Supplement information

Large-scale assessment of oxic methane production in lakes using an isotopic mass balance approach

Authors and Affiliations

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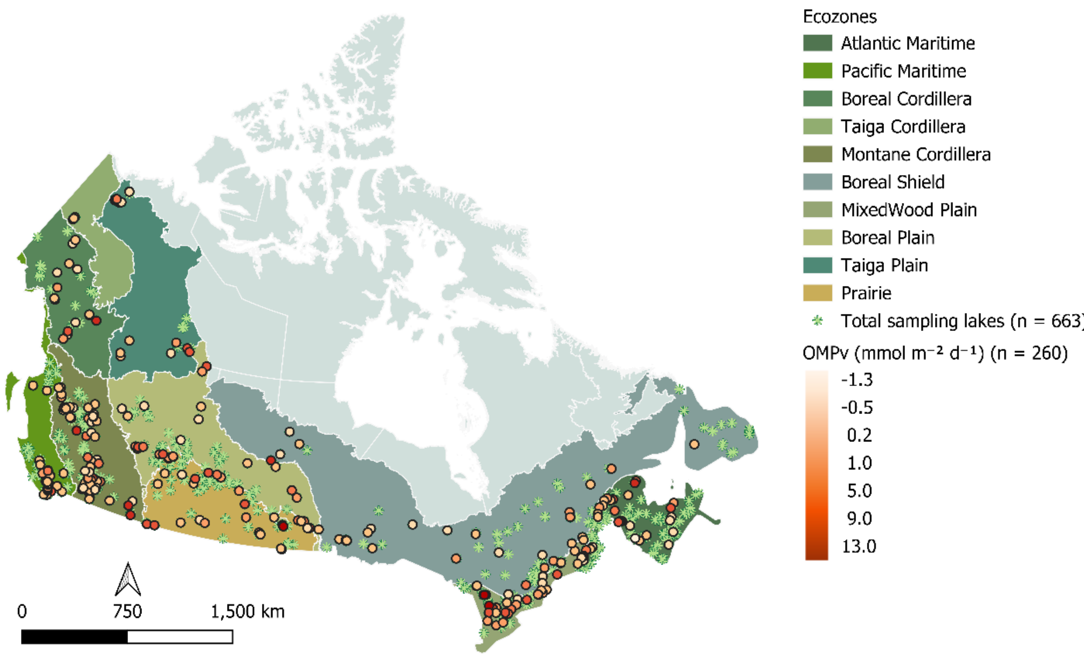
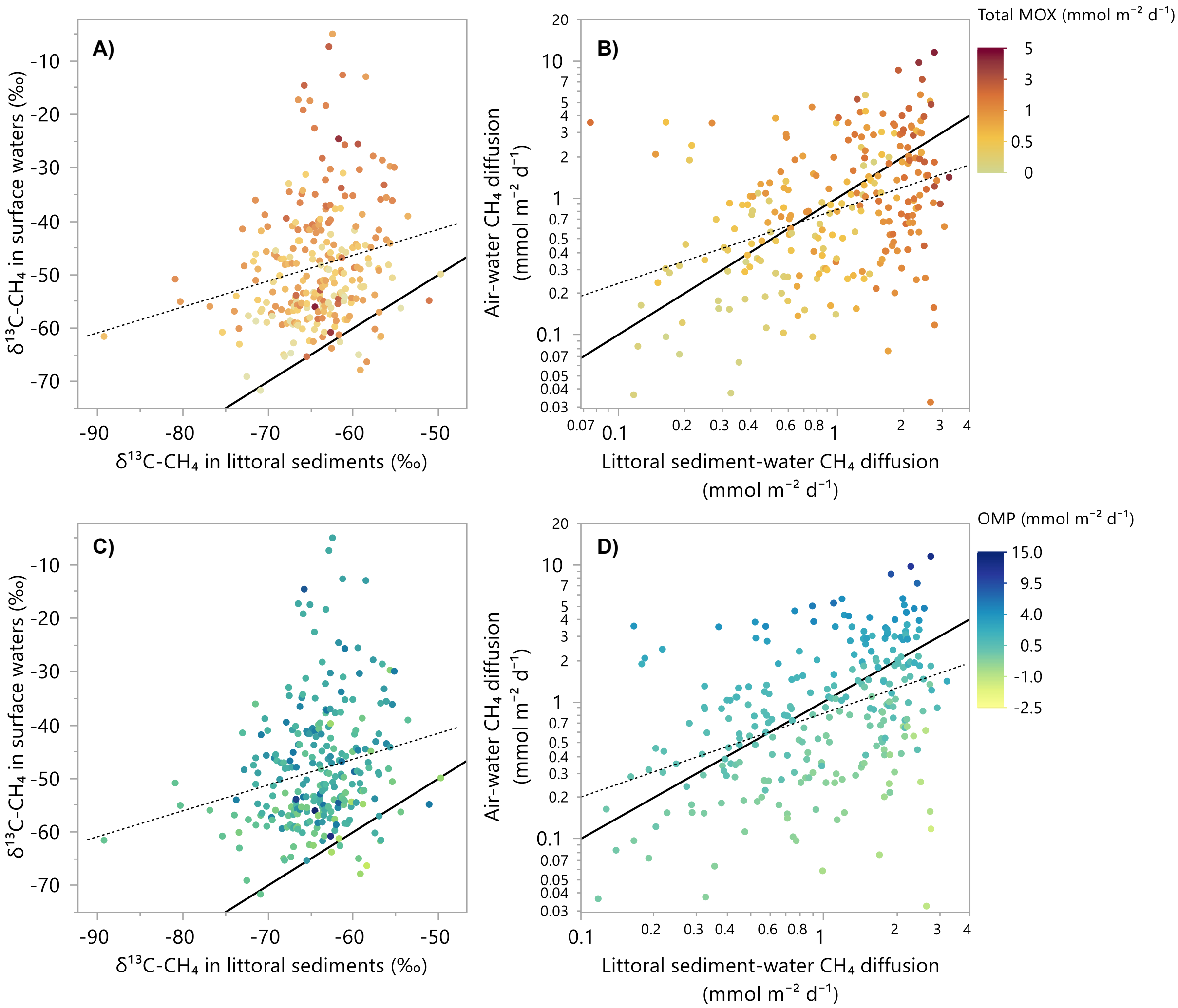
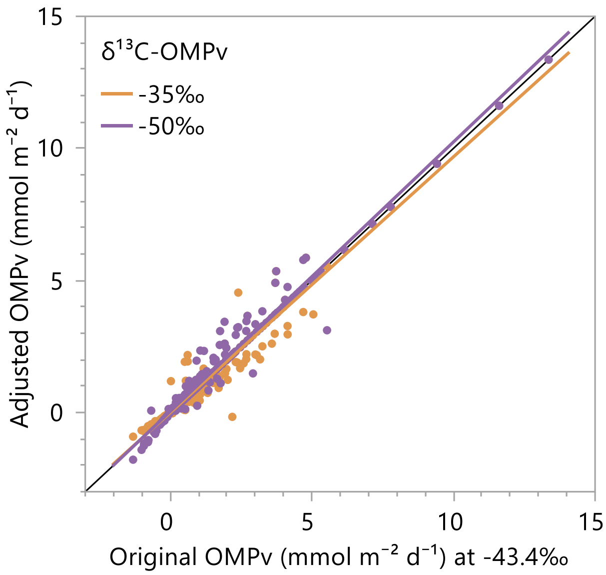


