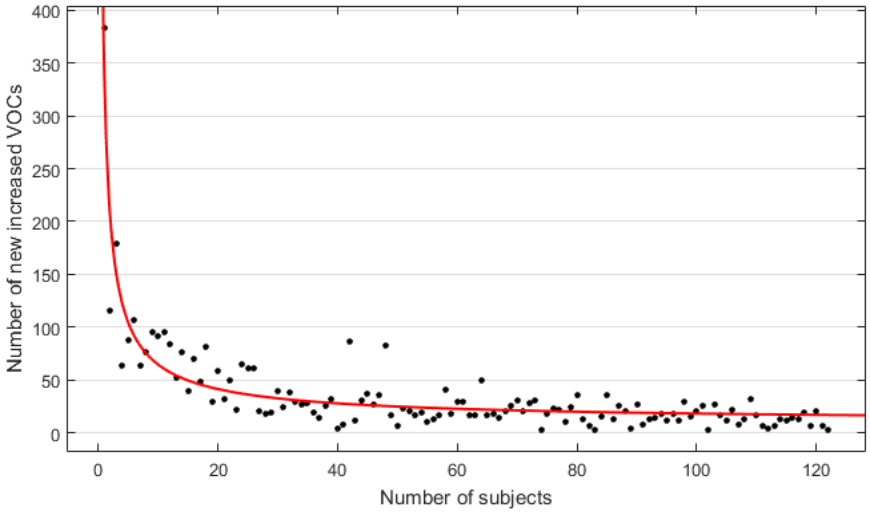


**Figure S1.** A downward trend of number of new identified VOCs.

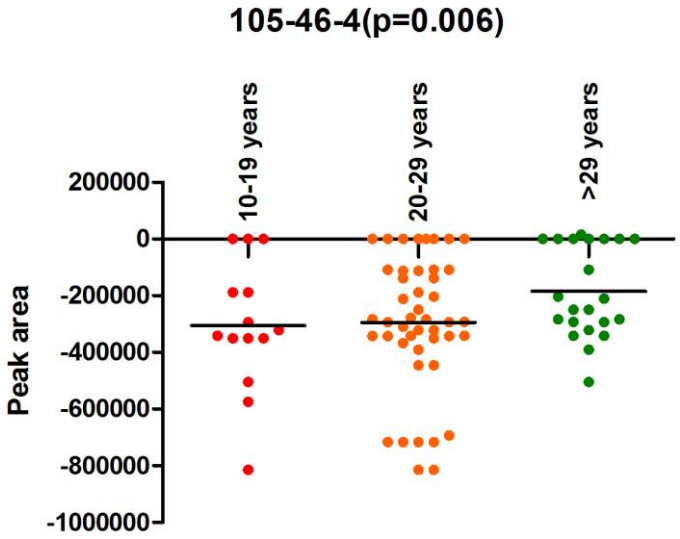


**Figure S2.** The VOC was strong correlated with years of smoking.

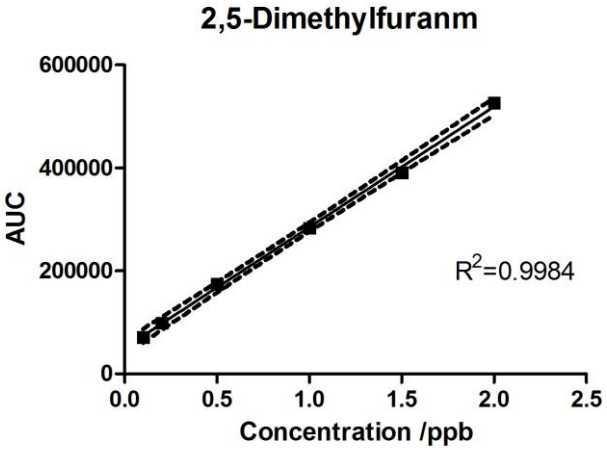


**Figure S3.** The results of calibration.

**Table S1.** The means of VOCs associated with smoking status.

| CAS No. | VOCs | SS | Number of Participants | *p*-Value |
|---|---|---|---|---|
| **111-84-2** * | Nonane | 1 | 41 | 0.047 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **465-24-7** * | Longiborneol | 1 | 41 | 0.022 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **112-39-0** * | Methyl hexadecanoate | 1 | 41 | 0.033 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **3075-84-1** * | 2,2′,5,5′-Tetramethylbiphenyl | 1 | 41 | 0.04 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **625-86-5** ** | 2,5-Dimethylfuran | 1 | 41 | <0.001 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **2612-46-6** ** | *cis*-1,3,5-Hexatriene | 1 | 41 | 0.002 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |
| **14676-29-0** * | 3-Ethyl-2-methylheptane | 1 | 41 | 0.032 |
| | | 2 | 5 | |
| | | 3 | 4 | |
| | | 4 | 72 | |

* $p < 0.05$, ** $p < 0.01$. SS: smoking status: never, former, former that quit less than 1 year, and current are signed as 1, 2, 3, and 4, respectively.

**Table S2.** The means of VOCs associated with smoking intensity.

| CAS No. | VOCs | SI | Number of Participants | *p*-Value |
|---|---|---|---|---|
| **123-86-4 *** | Butyl acetate | 1 | 53 | 0.035 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **100-41-4 *** | Ethylbenzene | 1 | 53 | 0.043 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **620-14-4 *** | 3-Ethyltoluene | 1 | 53 | 0.046 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **112-31-2 **** | Decanal | 1 | 53 | 0.005 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **138-86-3 *** | Cinene | 1 | 53 | 0.026 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **98-83-9 *** | 2-Phenyl-1-propene | 1 | 53 | 0.026 |
