Appendix

The diffusion equation with zero-order reactor is

$$\frac{\partial^2 C}{\partial z^2} = \frac{1}{D}\frac{\partial C}{\partial t} + f(z,t) \qquad \textbf{(A.1)}$$

With starting profile C(z,0)=φ(z) for 0 ≤ z ≤ L, initial condition, and values C(0,t)=A(t) and C(L,t)=B(t) for t≥0, boundary conditions.

The Fourier expansion in sin(β_nz) has norm 2/L and sin(β_nL) is null in the zeroes β_nL=nπ, therefore, β_n=nπ/L.

From the Fourier series the solution results

$$C(z,t) = \sum_{n=1}^{\infty} C_n(t)\sin\frac{n\pi}{L}z \qquad \textbf{(A.2)}$$

With Fourier coefficients given by

$$C_n(t) = \frac{2}{L}\int_0^L dz C(z,t)\sin\frac{n\pi}{L}z \qquad \textbf{(A.3)}$$

For obtaining the coefficient C_n(t), we multiply both sides of the partial differential equation time (2/L)sin(nπz/L) and integrate in the interval 0 ≤ z ≤ L (Amerio, 1976).

We obtain, after integrating twice the second-order partial differential equation:

$$\frac{2}{L}\int_0^L dz\frac{\partial^2 C(z,t)}{\partial z^2}\sin\frac{n\pi}{L}z = \frac{2n\pi}{L^2}[A(t)-(-1)^n B(t)] - \frac{n^2\pi^2}{L^2}C_n(t)$$

Applying the rule of derivation under the integral sign, the other terms become

$$\frac{2}{DL}\int_0^L dz\left[\frac{\partial C(z,t)}{\partial t} - f(z,t)\right]\sin\frac{n\pi}{L}z = \frac{1}{D}\frac{dC_c}{dt} + f_n(t)$$

after the definition

$$f_n(t) = \frac{2}{L}\int_0^L dz f(z,t)\sin\frac{n\pi}{L}z$$

Thus, $C_n(t)$ satisfies the first-order linear differential equation

$$\frac{dC_n(t)}{dt} = -\frac{n^2\pi^2 D}{L^2}C_n(t) + \frac{2n\pi D}{L^2}[A(t) - (-1)^n B(t)] - Df_n(t)$$

And integrating with respect to the time

$$C_n(t) = e^{-t\frac{n^2\pi^2 D}{L^2}}\left\{H_n + D\int_0^t d\tau\left[\frac{2n\pi}{L^2}A(\tau) - (-1)^n\frac{2n\pi}{L^2}B(\tau) - f_n(\tau)\right]e^{\tau\frac{n^2\pi^2 D}{L^2}}\right\}$$

For the initial concentation

$$C_n(t=0) = H_n$$

and for the initial condition

$$C_n(t=0) = \frac{2}{L}\int_0^L dz\varphi(z)\sin\frac{n\pi}{L}z = \frac{2}{L}\varphi_L$$

we obtain the expression

$$C_n(t) = \frac{2}{L}e^{-t\frac{n^2\pi^2 D}{L^2}}\int_0^L dz\varphi(z)\sin\frac{n\pi}{L}z + D\int_0^t d\tau\left\{\frac{2n\pi}{L^2}[A(\tau) - (-1)^n B(\tau)] - f_n(\tau)\right\}e^{(\tau-t)\frac{n^2\pi^2 D}{L^2}}$$

that gives the solution of the equation A.1 under the given conditions.

For every time t, the explicit solution is

$$C(z,t)=\sum_{n=1}^{\infty} C_n(t)\sin\frac{n\pi}{L}z=$$

$$=\frac{2}{L}\sum_{n=1}^{\infty} e^{-t\frac{n^2\pi^2 D}{L^2}}\sin\frac{n\pi}{L}z\left\{\int_0^L dz\varphi(z)\sin\frac{n\pi}{L}z+D\int_0^t d\tau\left[\frac{n\pi}{L}A(\tau)-(-1)^n\frac{n\pi}{L}B(\tau)-\int_0^L dzf(z,\tau)\sin\frac{n\pi}{L}z\right]e^{\tau\frac{n^2\pi^2 D}{L^2}}\right\}$$

and represents the evolution of the second 2.1 example.

For long-term evolution, the steady-state concentration solution of this expression, asymptotically attained and maintained by the ecosystem.