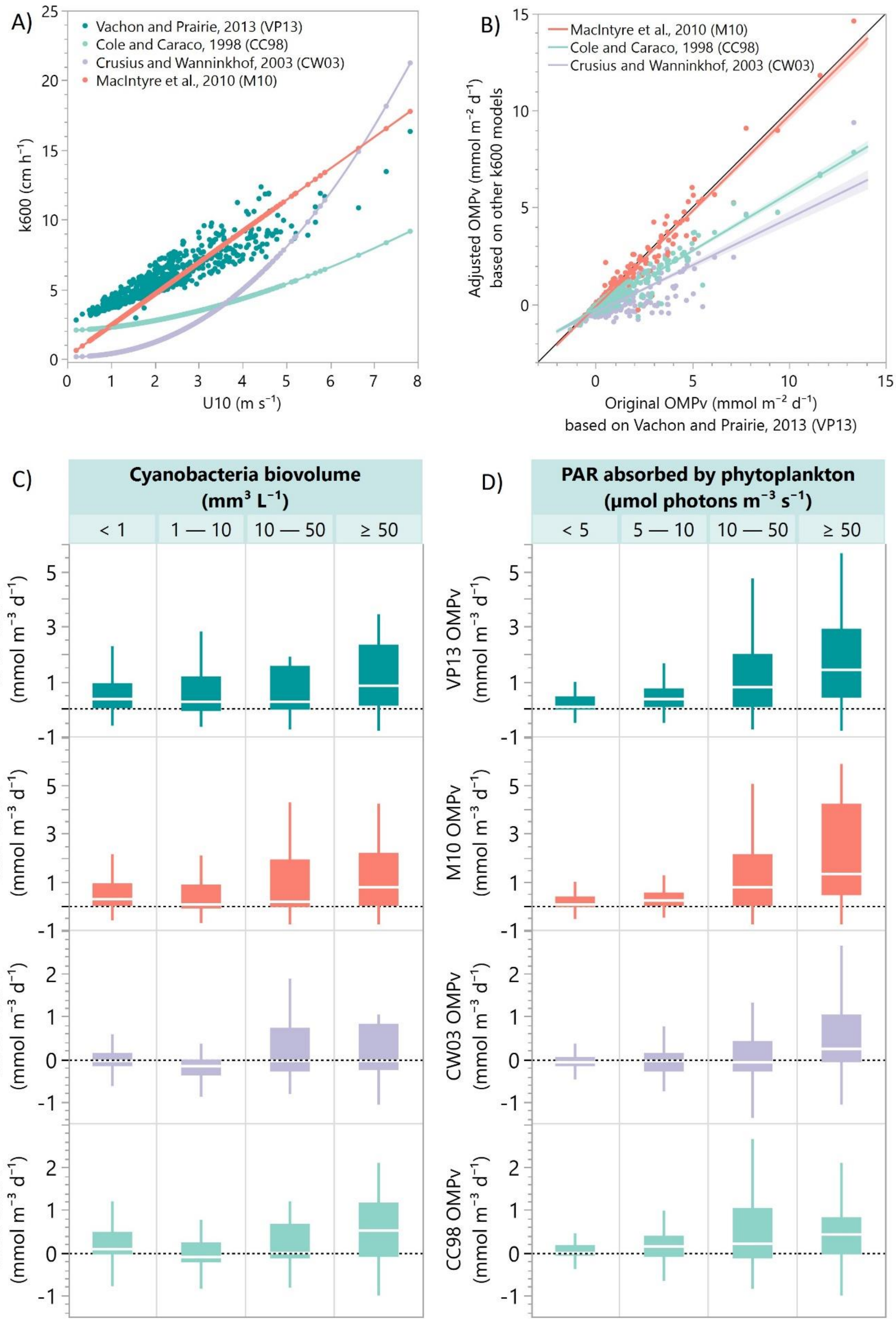
Supplementary Fig. 1 | Map of sampling lakes, covering 10 provinces and 2 territories (42°N to 69°N and 52°W to 141°W) across Canada. As part of the national-scale lakes assessment (NSERC Lake Pulse Project), a total of 663 lakes were sampled over three summers (2017 to 2019). Among them, OMPv rates were estimated in 260 lakes with complete CH_4-related measurements using our extended mass balance approach.



