for $\delta^{18}\text{O}$. The previous data are mostly included in the range found in this study. Assuming the Japanese 10·15 driving cycle as already described for gasoline automobiles also holds in the case of diesel engines for average driving cycle, we can estimate the average

Table 4 The estimated average concentration and isotopic composition of CO emitted from each type of automobile [1].

Engine	Conc. (ppm)	$\delta^{13}\text{C}$ (‰PDB)	$\delta^{18}\text{O}$ (‰SMOW)
Gasoline	2100	-23.8 ± 0.8	$+25.3 \pm 1.0$
Diesel	230	-19.5 ± 0.7	$+15.1 \pm 1.0$

Table 5 Estimated average isotopic compositions of CO emitted from gasoline automobiles [1].

$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Data source	Reference
-27.4 ± 0.3	$+24.6$	Urban atmosphere	Stevens et al. (1972) [16]
-29.9 ± 0.3	$+22.3 \pm 0.3$	Tail pipe	Kato et al. (1999) [6]
-23.8 ± 0.8	$+25.3 \pm 1.0$	Tail pipe (catalyst)	This study
-25.2 ± 1.5	$+23.7 \pm 1.8$	Road atmosphere	This study

isotopic compositions of CO from diesel automobiles to be $-19.5 \pm 0.7\text{‰PDB}$ for $\delta^{13}\text{C}$ and $+15.1 \pm 1.0\text{‰SMOW}$ for $\delta^{18}\text{O}$.

The striking feature of these results is that they clearly show different $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from those of gasoline automobiles as also pointed out by Kato et al. [6]. The values are higher in $\delta^{13}\text{C}$ while lower in $\delta^{18}\text{O}$ compared with those of gasoline automobiles. As the total $\delta^{13}\text{C}$ values of the source diesel fuel are almost identical with those of gasoline fuel [21–22], the difference might reflect some special generation and/or destruction processes in each engine. The diesel engines in general can be characterized by higher combustion efficiency than gasoline automobiles. During the combustion of fuel, carbon monoxide would possibly be formed by thermal decomposition of fuel, and/or reaction of carbon in fuel with atmospheric oxygen. This initially produced CO must have almost same or somewhat depleted ^{13}C and ^{18}O compared to the source material. At least part of the produced CO, however, ought to be oxidized to CO_2 through the subsequent reactions with reactive radicals such as OH etc. within the combustion flame. Although no data is available for the KIE values of the reactions occurring in flames, the KIEs during $\text{CO} + \text{OH}$ reaction under atmospheric conditions have been estimated to be $\text{KIE}_\text{C} = +7$ and $\text{KIE}_\text{O} = -10$. That is to say, the residual CO after the $\text{CO} + \text{OH}$ reaction will be enriched in ^{13}C while being depleted in ^{18}O . The KIEs during CO destruction processes in flames could account for the relation between $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ in the exhaust of gasoline and diesel engines (Fig. 1).

Even in diesel engines, we can recognize a trend to ^{13}C and ^{18}O enrichment when the CO depletes during idling (Table 2). Because both of the automobiles have EGR cleaning-up systems to reduce CO content in exhaust, the system may be responsible for the trend.

Comparison with CO in Trunk Road Atmosphere

During the whole sampling period, the average CO concentration on the trunk road was 0.66 ± 0.49 (1σ) ppmv (from 0.19 ppmv to 1.7 ppmv), while the average CO concentration in the urban atmosphere of Sapporo during the same period was 0.33 ± 0.25 (1σ) ppmv. The average contribution ratio of CO from automobiles in samples, therefore, can be roughly estimated to be ca. 0.5.

As shown in Fig. 5, the reciprocal of CO content in the trunk road atmosphere shows a good linear relationship with the isotopic compositions, irrespective to their sampling points and time. Similar linear

relationship between reciprocal of CO content and their isotopic compositions have been recognized to CO in urban atmosphere in past studies [3, 6]. The linear relationships suggest that all the samples are contaminated by CO classified, at least isotopically, to a single category, which must be automobile exhaust in this case. While the isotopic compositions of CO emitted from tail pipes of automobiles are heterogeneous as presented in this study, the good linear relation suggests that they can be characterized by a single isotopic composition at the sampling station at least 5 meters apart from tail pipes. The contaminated CO in each sample is not the CO that was emitted from a single tail pipe, but comprises the weighted average for many automobiles that have already passed through the sampling points. Besides, the composition is homogeneous at least for the sampling point for the sampling period. Because we can rate the trunk road as a representative road in Japan, we can also rate the isotopic composition of the source CO from the weighted average of $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ emitted from automobiles currently running Japanese roads.

