Estimating phytoplankton $\delta^{13}C$ in aquatic systems

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Abstract:	Carbon stable isotope ratio ($\delta^{13}C$) is a tool widely used in aquatic biogeochemistry and ecology. Phytoplankton $\delta^{13}C$ deeply varies over time and space and is not easy to measure since phytoplankton cannot be sampled or extracted from the pool of particulate organic matter (POM) as 'pure' material. The present study aims at providing firstly an approach for estimating phytoplankton $\delta^{13}C$ in aquatic systems and secondly a set of equations useful for the tested systems. The basic assumption is that POM of low particulate organic carbon-to-chlorophyll a (POC:Chl a) ratio is phytoplankton-dominated and thus that $\delta^{13}C$ of POM of low POC:Chl a ratio is a good estimate of phytoplankton $\delta^{13}C$. Empirical models based on multi-regressions between $\delta^{13}C$ of phytoplankton-dominated POM and environmental parameters were performed. The tested parameters are classically measured in aquatic studies and have theoretical direct or indirect relationships with phytoplankton $\delta^{13}C$: POC, chlorophyll a, pheopigments, temperature, salinity, oxygen and pH. This approach was tested on 22 data sets from man-managed marshes and from riverine, estuarine and marine coastal systems of mid-latitudes. These systems exhibit a large diversity of physical, biogeochemical and ecological functioning. This empirical approach was successful in estimating phytoplankton $\delta^{13}C$ in the 20 data sets originating from the natural systems, but not in the two data sets originating from the man-managed marshes. The robustness of the method and the extrapolation of the models over time and space are discussed. This approach could be attempted in other environments as lakes and systems of low and high latitudes.

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Table 2: Results of the models and characteristics of the data sets.