Supplementary Fig. 2 | In line with Fig 1 of main context, our mass balance-based estimates of **A)** total MOX and **B)** OMP further elucidate the quantitative mechanisms underlying the interplay between OMP and total MOX as a key control on diffusive CH_4 emissions to the atmosphere, beyond littoral sediment inputs.

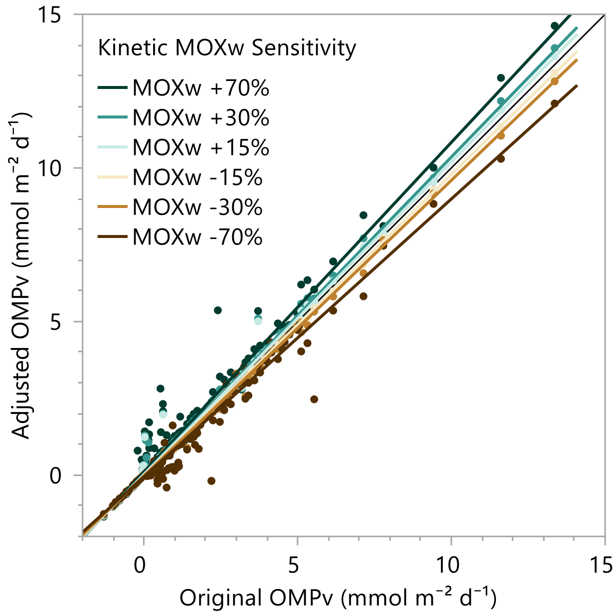


Supplementary Fig. 3 | Sensitivity analysis of our mass balance to potential variability in $\delta^{13}C_{OMP_V}$. The x-axis shows OMP_V estimates assuming $\delta^{13}C_{OMP_V}$ = -43.4‰ (literature average), while the y-axis shows corresponding estimates when $\delta^{13}C_{OMP_V}$ is adjusted to -35‰ and -50‰, respectively. The black line indicates the 1:1 line, while colored lines represent fitted regression line.

