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NOTES AND CORRESPONDENCE

A Three End-Member Mixing Model Based on Isotopic Composition and Elemental Ratio

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ABSTRACT

A three end-member mixing model based on nitrogen isotopic composition and organic carbon to nitrogen ratio of suspended particulate matter in an aquatic environment has been developed. Mathematical expressions have been derived for the calculation of the fractions of nitrogen or organic carbon originating from three different sources of distinct isotopic and elemental compositions. The model was successfully applied to determine the contributions from anthropogenic wastes, soils and bedrock-derived sediments to particulate nitrogen and particulate organic carbon in the Danshuei River during the flood caused by Typhoon Bilis in August 2000. The model solutions have been expressed in a general form that allows applications to mixtures with other types of isotopic compositions and elemental ratios or in forms other than suspended particulate matter.

(Key words: Carbon isotope, Particulate organic matter, Typhoon flood, Danshuei River, Taiwan)

1. INTRODUCTION

Geochemical properties, such as isotopic compositions and elemental concentrations, are often used to determine contributions of materials from different sources. Two end-member mixing models based on one geochemical variable, such as carbon or nitrogen isotopic composition, are most widely used (e.g., Shultz and Calder 1976; Kao et al. 2006). Three end-

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member mixing models based on two geochemical variables, such as carbon and nitrogen isotopic compositions or various radio-nuclides, are also in common use (e.g., Phillips 2001). Recently, a four end-member mixing model based on three radio-nuclide concentrations has been used to delineate the geochemical properties of different types of source materials (Li 2005).

In this study, a three end-member mixing model based on the δ^{15}N value and the organic carbon to nitrogen ratio in SPM is presented. Because inorganic carbon is effectively removed from particulate materials in the pretreatment of samples for chemical analysis, the carbon determined is referred to as particulate organic carbon (POC) in this study. By contrast, the inorganic nitrogen that may exist in mineral phases of the particulate materials, albeit in minute amounts, cannot be effectively removed; therefore, the nitrogen analyzed is referred to as particulate nitrogen (PN) in this study. The POC to PN ratio is referred to as the C/N ratio for brevity.

The three end-member mixing model of this study was established for water borne SPM in the Danshuei River collected under flooding conditions caused by Typhoon Bilis in 2000 (Chen et al. 2001). Because typhoon induced floods are responsible for a majority of riverine discharge of terrigenous organic matter from the small mountainous watersheds of Taiwan (Kao and Liu 1996), it is desirable to better understand the sources of materials in the river load. The major terrestrial sources of POC and PN in the Danshuei River have been identified as anthropogenic wastes, soils and bed-rock derived sediments (Liu et al. 2007). The range of the $\delta^{13}C_{POC}$ values (-24.9 ~ -23.8‰) observed during the flood was quite narrow, whereas the $\delta^{15}N_{PN}$ values (-2.7 ~ +3.0‰) and the C/N ratios (7.2 ~ 11.3) are more variable. Therefore, the latter two geochemical variables were chosen for the modeling exercise.

Although the δ^{13}C and δ^{15}N values and the C/N ratio have often been used to indicate the origin of materials (e.g., Andrews et al. 1998; Middelburg and Nieuwenhuize 1998), the contributions from different sources have not been quantified by mean of a multiple end-member mixing model based on the C/N ratio and any of the isotopic compositions. The model has been applied to trace the origins of particulate organic matter (POM) in the Danshuei Estuary (Liu et al. 2007). In this note, the derivation of the mathematical expressions of the model is reported and an example is given to illustrate the usefulness of the model. The limitations of the model and the uncertainties of the model results are also presented.