For obtaining it, we limit the summation behaviour

$$\sum_{n=1}^{\infty} e^{-tn^2\pi^2 D/L^2}\sin\frac{n\pi}{L}z$$

substituting as unitary the sinus coefficients

$$\sum_{n=1}^{\infty} e^{-tn^2\pi^2 D/L^2}\sin\frac{n\pi}{L}z\le\sum_{n=1}^{\infty} e^{-tn^2\pi^2 D/L^2}$$

This inequality is valid for all the sinus values.

$$\sum_{n=1}^{\infty} e^{-tn^2\pi^2 D/L^2}=$$

$$=e^{-t\pi^2 D/L^2}+e^{-t4\pi^2 D/L^2}\sum_{n=2}^{\infty} e^{-t(n-2)(n+2)\pi^2 D/L^2}=$$

$$=e^{-t\pi^2 D/L^2}+e^{-t4\pi^2 D/L^2}\left(1+\sum_{n=3}^{\infty} e^{-t(n-2)(n+2)\pi^2 D/L^2}\right)$$

Taking into account that for α>β it follows

$$e^{-\alpha}<e^{-\beta}$$

and that for n>3 it results

$$n^2-4\ge(n-1)^2$$

The final inequality is

$$\sum_{n=1}^{\infty} e^{-tn^2\pi^2 D/L^2} \sin\frac{n\pi}{L} z \leq$$
$$\leq e^{-t\pi^2 D/L^2} + e^{-t4\pi^2 D/L^2}\left(1+\sum_{n=3}^{\infty} e^{-t(n-1)^2\pi^2 D/L^2}\right)$$

The second-member series in the inequality is convergent as it follows from the D'Alembert criterion that

$$\frac{a_{n+1}}{a_n} = \frac{e^{-tn^2\pi^2 D/L^2}}{e^{-t(n-1)^2\pi^2 D/L^2}} = e^{-t(2n-1)\pi^2 D/L^2} \rightarrow 0$$

for n going to infinity. Thus, the starting series is convergent toward the first-order term of a time-negative exponential function, a first-order infinitesimal of the time step plus a quartic-order infinitesimal of the same time function.

The renewal of the variable *C(z,t)* after the period $t+\Delta t$ is

$$C(z,t+\Delta t) = \frac{2}{L} e^{-t\pi^2 D/L^2}(1-\Delta t\pi^2 D/L^2)\sin\frac{\pi}{L} z\left\{\varphi_L + \int_0^t d\tau(1+\Delta t\pi^2 D/L^2)e^{\tau\pi^2 D/L^2}\left[\frac{\pi D}{L}A(\tau)+\frac{\pi D}{L}B(\tau)-\frac{L}{2}f_1\right]\right\}$$

with both factors at first-order approximation in the time increment.

The cross-product term with $(\Delta t)^0$ gives C(z,t)

$$\frac{2}{L} e^{-t\pi^2 D/L^2} \sin\frac{\pi}{L} z\left\{\varphi_L + \int_0^t d\tau e^{\tau\pi^2 D/L^2}\left[\frac{\pi D}{L}A(\tau)+\frac{\pi D}{L}B(\tau)-\frac{L}{2}f_1\right]\right\} = C(z,t)$$

Finally, the cross-product terms in $(\Delta t)^2$ are of higher-order infinitesimals and therefore not giving contributions to this first order approximation.

Thus, the time increment at first order $(\Delta t)^1$ gives

$$-\frac{2}{L}e^{-t\pi^2 D/L^2}\ \Delta t\pi^2 D/L^2 \sin\frac{\pi}{L}z\left\{\varphi_L+\int_0^t d\tau e^{\tau\pi^2 D/L^2}\left[\frac{\pi D}{L}A(\tau)+\frac{\pi D}{L}B(\tau)-\frac{L}{2}f_1\right]\right\}=-\Delta t\pi^2 DC(z,t)/L^2$$

multiplying the starting value times the coefficient $-\pi^2 D/L^2$.

Finally, the second first-order term $(\Delta t)^1$ multiplies the time integrated terms

$$\frac{2}{L}e^{-t\pi^2 D/L^2}\ \sin\frac{\pi}{L}z\left\{\int_0^t d\tau\Delta t\pi^2 D/L^2 e^{\tau\pi^2 D/L^2}\left[\frac{\pi D}{L}A(\tau)+\frac{\pi D}{L}B(\tau)-\frac{L}{2}f_1\right]\right\}=\Delta t\,\pi^2 D\underline{C_S(z,t)}/L^2$$

giving the stationary solution, $C_S(z,t)$, times the coefficient $\Delta t\pi^2 D/L^2$ and independent of the initial condition that does not contribute to this term also.