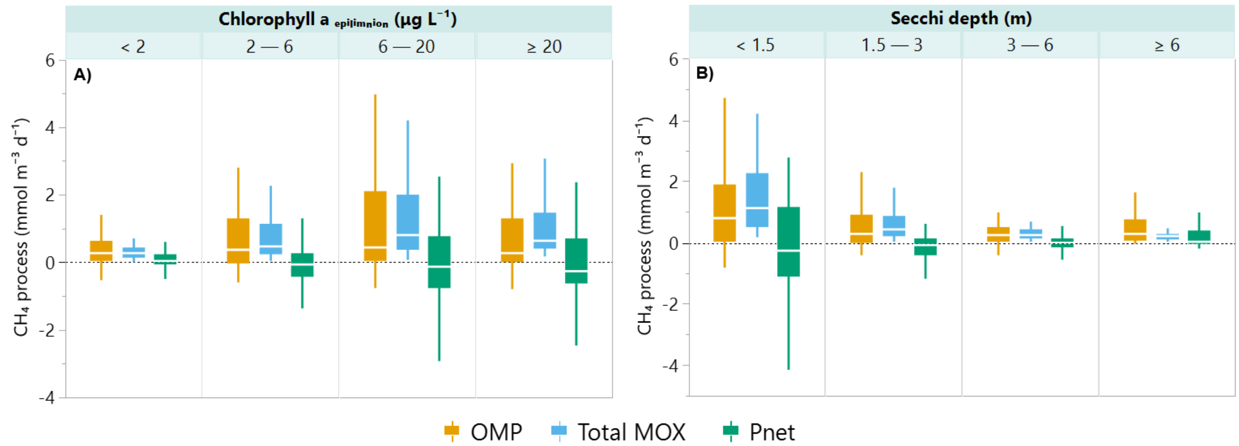


A)
Vachon and Prairie, 2013 (VP13)
Cole and Caraco, 1998 (CC98)
Crusius and Wanninkhof, 2003 (CW03)
MacIntyre et al., 2010 (M10)
k600 (cm h⁻¹)
U10 (m s⁻¹)
B)
MacIntyre et al., 2010 (M10)
Cole and Caraco, 1998 (CC98)
Crusius and Wanninkhof, 2003 (CW03)
Adjusted OMPv (mmol m⁻² d⁻¹) based on other k600 models
Original OMPv (mmol m⁻² d⁻¹) based on Vachon and Prairie, 2013 (VP13)
C)
Cyanobacteria biovolume (mm³ L⁻¹)
< 1
1 — 10
10 — 50
≥ 50
D)
PAR absorbed by phytoplankton (µmol photons m⁻³ s⁻¹)
< 5
5 — 10
10 — 50
≥ 50
VP13 OMPv (mmol m⁻³ d⁻¹)
M10 OMPv (mmol m⁻³ d⁻¹)
CW03 OMPv (mmol m⁻³ d⁻¹)
CC98 OMPv (mmol m⁻³ d⁻¹)

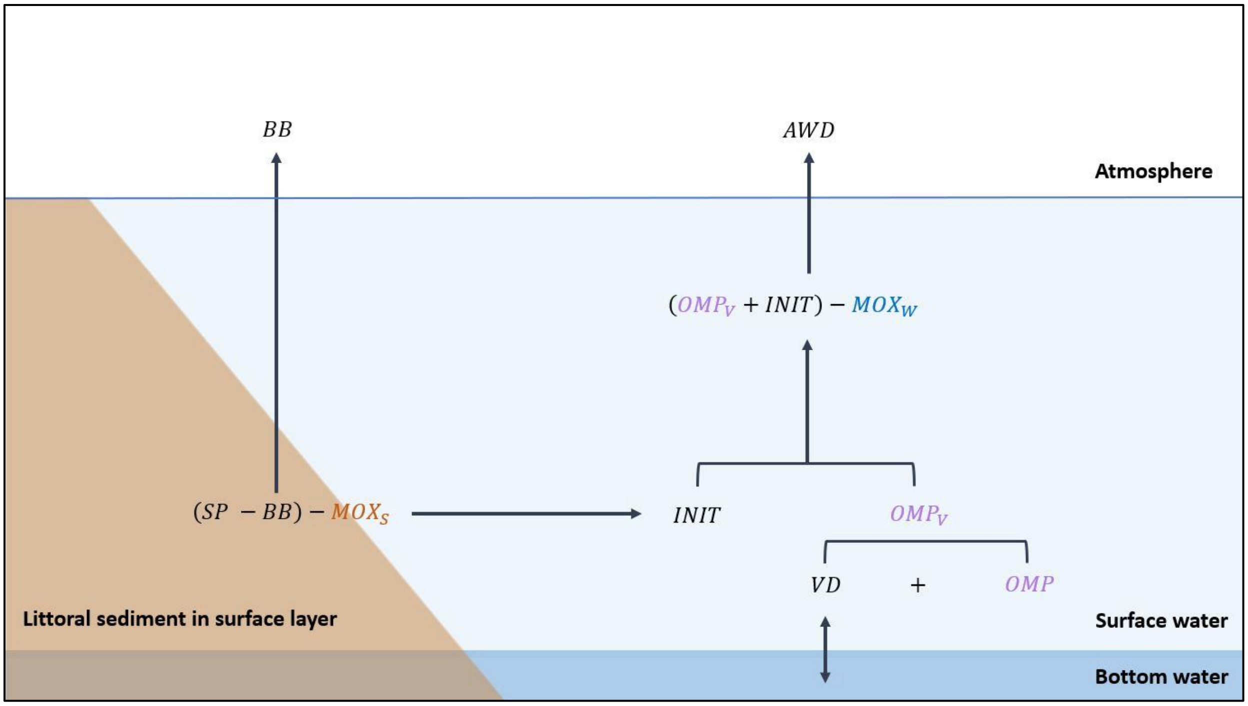
Supplementary Fig. 4 | Sensitivity analysis of our mass balance to potential variability in k_{600} models for AWD. **A)** The x-axis shows the average wind speeds at 10 m, and the y-axis shows the corresponding k_{600} derived from four different models: MacIntyre et al. (2010; based on eddy covariance estimates, mixed buoyancy-derived), Cole and Caraco (1998), and Crusius and Wanninkhof (2003) (both derived from wind speed based on SF_6 tracer experiments). The colored lines represent smoother fits **B)** The x-axis shows OMP_V estimates in this study using the k_{600} model derived from Vachon and Prairie (2013; based on lake size and wind speed). The y-axis shows estimates adjusted using the three alternative models. The black line indicates the 1:1 line, while colored lines represent fitted regression lines. **C)** Boxplots illustrate the variability in OMP_V derived from each model as a function of total biomass volume of cyanobacteria, and **D)** as a function of PAR absorbed by cyanobacteria and algae. Boxes show the 1st and 3rd quartile with the median (white line), whiskers extend to most extreme data point within 1.5 times the IQR from the box.