2. DERIVATION OF THE MODEL

The model is based on mass balance equations for POC and PN in SPM originating from the afore-mentioned three sources. First the mass balances for the two elements are established:

$$N = N_1 + N_2 + N_3 \quad , \tag{1}$$

$$C = C_1 + C_2 + C_3 \quad , \tag{2}$$

where C and N represent PN and POC, respectively in the sample and the subscripts represent the three different sources. The C/N ratio of the sample is expressed as:

$$r = C/N \quad . \tag{3}$$

The fraction of PN originating from each source is denoted as follows:

$$f_i = N_i/N \quad . \tag{4}$$

Equation (2) may be re-written as follows:

$$C = r_1N_1 + r_2N_2 + r_3N_3 \quad , \tag{5}$$

where r_i represents the C/N ratio of the material from the i^{th} source. Then the C/N ratio may be expressed as:

$$r = (r_1N_1 + r_2N_2 + r_3N_3)/N \quad , \tag{6}$$

which can be reduced to:

$$r = f_1r_1 + f_2r_2 + f_3r_3 \quad . \tag{7}$$

The mass balance equation for the isotope ^{15}N in PN, designated as M, is as follows:

$$M = M_1 + M_2 + M_3 \quad . \tag{8}$$

It is noted that $N = {}^{14}N + {}^{15}N \approx {}^{14}N$, because ^{15}N accounts for only about 0.36% of nitrogen in the air (Nier 1950). Modifying the definition,

$$\delta^{15}N = \left[\left({}^{15}N/{}^{14}N\right)_{sam} \Big/ \left({}^{15}N/{}^{14}N\right)_{air} - 1\right] \times 1000 \quad ,$$

one gets the approximate expression for the $\delta^{15}N$ value of the sample as follows:

$$\delta \approx \left[(M/N)/R_{air} - 1\right] \times 1000 \quad . \tag{9}$$

Then Equation 8 can be expressed as:

$$M = \left[N_1(1+\delta_1/1000) + N_2(1+\delta_2/1000) + N_3(1+\delta_3/1000)\right] R_{air} \quad , \tag{10}$$

where δ_i represents the $\delta^{15}N$ value of the PN from the i^{th} source. Plugging the above relation into Equation 9 results in the following:

$$\delta = \left[N_1 \left(1000 + \delta_1 \right) + N_2 \left(1000 + \delta_2 \right) + N_3 \left(1000 + \delta_3 \right) \right] \Big/ N - 1000 \quad , \tag{11}$$

which can be reduced to:

$$\delta = f_1 \delta_1 + f_2 \delta_2 + f_3 \delta_3 \quad . \tag{12}$$

Then the fraction of PN originating from each source may be solved from the set of simultaneous equations, namely, Equations 7 and 12 and the following:

$$1 = f_1 + f_2 + f_3 \quad . \tag{13}$$

The nitrogen-based fraction of each end-member may be calculated as follows:

$$f_1 = \left[Q \left(r - r_2 \right) - \left(\delta - \delta_2 \right) \right] \Big/ \left[r \left(r_3 - r_2 \right) - \left(\delta_3 - \delta_2 \right) \right] \quad , \tag{14}$$

$$f_3 = \left(\delta - \delta_2 \right) / \left(\delta_1 - \delta_2 \right) - f_1 \left(\delta_3 - \delta_2 \right) / \left(\delta_1 - \delta_2 \right) \quad , \tag{15}$$

$$f_2 = 1 - f_1 - f_3 \quad . \tag{16}$$

The parameter, Q, is defined as follows:

$$Q = \left(\delta_1 - \delta_2 \right) / \left(r_1 - r_2 \right) \quad . \tag{17}$$

It is noted that end-members 1 and 2 must be chosen such that they have different C/N ratios and $\delta^{15}N_{PN}$ values. For carbon-based fractions (g), the following relationship may be used for the conversion:

$$g_i = f_i \cdot r_i / \Sigma_i (f_i \cdot r_i) \quad , \tag{18}$$

where i denotes the i^{th} end-members.

3. APPLICATION TO THE DANSHUEI RIVER

The model has been applied to the time-series dataset obtained during the invasion of Typhoon Bilis between 22^{nd} and 31^{st} of August 2000 by intensive sampling on the Chung-Yang Bridge over the Danshuei River. The sampling and analytical methods and the results have been reported in detail previously (Chen et al. 2001). The time-series of observed

$\delta^{15}N_{PN}$ values and C/N ratios are shown in Fig. 1. The abrupt rise of the C/N ratio and $\delta^{15}N_{PN}$ value coincided with the rapid increase in discharge rate from about 200 to 3000 m^3 s^{-1}.