Defining $C(z)=\lim C_S(z,t)$, the first-order approximation in $(\Delta t)^1$ is obtained as the long-term solution for $t>>L^2/\pi^2 D$, given in the text,

$$C(z,t+\Delta t)=C(z,t)+\Delta t(\pi^2 D/L^2)\underline{C}-\Delta t(\pi^2 D/L^2)C(z,t)$$

We consider that the system starts at an initial homogeneous concentration, $C(z,0)=C_0$, and that $f(z,t)=-S/LD$.

The steady-state solution of the time-independent partial differential equation with sum of all internal sources and sinks, S in mmol C m^{-3} s^{-1}, b.e. primary production vertically integrated along the layer, considered in the following constant in time, and with time-independent boundary concentrations A and B is

$$D\frac{\partial^2 C}{\partial z^2}+\frac{S}{L}=0$$

Thus, in this notation

$$f(z,t)=f=-\frac{S}{LD}$$

The general solution is

$$C(z)=-\frac{S}{2DL}z^2+az+b$$

and a and b result

$$a=\frac{B-A}{L}+\frac{S}{2D}$$
$$b=A$$

Substituting these values, the stationary solution is

$$C(z)=-\frac{S}{2DL}z^2+(\frac{B-A}{L}+\frac{S}{2D})z+A$$

On the other hand, the long-term Fourier integration requires the term f_n which is

$$f_n=\frac{2}{L}\int_0^L(-\frac{S}{LD})\sin\frac{n\pi}{L}zdz=$$
$$=-\frac{2S}{L^2D}\int_0^L\sin\frac{n\pi}{L}zdz=$$
$$=\frac{2S}{n\pi LD}(-\cos\frac{n\pi}{L}z)\Big|_0^L=\frac{2S}{n\pi LD}[(-1)^n-1]$$

The solution, considering $t \gg L^2/D\pi^2$, is the series summation

$$C(z,t)=\sum_{n=1}^{\infty} e^{-\frac{n^2\pi^2 Dt}{L^2}} \frac{2C_0}{n\pi}[1-(-1)^n]+\sum_{n=1}^{\infty}(1-e^{-\frac{n^2\pi^2 Dt}{L^2}})\left(\frac{2}{n\pi}A-\frac{2}{n\pi}(-1)^n B-\frac{2LS}{n^3\pi^3 D}((-1)^n-1)\right)\sin\frac{n\pi}{L}z$$

where C_0 is the homogeneous initial condition, and A, B, S are the boundary condition at the top of the layer, the boundary condition at the bottom of the layer, the vertically integrated sum of all sources and sinks in the layer, respectively. The first series does no contribute for long-term integration; the other three series give the following positive contributions to the asymptotic concentration:

a) First Term

$$\sum_{n=1}^{\infty}\frac{2A}{n\pi}\sin\frac{n\pi}{L}z=$$

$$=\frac{2A}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\frac{n\pi}{L}z=$$

$$=\frac{2A}{\pi}\frac{\pi-\frac{\pi z}{L}}{2}=A-\frac{Az}{L}$$

b) Second Term

$$-\sum_{n=1}^{\infty}\frac{2B}{n\pi}(-1)^n\sin\frac{n\pi}{L}z=$$

$$=\frac{B}{\pi}\sum_{n=1}^{\infty}\frac{2(-1)^{1+n}}{n}\sin\frac{n\pi}{L}z=$$

$$=\frac{B}{\pi}\frac{\pi z}{L}=\frac{Bz}{L}$$

c) Third Term

$$\sum_{n=1}^{\infty}(-\frac{L^2}{n^2\pi^2}f_n)\sin\frac{n\pi}{L}z=$$

$$=\frac{2LS}{\pi^3 D}\sum_{n=1}^{\infty}\frac{1}{n^3}[1-(-1)^n]\sin\frac{n\pi}{L}z=$$

$$=\frac{4LS}{\pi^3 D}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^3}\sin\frac{(2n-1)\pi}{L}z=$$

$$=\frac{4LS}{\pi^3 D}\frac{\pi}{8}\frac{\pi z}{L}(\pi-\frac{\pi z}{L})=\frac{Sz}{2D}(1-\frac{z}{L})$$

Grouping all power terms of the spatial variable z, we obtain q.e.d., the asymptotic solution

$$C(z,t)=C(z)=A-\frac{Az}{L}+\frac{Bz}{L}+\frac{Sz}{2D}(1-\frac{z}{L})=$$
$$=-\frac{S}{2DL}z^2+(\frac{B-A}{L}+\frac{S}{2D})z+A$$

This is equal to the steady-state solution obtained without the time-derivative term in the partial differential equation.