Supplementary Fig. 5 | Sensitivity analysis of our mass balance to potential variability in MOX_W. The x-axis shows OMP_V estimates assuming MOX_W derived from aerobic oxidation kinetics that integrate the effects of surface CH_4, O_2, and temperature, following Thottathil et al. (2019), while the y-axis shows corresponding estimates when MOX_W is adjusted to ±15%, ±30%, and ±70%, respectively. The black line indicates the 1:1 line, while colored lines represent fitted regression line.



Supplementary Fig. 6 | Boxplots illustrate the variability in $\boldsymbol{OMP_V}$, total MOX (as sum of $\boldsymbol{MOX_S}$ and $\boldsymbol{MOX_w}$), and $\boldsymbol{P_{net}}$ (all rates are normalized to surface-water volume) as a function of **A)** chlorophyll a (in µg L^{-1}) and **B)** Secchi depth (in m) in surface layers. Boxes show the 1st and 3rd quartile with the median (white line), whiskers extend to most extreme data point within 1.5 times the IQR from the box.



Supplementary Fig. 7 | Conceptual schematic of the extended mass balance approach. CH_4 mass balance components (in mol d^{-1}) in surface water and littoral sediment: sedimentary CH_4 production (SP), ebullitive CH_4 emission (BB), air-water diffusive CH_4 emission to the atmosphere (AWD), CH_4 oxidized at the sediment-water interface (MOXs), CH_4 oxidized in surface waters (MOXw), CH_4 reaching the water column after MOXs (INIT), vertical CH_4 diffusion between surface and bottom water layers (VD), oxic CH_4 production (OMP), and the net CH_4 as sum of OMP and VD (OMPv).

Detailed calculations to derive equation (11) in the extended mass balance approach

In the main context, equations (2) – (10) were then sequentially combined to derive an integrative function of the unknown MOX_S (i.e., equation (11)) as follows.

In equation (8), isolate the unknown $\delta^{13}C_{INIT}$.

SEq 1

$$\delta^{13}C_{INIT} = \left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000$$

In equation (10), $frac_{INIT}$ is the fraction of $INIT$ and defined as $\frac{INIT}{INIT + OMP_V}$. Then, substitute equation (7) into this,

SEq 2

$$frac_{INIT} = \frac{AWD + MOX_w - OMP_V}{AWD + MOX_w}$$

Substitute SEq 1 and SEq 2 into equation (10).

SEq 3

$$\delta^{13}C_{INIT+OMP} = \left(\frac{AWD + MOX_w - OMP_V}{AWD + MOX_w}\right) \times \left\{\left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000\right\}$$

$$+ \left(\frac{OMP_V}{AWD + MOX_w}\right) \times \delta^{13}C_{OMP_V}$$

Similarly, in equation (9), isolate the unknown $\delta^{13}C_{INIT+OMP_V}$.

SEq 4

$$\delta^{13}C_{INIT+OMP_V} = \frac{(\delta^{13}C_{SURF} + 1000)}{\left(\frac{OMP_V + INIT - MOX_w}{OMP_V + INIT}\right)^{\frac{1-\alpha}{\alpha}}} - 1000$$

Substitute equation (7) into SEq 4.