Id	Data set	Uncertainty (/‰)		Model ($\delta^{13}C$ =) (/‰)	n(m)[3]	Outliers (av.±s.d.) (/‰)	POC:Chl *a* (g/g)	Salinity range	Time period of model validity
		Data[1]	Model[2]						
1	Côte	1.4	1.0	0.684 Ln([Chl *a*]) + 0.0603 (%O_2) – 28.4	64(4)	-25.2±1.9	≤ 200	33.1-34.7	Jan.-Dec.
	Large	1.4	1.2	0.901 Ln([Chl *a*]) – 21.9	52(2)	-24.6±0.8	≤ 200	33.9-35.3	Jan.-Dec.
	Côte+Large	1.4	1.1	0.504 Ln ([Chl *a*]) + 0.0613 (%O_2) – 28.1	116(6)		≤ 200	33.1-35.3	Jan.-Dec.
2	Eastern Bay of Seine	2.5	0.7	0.613 temp + 2.641 Ln([POC]) + 0.835 S – 73.7	26(0)		≤ 200	30.4-34.7	Apr., June, Oct.
3	Luc/Mer	1.3	0.8	0.146 temp + 0.547 Ln([Chl *a*]) + 4.39 pH – 59.5	64(8)	-23.3±1.0	≤ 200	30.5-33.8	Jan.-Dec.
4	Bizeux	1.1	0.8	1.430 Ln([Chl *a* + pheo]) – 23.7	43(2)	-26.4±1.7	≤ 200	33.6-35.3	March-Dec.
	Le Buron	0.9	0.6	1.228 Ln([Chl *a* + pheo]) – 23.3	10(2)	-27.1±0.8	≤ 200	34.5-34.8	Jan.-Oct.
	Cézembre	1.3	0.9	2.280 Ln([Chl *a* + pheo]) – 24.8	23(1)	-26.1	≤ 200	34.5-34.7	March-Sept.
	All 3 stations	1.1	0.8	1.523 Ln([Chl *a* + pheo]) – 23.8	76(5)		≤ 200	33.6-35.3	Jan.-Dec.
5	Astan	0.8	-	–22.9[4]	93(8)	-25.6±0.5	≤ 200	34.8-35.5	Jan.-Nov.
	Estacade	0.8	-	–22.3[4]	75(1)	-24.9	≤ 200	34.8-35.5	Jan.-Dec.
	Astan + Estacade	0.9	-	–22.6[4]	168(9)		≤ 200	34.8-35.5	Jan.-Dec.
6	Portzic	1.3	0.8	2.441 Ln([POC]) – 33.2	204(27)	-22.4±0.6	≤ 200	33.5-35.5	Jan.-Dec.
1, 3-6	English Channel	1.4	1.1	0.830 Ln([Chl *a* + pheo]) – 22.6	546(52)		≤ 200	30.4-35.5	Jan.-Dec.
7	Antioche	1.1	0.7	1.592 Ln([Chl *a*]) – 22.5	44(8)	-23.5±0.9	≤ 200	31.0-35.3	Jan.-Dec.
8	Bouée 13	0.95	0.87	1.006 Ln([Chl *a*]) – 22.4	63(6)	-22.8±0.8	≤ 200	32.0-35.5	Jan.-Dec.
	Eyrac	1.2	0.8	0.292 S + 1.341 Ln([Chl *a*]) – 31.9	88(0)		≤ 200	27.4-35.1	Jan.-Dec.
	Comprian	1.1	0.8	0.248 S + 1.336 Ln([Chl *a*]) – 30.2	71(2)	-24.5±0.2	≤ 200	23.1-34.8	Jan.-Dec.
	All 3 stations	1.1	0.9	0.169 S + 1.281 Ln([Chl *a*]) – 27.9	220(8)		≤ 200	23.1-35.5	Jan.-Dec.
7-8	Atlantic systems	1.1	0.9	1.378 Ln([Chl *a*]) – 22.4	280(16)		≤ 200	23.1-35.5	Jan.-Dec.
9	SOLA	1.0	-	-22.6[4]	26(0)		≤ 200	34.7-38.3	Jan.-Dec.
10	Frioul	1.1	0.9	0.113 temp + 0.634 [Chl *a* + pheo] – 25.2	50(0)		≤ 200	36.5-38.4	Jan.-Dec.
11	Point B	1.0	-	–23.8[4]	8(0)		≤ 200	37.6-38.2	Feb.-Apr.
9-11	Mediterranean systems	1.1	1.0	0.559 Ln([Chl *a*]) – 23.2	84(0)		≤ 200	34.7-38.4	Jan.-Dec.
1, 3-11	Coastal systems	1.3	1.0	0.047 temp + 0.945 Ln[Chl *a* + pheo] – 23.2	844(68)		≤ 200	23.1-38.4	Jan.-Dec.
12	Seine Estuary	2.5	0.3	0.250 S + 1.204 [POC] – 32.4	8(0)		≤ 200	0-25.7	Apr., June, Oct.
13	Gironde Estuary	2.8	1.2	$-5.98.10^{-3}$ S^2 + 0.626 S + 0.888 [pheo] – 35.7	40(0)		≤ 150	0-31.7	Apr.-Nov.
14	Loire River	1.2	0.7	0.0483 [Chl *a*] + 7.81 P_{pheo} – 32.2	33(0)		≤ 200	freshwater	Feb.-Nov.
15	Replenished marshes	2.2	-	-	-		≤ 150	freshwater	Jan.-Dec.
16	Unreplenished marshes	2.8	1.9	0.329 temp + 2.490 Ln([Chl *a*]) – 49.9	23(2)		≤ 110	freshwater	Feb.-Dec.

[1] standard deviation of measured data ($\delta^{13}C$ of phytoplankton-dominated POM). [2] standard deviation of the difference between model output (phytoplankton $\delta^{13}C$) and data. [3] n: number of data used for running the model; m: number of data excluded before running the model (outliers). [4] average of the measured data. POC: particulate organic carbon (µg/L); Chl *a*: chlorophyll *a* (µg/L); %O_2: concentration of dissolved oxygen expressed against the saturation concentration; temp: temperature (°C); pheo: pheopigments (µg/L); S: salinity; P_{pheo}: [pheo]/[Chl *a*+pheo]; av.: average; s.d.: standard deviation; -: no model was able to improve the uncertainty.