| | | 2 | 22 | |
| | | 3 | 6 | |
| **17671-27-1 *** | Behenyl behenate | 1 | 53 | 0.04 |
| | | 2 | 22 | |
| | | 3 | 6 | |

* $p < 0.05$, ** $p < 0.01$. SI: smoking intensity. 1: 1–20 cigarettes per day, 2: 21–40 cigarettes per day, 3: 41–60 cigarettes per day.

**Table S3.** The means of VOCs associated with years of smoking.

| CAS No. | VOCs | YS | Number of Participants | *p*-Value |
|---|---|---|---|---|
| **111-84-2** * | N-Nonane | 1 | 14 | 0.028 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **19549-87-2** ** | 2,4-Dimethyl-1-heptene | 1 | 14 | 0.001 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **105-46-4** ** | DL-sec-Butyl acetate | 1 | 14 | 0.006 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **589-81-1** * | 3-Methylheptane | 1 | 14 | 0.014 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **3074-71-3** ** | 2,3-Dimethylheptane | 1 | 14 | 0.001 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **17312-77-5** * | 2,3-dimethylundecane | 1 | 14 | 0.013 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **2492-18-4** * | Hexanoic acid, 1,1-dimethylethyl ester | 1 | 14 | 0.049 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **17302-37-3** * | 2,2-Dimethyldecane | 1 | 14 | 0.011 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **16397-79-8** * | Acetic acid,2,2,2-trichloro-, 2-ethylhexyl ester | 1 | 14 | 0.01 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **2216-34-4** ** | 4-Methyloctane | 1 | 14 | 0.001 |
| | | 2 | 45 | |
| | | 3 | 22 | |
| **79-01-6** * | Trichloroethylene | 1 | 14 | 0.021 |
| | | 2 | 45 | |
| | | 3 | 22 | |

* $p < 0.05$, ** $p < 0.01$. YS: years of smoking years of smoking. 1: 10–19 years, 2: 20–29 years, 3: >29 years.