The concentrations of POC and PN peaked at 4325 and 420 μM, respectively, corresponding to the peak flow. The C/N ratio increased sharply from around 7.5 to 11.3 in the flooding phase and fluctuated between 7.2 and 11 in the receding phase. The carbon isotopic composition of POC fluctuated between δ^{13}C values of -24.9‰ and -23.8‰ with no clear

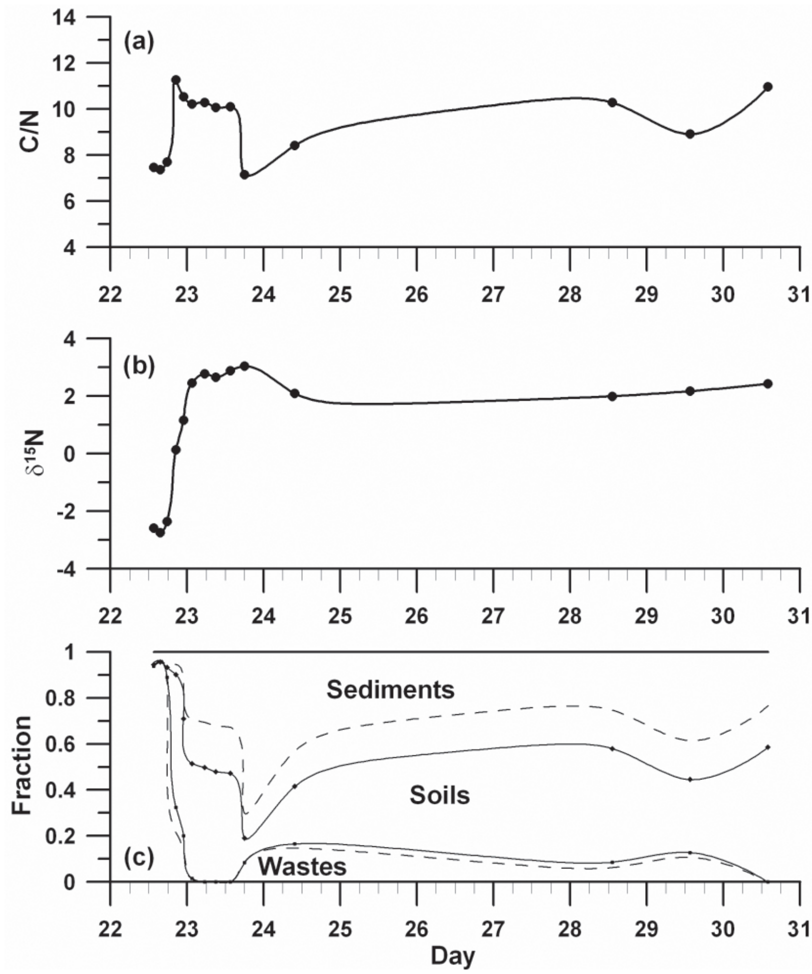

Fig. 1. Time-series plots of (a) C/N ratio and (b) δ^{15}N observed during the invasion of Typhoon Bilis in August 2000. The abscissa shows the date. (c) The solid curves indicate the fractions of particulate nitrogen attributed to the three major sources: anthropogenic wastes, soils and bedrock derived sediments. The dashed curves indicate the fractions of particulate organic carbon.

trend (not shown). By contrast, the $\delta^{15}N$ value of PN increased sharply from -2.5‰ to +3‰ responding to the flood. When the flood subsided, the $\delta^{15}N$ value of PN persisted for one day and then dropped slightly to +2‰ and remained nearly constant in the post-typhoon condition. Both POC and PN concentrations dropped dramatically after peak flow, but stayed at levels of 400 - 1500 μM for POC and 75 - 140 μM for PN. These levels were generally higher than the normal range of 500 μM or less for POC and 70 μM or less for PN, while the discharge rate fluctuated between 500 and 1000 $m^3 s^{-1}$ (Chen et al. 2001), which was 3 - 5 times above the mean level.