The difference with respect to the text expression is given by the substitution of π/2 in the place of π in the above solution, because the orhogonal functions in this Appendix are given as an half-period and, on the other hand, as a quarter-period in the text solution for the two consistent boundary condition: due to the two different and consistent boundary conditions, i.e. a couple of Dirichlet conditions here with respect to mixed, Dirichlet-Neumann conditions in the text.

Explicitly, in the first 2.1 example the transformation of the diffusive term is after integration along z

$$\frac{2}{L}\int_0^L dz\frac{\partial^2 C(z,t)}{\partial z^2}\sin\frac{z(2n-1)\pi}{2L}=$$
$$=(-1)^{n+1}\frac{2}{L}\frac{F(t)}{\phi D}-\frac{(2n-1)\pi}{L^2}\int_0^L dz\frac{\partial C(z,t)}{\partial z}\cos\frac{(2n-1)\pi}{2L}z$$

Integrating the second time along z we obtain

$$\frac{2}{L}\int_0^L dz\frac{\partial^2 C(z,t)}{\partial z^2}\sin\frac{(2n-1)\pi}{2L}z =$$

$$=(-1)^{n+1}\frac{2}{L}\frac{F(t)}{\phi D}+\frac{(2n-1)\pi}{L^2}A(t)-\frac{(2n-1)^2\pi^2}{4L^2}C_n(t)$$

And, writing the solution in terms of C_n, we obtain

$$C(z,t)=\sum_{n=1}^{\infty}C_n(t)\sin\frac{(2n-1)\pi}{2L}z=$$

$$=\frac{2}{L}\sum_{n=1}^{\infty}e^{-t\frac{(2n-1)^2\pi^2 D}{4L^2}}\sin\frac{(2n-1)\pi}{2L}z\left\{\int_0^L dz\varphi(z)\sin\frac{(2n-1)\pi}{2L}z+D\int_0^t d\tau\left[\frac{(2n-1)\pi}{2L}A(\tau)+(-1)^{n+1}\frac{F(\tau)}{\phi D}-\int_0^L dzf(z,\tau)\sin\frac{(2n-1)\pi}{2L}z\right]e^{\tau\frac{(2n-1)^2\pi^2 D}{4L^2}}\right\}$$

Using the same notation, but in the 2.2 conditions and in the first 2.1 example, we obtain the asymptotic solution

$$C(z)=-\frac{S}{2DL}z^2+\frac{S}{D}z+\frac{F}{\phi D}z+A$$

With air-sea concentration A and inflowing flux from the bottom of the layer *F*. As in the above-solved Dirichlet case, *S* is the sum of all the sources and sinks in the layer, taking into account the thickness *L* of the layer and its porosity *Φ*, with the diffusion *D* in the layer.

Plate 1. Position of the **CO_2-GEO** scheme in the geochemical matrix; vertical displacements of the different model zones are shown in the three different environments: atmosphere, sea water column and benthos, top-down air-sea-sediment; relevant processes and research activities are cited next to each zone. **CO_2-GEO** topics concern the time and space variability of gas concentrations in benthic habitats and the description of the evolution of the sediment: in the aerobic zone, with the biological uptake of carbon, nitrogen, phosphorus, silica, and the oxidation of methane; in the sulfate and nitrate anaerobic reducing zone, with the methanotrophic processes; in the anaerobic carbonate reducing zone, with methanogenetic processes. The Systems Model subtasks consist in four top-down segments: Air-Sea Carbon Fluxes, Photic Zone Ecology, Bottom Boundary Layer Description, Sediment Geochemistry.

<table>
<tr><th>TOPICS
PHASES</th><th>ZONES</th><th>PROCESSES</th><th colspan="2">ACTIVITIES</th></tr>
<tr><td>AIR</td><td>TROPOSPHERE</td><td>AIR-SEA CARBON FLUXES</td><td colspan="2" rowspan="2">Fluxes developed exploiting and extending results from the European Union MTP Projects</td></tr>
<tr><td rowspan="2">SEA</td><td>PHOTIC ZONE</td><td>NATURAL COUPLING OF CO_2 AND NUTRIENT CYCLES</td></tr>
<tr><td>BOTTOM BOUNDARY LAYER</td><td>TIME AND SPACE VARIABILITIES OF GAS CONCENTRATION IN BENTHOS HABITAT</td><td>BBL</td><td rowspan="4">INTEGRATED HERE THROUGH CO_2-GEO</td></tr>
<tr><td rowspan="3">SEDIMENT</td><td>AEROBIC ZONE</td><td>BIOLOGICAL UPTAKE OF C, N, P, Si</td><td>OXIC</td></tr>
<tr><td>SULFATE REDUCING ZONE</td><td>METHANOTROPHY:
$SO_4^{2-} + CH_4 \rightarrow H_2O + HS^- + HCO_3^-$</td><td>REDOX</td></tr>
<tr><td>ANAEROBIC ZONE</td><td>METHANOGENESIS:
$CO_2 + 4H_2 \rightarrow CH_4 + 2\ H_2O$</td><td>ANOXIC</td></tr>
</table>