By extrapolating the relationship between $1/\text{CO}$ and $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ to $1/\text{CO} = 0$, we can estimate the average isotopic compositions of CO from automobiles using the trunk road. The estimated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ was $-25.2 \pm 1.5\text{‰PDB}$ and $+23.7 \pm 1.8\text{‰SMOW}$, respectively. They correspond to the average values

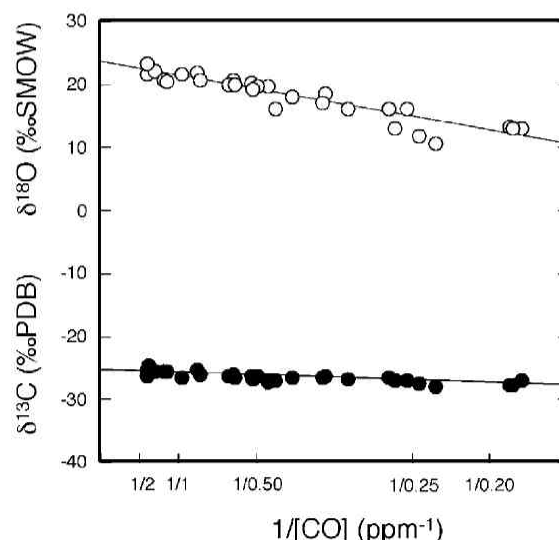


Fig. 5 Relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO and reciprocal of CO concentration in trunk road atmosphere. The solid lines are the least square fitting of all measured values. The average isotopic compositions of automobile sources can be estimated to be $\delta^{13}\text{C} = -25.2 \pm 1.5\text{‰PDB}$ and $\delta^{18}\text{O} = +23.7 \pm 1.8\text{‰SMOW}$ from the intercepts [1].

for catalyst automobiles estimated from tail pipes of gasoline automobiles ($-23.8 \pm 0.8\text{‰}_{\text{PDB}}$, and $+25.3 \pm 1.0\text{‰}_{\text{SMOW}}$) within 1σ error, while being far different from the diesel automobiles ($-19.5 \pm 0.7\text{‰}_{\text{PDB}}$, and $+15.1 \pm 1.0\text{‰}_{\text{SMOW}}$) and also from the estimates of gasoline automobiles in earlier reports [3, 6]. Besides, they are also different to the old, non-catalyst automobiles determined in this study ($-27.9 \pm 1.1\text{‰}_{\text{PDB}}$, and $+18.7 \pm 3.2\text{‰}_{\text{SMOW}}$). Tsunogai et al. [1] concluded that i) the major source of CO in trunk roads will still be gasoline automobiles and ii) the estimated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ arising from tail pipes fairly represent the present CO contribution from automobiles. The maximum possible contribution of diesel automobiles to the trunk road CO level can be estimated to be $< 5\%$.

In order to verify this final conclusion, Tsunogai et al. [1] performed an approximate traffic-count to determine the ratio of diesel automobiles to all the automobiles passing the sampling points during the sampling period with the aim of calculating CO emission ratio between gasoline and diesel automobiles. The ratio was roughly estimated to be $< 2\%$, after correcting for the CO content difference between gasoline and diesel automobiles. Thus, these isotopes can also act as highly reliable tracers to evaluate the CO contribution ratio between gasoline and diesel automobiles.

Implications for Future $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ Values from Automobiles

Tsunogai et al. [1] suggest that the average isotopic composition of CO will be gradually enriched in heavy isotopes following the advancements of functional catalytic converters in automobiles and the increase of automobiles equipped with efficient catalytic converters. Future gasoline automobiles will emit CO with more enriched ^{13}C and ^{18}O . Assuming the KIE_{C} and KIE_{O} for CO destruction at catalytic surface as $+2.6$ and $+1.3$ as estimated from Figs. 2 and 3, the average isotopic compositions of CO can be roughly estimated to be $+3$ and $+1\text{‰}$ enriched if the average CO content in each tail pipe is reduced to ca. $1/3$ of the present level. While the average CO emission from each automobile has been decreasing, the total number of automobiles in the world has been on the increase [23]. We must re-evaluate the value successively to determine the latest average isotopic composition. On the other hand, by determining $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ together with the CO mixing ratio in a trunk road atmosphere and by estimating source $\delta^{13}\text{C}_{\text{CO}}$ and $\delta^{18}\text{O}_{\text{CO}}$ of automobile exhaust as done by Tsunogai et al. [1], we can quan-

titatively estimate the progress of CO reduction in automobile exhaust. Furthermore, the method will be also valid to estimate the popularization of functional catalytic converters in engines for many regions and countries.