During typhoon floods, the allochthonous sources dominated POC and PN in the river (Liu et al. 2007). Most data points fall within or near the domain defined by the mixing of the three end-members, which is depicted by the triangle in Fig. 2. The properties of the end-members (Table 1) are adopted from observed or derived values reported in previous studies (Kao and Liu 2000; Liu et al. 2007). A discussion of the selection of end-member properties is given in the Concluding Remarks.

For any sample that has a composition outside of the triangular domain defined by the three end-members (Fig. 2), the model generates a negative value for one of the fractions. Such conditions could be caused by non-uniform end-member compositions or uncertainties in the measurements. The negative values produced from the model were all quite small in magnitude with an average value of -0.02. For those samples that produced negative fractions, we re-did the calculation using only the end-members with non-negative fractions in the fashion of a two end-member mixing model.

The contributions from the three sources to the PN during the passage of Typhoon Bilis over northern Taiwan were calculated by means of the three end-member mixing model presented above. The results are quite interesting (Fig. 1c). The anthropogenic wastes, which are the predominant source of POC and PN under non-typhoon conditions (Liu et al. 2007), accounted for about 95% of PN in the Danshuei River at the beginning of the flood brought about by Typhoon Bilis. In fact, this very high contribution from anthropogenic wastes was above the average (87%) of the non-typhoon conditions (Liu et al. 2007). The recorded discharges were above 300 $m^3 s^{-1}$ (Chen et al. 2001), which was considerably higher than the average discharge. This phenomenon suggests that the first wave of typhoon rain probably washed down a large amount of anthropogenic wastes from land. When the flood rose further, the anthropogenic wastes were rapidly washed away and the supply could not keep up. The abrupt increase in POC and PN were attributed to soils and bed-rock derived sediments washed down from the upstream watershed. During flooding conditions, the combined fractions of soils and sediments account for more than 80% of PN. The plot of organic carbon based fractions indicates that soils dominated the contributions to POC under flood conditions. This is conceivable in light of exacerbated soil erosion during typhoon flooding and the high C/N ratio in soil organics.

In the late afternoon on August 23, there occurred an insurgence of sediments' contribution to the PN reaching a maximum fraction of 0.8 (Fig. 1), suggesting an enhanced downstream transport of resuspended sediments from the upstream river channel. More studies are warranted to further investigate the meaning of the time-varying contributions from different sources in sediment transport during flood conditions.

4. CONCLUDING REMARKS

The ideal condition for the successful application of the model is the uniformity in compositions of source material. In reality, materials from any single source could have a range of compositions. For instance, the soil profiles in northern Taiwan often show varying isotopic

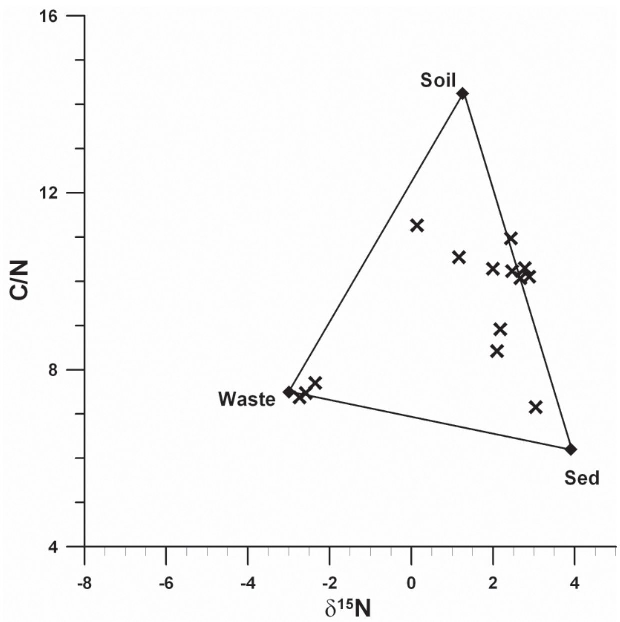

Fig. 2. Plot of C/N ratio vs. $\delta^{15}N_{PN}$ value observed in the Danshuei Estuary. The triangle represents the field covered by the mixing of the three major end-members, for which the three end-member mixing model was developed.