**Table S4.** The means of VOCs associated with depth of smoke inhalation.

| CAS No. | VOCs | DS | Number of Participants | *p*-Value |
|---|---|---|---|---|
| **111-84-2 *** | n-Nonane | 1 | 27 | 0.013 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **98-86-2 *** | Acetophenone | 1 | 27 | 0.027 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **112-31-2 *** | Decyl aldehyde | 1 | 27 | 0.042 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **24959-83-9 *** | 2,4-Methano-1H-indene,octahydro-7a-methyl-1-methylene-5-(1-methylethyl)-, (2R,3aR,4R,5S,7aS)-rel- | 1 | 27 | 0.042 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **719-22-2 *** | 2,6-Di-tert-butylcyclohexa-2,5-diene-1,4-dione | 1 | 27 | 0.042 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **3892-00-0 *** | 2,6,10-Trimethylpentadecane | 1 | 27 | 0.049 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **17302-01-1 *** | 3-Ethyl-3-methylheptane | 1 | 27 | 0.049 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **2051-30-1 *** | 2,6-Dimethyloctane | 1 | 27 | 0.033 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **83704-03-4 *** | Heptane,3-[(1,1-dimethylethoxy)methyl]- | 1 | 27 | 0.02 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **92-52-4 *** | Biphenyl | 1 | 27 | 0.027 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **4443-59-8 *** | 5-Cyclohexylicosane | 1 | 27 | 0.044 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **62183-79-3 **** | 2,2,4,4-Tetramethyloctane | 1 | 27 | 0.001 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **111-66-0 *** | 1-Octene | 1 | 27 | 0.02 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **625-86-5 *** | 2,5-Dimethylfuran | 1 | 27 | 0.01 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **2612-46-6 **** | 1,3,5-Hexatriene, (3Z)- | 1 | 27 | 0.001 |
| | | 2 | 42 | |

| | | | | |
|---|---|---|---|---|
| | | 3 | 11 | |
| **51655-64-2 *** | 3-Methylene-nonane | 1 | 27 | 0.033 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **1002-43-3 **** | 3-Methylundecane | 1 | 27 | 0.008 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **1067-20-5 *** | 3,3-Diethylpentane | 1 | 27 | 0.014 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **108-95-2 *** | Phenol | 1 | 27 | 0.02 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **13287-21-3 *** | 6-Methyltridecane | 1 | 27 | 0.043 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **17302-27-1 *** | 2,5-Dimethylnonane | 1 | 27 | 0.037 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **571-61-9 *** | 1,5-Dimethylnaphthalene | 1 | 27 | 0.049 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **17301-28-9 *** | 3,6-Dimethylundecane | 1 | 27 | 0.033 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **124-18-5 *** | Decane | 1 | 27 | 0.031 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **7146-60-3 *** | 2,3-Dimethyloctane | 1 | 27 | 0.015 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **17301-24-5 *** | 2,7-Dimethylundecane | 1 | 27 | 0.033 |
| | | 2 | 42 | |
| | | 3 | 11 | |
| **71138-64-2 *** | 3-Methyleneundecane | 1 | 27 | 0.03 |
| | | 2 | 42 | |
| | | 3 | 11 | |

* $p < 0.05$, ** $p < 0.01$. DS: depth of smoke inhalation. 1: inhale into lung, 2: only inhale into mouth, and throat, 3: non-inhale.

**Table S5.** Correlations between VOCs and "engine oil" reported.

| CAS No. | VOCs | *p*-Value |
|---|---|---|
| **95-47-6** | 1,2-Dimethylbenzene | 0.042 |
| **1120-21-4** | n-Hendecane | 0.004 |
| **620-14-4** | 1-ethyl-3-methyl-Benzene | 0.028 |
| **294-62-2** | Cyclododecane | <0.001 |
| **77-53-2** | Cedrol | <0.001 |
| **123-51-3** | 1-Hydroxy-3-methylbutane | 0.014 |
| **2958-76-1** | Naphthalene,decahydro-2-methyl- | <0.001 |

**Table S6.** Correlations between VOCs and "automobile exhaust" reported.

| CAS No. | VOCs | *p*-Value |
|---|---|---|
| **95-47-6** | 1,2-Dimethylbenzene | 0.030 |
| **13475-82-6** | 2,2,4,6,6-pentamethyl-Heptane | <0.001 |
| **80-56-8** | 2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene | 0.013 |
| **88-18-6** | 2-tert-Butyl-1-hydroxybenzene | 0.058 |
| **535-77-3** | 1-methyl-3-(1-methylethyl)-benzen | 0.023 |
| **2958-76-1** | Naphthalene,decahydro-2-methyl- | 0.031 |