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REFERENCES

1. Tsunogai, U., Hachisu, Y., Komatsu, D.D., Nakagawa, F., Gamo, T. and Akiyama, K., 2003. An updated estimation of the stable carbon and oxygen isotopic compositions of automobile CO emissions. *Atmos. Environ.*, 37, 4901–4910.
2. Brenninkmeijer, C.A.M., Röckmann, T., Bräunlich, M., Jöckel, P. and Bergamaschi, P., 2000. Review of progress in isotope studies of atmospheric carbon monoxide. *Chemosphere: Global Change Science*, 1, 33–52.
3. Stevens, C.M., Krout, L., Walling, D., Venters, A., Engelke-meir, A. and Ross, L.E., 1972. The carbon isotopic composition of atmospheric carbon monoxide. *Earth Planet. Sci. Lett.*, 16, 147–165.
4. Brenninkmeijer, C.A.M. and Röckmann, T., 1997. Principal factors determining the $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric CO as derived from observations in the southern hemispheric troposphere and lowermost stratosphere. *J. Geophys. Res.*, 102, 25477–25485.
5. Huff, A.K. and Thiemens, M.H., 1998. $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ isotope measurements of atmospheric carbon monoxide and its sources. *Geophys. Res. Lett.*, 25, 3509–3512.
6. Kato, S., Akimoto, H., Bräunlich, M., Röckmann, T. and Brenninkmeijer, C.A.M., 1999. Measurements of stable carbon and oxygen isotopic compositions of CO in automobile exhausts and ambient air from semi-urban Mainz, Germany. *Geochim. J.*, 33, 73–77.
7. Mak, J.E. and Yang, W., 1998. Technique for analysis of air samples for ^{13}C and ^{18}O in carbon monoxide via continuous-flow isotope ratio mass spectrometry. *Anal. Chem.*, 70, 5159–5161.
8. Tsunogai, U., Nakagawa, F., Hachisu, Y. and Yoshida, N., 2000. Stable carbon and oxygen isotopic analysis of carbon monoxide in natural waters. *Rapid Commun. Mass Spectrom.*, 14, 1507–1512.

9. Tsunogai, U., Nakagawa, F., Komatsu, D.D. and Gamo, T., 2002. Stable carbon and oxygen isotopic analysis of atmospheric carbon monoxide using continuous-flow isotope ratio MS by isotope monitoring of CO. *Anal. Chem.*, 74, 5695–5700.
10. Schuetzle, D., Jensen, T.E., Nagy, D., Probst, A. and Hochhauser, A., 1991. Analytical chemistry and auto emissions. *Anal. Chem.*, 63, 1, 149A–I, 159A.
11. Röckmann, T. and Brenninkmeijer, C.A.M., 1998. The error in conventionally reported $^{13}\text{C}/^{12}\text{C}$ ratios of atmospheric CO due to the presence of mass independent oxygen isotope enrichment. *Geophys. Res. Lett.*, 25, 3163–3166.
12. Kroopnick, P. and Craig, H., 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science*, 175, 54–55.
13. Thiemens, M.H., Jackson, T., Zipf, E.C., Erdman, P.W. and Egmond, C.V., 1995. Carbon Dioxide and Oxygen Isotope Anomalies in the Mesosphere and Stratosphere. *Science*, 270, 969–972.
14. Smit, H.G.J., Volz, A., Ehle, D.H. and Knappe, H., 1981. The isotopic fractionation during the oxidation of carbon monoxide. In: Schmidt, H.-L., Forstel H., Heinzinger K. (Eds.), *Stable isotopes : Proceedings of the 4th international conference* (Jülich, March 23–26). Elsevier, Amsterdam, 147–152.
15. Röckmann, T., Brenninkmeijer, C.A.M., Saueressig, G., Bergamaschi, P., Crowley, J.N., Fischer, H. and Crutzen, P.J., 1998. Mass-independent oxygen isotope fractionation in atmospheric CO as a result of the reaction $\text{CO} + \text{OH}$. *Science*, 281, 544–546.
16. Stevens, C.M., Kaplan, L., Gorse, R., Durkee, S., Compton, M., Cohen, S. and Bielling, K., 1980. The kinetic isotope effect for carbon and oxygen in the reaction $\text{CO} + \text{OH}$. *J. Chem. Kinetics*, 12, 935–948.
17. Tsunogai, U., Yoshida, N. and Gamo, T., 1999. Carbon isotopic compositions of C_1 – C_5 hydrocarbons and methyl chloride in urban, coastal and maritime atmosphere over western North Pacific. *J. Geophys. Res.*, 104(D13), 16033–16039.
18. Ogrinc, N., Kobal, I. and Senegacnik, M., 1997. Carbon-13 kinetic isotope effects in the catalytic oxidation of Carbon Monoxide over $\text{Pd}/\text{Al}_2\text{O}_3$. *J. Phys. Chem. A*, 101, 7236–7242.
19. Kato, S., Akimoto, H., Röckmann, T., Bräunlich, M. and Brenninkmeijer, C.A.M., 1999. Stable isotopic compositions of carbon monoxide from biomass burning experiments. *Atmos. Environ.*, 33, 4357–4362.
20. Chanton, J.P., Rutkowski, C.M., Schwartz, C.C., Ward, D.E. and Boring, L., 2000. Factors influencing the stable carbon isotopic signature of methane from combustion and biomass burning. *J. Geophys. Res.*, 105(D2), 1867–1877.
21. Recio, C., Etcheverry, R.O., Redondo, R. and Rubio, A., 2001. Isotopic characterization of beach tar: Is it possible to determine its provenance? In: M. Lago, E. Arranz and C. Galé (eds.), *Proceedings of III Congreso Ibrico de Geoquímica and VIII Congreso de Geoquímica de España (ISBN: 84-930635-8-4)*, 247–252.
22. Widory, D., 1999. Etude de la pollution urbaine a l'aide des isotopes du carbone et de l'azote. Ph.D. thesis, *University Paris 7 - IPGP*, 281 pp.
23. Pemberton, M.J., 1991. World vehicle market: strategic review and forecast databook, *Euromotor Reports*, London, 385 pp.