Table 1. Properties of end-members.

End-members	**Observed $\delta^{15}N_{PN}$ (‰)**	**Adopted $\delta^{15}N_{PN}$ (‰)**	**Observed C/N**	**Adopted C/N**	**Data sources**
Bed-rock derived sediments	3.9 ± 0.1	3.9	5.8 ± 0.5	6.2	Kao and Liu (2000)
Soils	-0.0 ± 1.3	1.25	13.6 ± 4.5	14.25	Kao and Liu (2000)
Anthropogenic wastes	-3.0 ± 0.1	-3.0	8.0 ± 1.4	7.5	Liu et al. (2007)

compositions of POC and PN (S. J. Kao, unpublished data). Non-uniformity in composition may result in errors in the estimated results. For selection of an end-member composition, the optimal choice is to pick the actual average composition of materials coming out of a common source. For limited observations, it is often difficult to accurately determine the true mean value. For this study, the end-member compositions were determined as the set of compositions that fulfill two criteria: (1) Each of the three end-member compositions falls within one standard deviation of the observed or derived mean values of materials originating from the source; and (2) The observed compositions of the majority of mixtures fall within the domain defined by the three end members or very close to the domain such that the differences are within one standard deviation of the analytical uncertainty.

It is noted that the compositions of the soil and sediment end-members adopted in this study (Table 1) are based on results of soil and sediment samples collected from the Lanyang Hsi watershed and the the Fushan Experimental Forest (Kao and Liu 2000), which is in the headwaters of one major tributary of the Danshuei River. Because of the juxtaposition of the two catchment basins we assume that their soils and bedrock-derived sediments are similar in composition. However, future study is warranted to check the validity of this assumption.

It has been tested how selection of the end-member properties may alter the results of the calculation. For the nitrogen based fractions, a change of the $\delta^{15}N_{PN}$ value of any end-member by 0.5‰ may result in changes in the fractions by 0.07 or less; a change of the C/N ratio of any end-member by 0.5 may result in changes in the fractions by 0.06 or less.

Because all measured values are subject to uncertainties associated with the analytical methods as well as random error. The estimated error associated with the nitrogen isotopic analysis was ±0.2‰ (Chen et al. 2001). The estimated error associated with the elemental analysis was ±5%, which may result in a mean error of ±0.7 in the C/N ratio. It has been examined how errors in the measured values may alter the results of the calculation. For the nitrogen based fractions, a change of the $\delta^{15}N_{PN}$ value of a sample by 0.2‰ may result in changes in the fractions by 0.03 or less; a change of the C/N ratio of any end-member by 0.7 may result in changes in the fractions by 0.08 or less.

Although the model is based on the $\delta^{15}N$ value and C/N ratio in SPM, it may be applied to systems with other combination of biochemical properties, such as the $\delta^{13}C$ value and N/C ratio, or the $\delta^{34}S$ value and C/S ratio. The sample can be in forms other than SPM, such as sediments in aquatic environments, soils in terrestrial environments or even solutions. For solutions, the geochemical properties could be $\delta^{13}C_{DIC}$ and X/DIC ratios, where X could be any solute species, such as chloride or calcium ions.

It is cautioned that the model is only applicable to systems with three end-members each of which is rather uniform in composition. If the composition of an end-member does not remain constant strictly, the model is still useful for cases that have a rather constant mean composition for the end-member in question. In addition, any two of the end-members should have at least one tracer composition sufficiently different from each other; i.e., the difference should be significantly greater than the standard deviation of the compositional measurement of that tracer. If end-members with highly variable compositions, such as the autochthonous POM from the river-estuary-coastal system, are present in significant amounts, the model would not be useful. Aside from the typhoon conditions presented in this report, it has been demonstrated that the model is applicable for highly polluted waters in the Danshuei Estuary, where anthropogenic wastes dominant the system (Liu et al. 2007).

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