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The foreground, called CO_2-GEO as a background carbon model in the oceanographic 2-phase geochemistry of a later European Union project, has been defined and verified in first-order contexts by the technical details given here in the Appendix. The contents not fully developed before, here from Fig. 3 to Fig. 13, are attributable only to this work including the Appendix, as a spin-off of the European Union 240837 - Research into Impacts and Safety of CO_2 Storage.
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Abstract

The dynamics of the aquatic ecosystem requires a thorough knowledge of the chemical and physical parameters in both the water column and the sediment. The constitutive equations of the former subsystem solve diffusion and transport processes in three-dimensional domains; the latter is described by one-dimensional and nonlinear differential equations whose solution strongly depends on slower diffusion parameters.

An evolution method, CO2-GEO, which minimises the squared deviation between the exact evolution and the consistent prediction with the transformation method, is developed and verified to estimate the single-layer evolution and the three-layer sediment description based on the diffusion parameters in the porewater. The method is generic and is extended here to the trophic behaviour of carbon dioxide and methane.

References

Amerio, L., 1976. Analisi matematica con elementi di analisi funzionale: Volume II. Tamburini Masson Editori, Centro Grafico Linate, Milano, IT, 503–538.

Blackford, J. C., 2002. The Influence of Microphytobenthos on the Northern Adriatic Ecosystem: A Modelling Study. Est. Coast. Shelf Sci., 55(1), 109–123.

Boetius, A., Ravenschlag, K., Schubert, C. J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B. B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature, 407, 623–626.

Boudreau, P. B., 1996. A method-of-lines code for carbon and nutrient diagenesis in aquatic sediments. Comp. Geosci., 22(5), 479–496.

Brandes, J. A., Devol, A. H., Deutsch, C., 2007. New Developments in the Marine Nitrogen Cycle. Chem. Rev., 107(2), 577–589.

Crispi, G., Pacciaroni, M., Viezzoli, D., 2006. Simulating biomass assimilation in a Mediterranean ecosystem model using SOFA: setup and identical twin experiments. Ocean Sci., 2(2), 123–136.

Gaidos, E., Dubuc, T., Dunford, M., McAndrew, P., Padilla-Gamiño, J., Studer, B., Weersing, K., Stanley, S., 2007. The Precambrian emergence of animal life: a geobiological perspective. Geobiology, 5(4), 351–373.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., Vörösmarty, C. J., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry, 70(2), 153–226.

Ebenhöh, W., Kohlmeier, C., Radford, P. J., 1995. The benthic biological submodel in the European Regional Seas Ecosystem Model. Neth. J. Sea Res., 33(3/4), 423–452.

Herndl, G. J., Peduzzi, P., Fanuko, N., 1989. Benthic community metabolism and microbial dynamics in the Gulf of Trieste (Northern Adriatic Sea). Mar. Ecol. Prog. Ser., 53, 169–178.

Luff, R., Moll, A., 2004. Seasonal dynamics of the North Sea sediments using a three-dimensional coupled sediment–water model system. Cont. Shelf Res., 24(10), 1099–1127.

Peng, T.-H., Takahashi, T., Broecker, W. S., Olafsson, J., 1987. Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North Atlantic surface water: observations and a model. Tellus, 39(B5), 439–458.

Ruardij, P., Van Raaphorst, W., 1995. Benthic nutrient regeneration in the ERSEM ecosystem model of the North Sea. Neth. J. Sea Res., 33(3/4), 453–483.

Vichi, M., Oddo, P., Zavatarelli, M., Coluccelli, A., Coppini, G., Celio, M., Fonda Umani, S., Pinardi, N., 2003. Calibration and validation of a one-dimensional complex marine biogeochemical flux model in different areas of the northern Adriatic shelf. Ann. Geophys., 21(1), 413–436.

Van Cappellen, P., 2004. Biomineralization and Global Biogeochemical Cycles. Rev. Mineral. Geochem., 54(1), 357–381.

Wanninkhof, R., 1992. Relationship Between Wind Speed and Gas Exchange Over the Ocean. J. Geoph. Res., 97(C5), 7373–7382.