SEq 5

$$\delta^{13}C_{INIT+OMP_V} = \frac{(\delta^{13}C_{SURF} + 1000)}{\left(\frac{AWD}{AWD + MOX_w}\right)^{\frac{1-\alpha}{\alpha}}} - 1000$$

Let SEq 3 equal SEq 5.

SEq 6

$$\frac{(\delta^{13}C_{SURF} + 1000)}{\left(\frac{AWD}{AWD + MOX_w}\right)^{\frac{1-\alpha}{\alpha}}} - 1000$$

$$= \left(\frac{AWD + MOX_w - OMP_V}{AWD + MOX_w}\right) \times \left\{\left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000\right\}$$

$$+ \left(\frac{OMP_V}{AWD + MOX_w}\right) \times \delta^{13}C_{OMP_V}$$

Rearrange equation (2) as $AWD + MOX_W - OMP_V = SP - BB - MOX_S$. Then, substitute this into SEq 6.

SEq 7

$$\frac{(\delta^{13}C_{SURF} + 1000)}{\left(\frac{AWD}{AWD + MOX_w}\right)^{\frac{1-\alpha}{\alpha}}} - 1000$$

$$= \left(\frac{SP - BB - MOX_S}{AWD + MOX_w}\right) \times \left\{\left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000\right\}$$

$$+ \left(\frac{OMP_V}{AWD + MOX_w}\right) \times \delta^{13}C_{OMP_V}$$

In SEq 7, isolate the unknown OMP_V.

SEq 8

$$OMP_V = \left[\frac{\delta^{13}C_{SURF} + 1000}{\left(\frac{AWD}{AWD + MOX_W}\right)^{\frac{1-\alpha}{\alpha}}} - 1000 - \left(\frac{SP - BB - MOX_S}{AWD + MOX_W}\right) \cdot \left\{ \left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000 \right\} \right] \cdot \frac{AWD + MOX_W}{\delta^{13}C_{OMP_V}}$$

Rearrange equation (2) as $OMP_V = AWD +\ MOX_W - SP + BB + MOX_S$. Then, let this equal SEq 8.

SEq 9

$$AWD +\ MOX_W - SP + BB + MOX_S = \left[\frac{\delta^{13}C_{SURF} + 1000}{\left(\frac{AWD}{AWD + MOX_W}\right)^{\frac{1-\alpha}{\alpha}}} - 1000 - \left(\frac{SP - BB - MOX_S}{AWD + MOX_W}\right) \cdot \left\{ \left(\frac{SP - BB - MOX_S}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000 \right\} \right] \cdot \frac{AWD + MOX_W}{\delta^{13}C_{OMP_V}}$$

In the left-hand side of SEq 9, move all variables except MOX_S to the right-hand side. Then, finally it derives an integrative function as equation (11), in which $\boldsymbol{MOX_S}$ appears on both sides.

SEq 10 (i.e., equation (11) in the main manuscript)

$$\boldsymbol{MOX_S} = \left[\frac{\delta^{13}C_{SURF} + 1000}{\left(\frac{AWD}{AWD + MOX_W}\right)^{\frac{1-\alpha}{\alpha}}} - 1000 - \left(\frac{SP - BB - MOX_S}{AWD + MOX_W}\right) \cdot \left\{ \left(\frac{SP - BB - \boldsymbol{MOX_S}}{SP - BB}\right)^{\frac{1-\alpha}{\alpha}} \cdot (\delta^{13}C_{SED} + 1000) - 1000 \right\} \right] \cdot \frac{AWD + MOX_W}{\delta^{13}C_{OMP_V}} - AWD - MOX_W + (SP - BB)$$

Due to its nonlinear form, MOX_S can be solved numerically using an iterative method. Lastly, substituting the calculated MOX_S into equation (2) yielded OMP_V as

SEq 11 (i.e., equation (12) in the main manuscript)

$$OMP_V = AWD - (SP - BB) + MOX_S + MOX_W$$