

ACTIONS CONCERTÉES EN OcéANOGRAPHIE

RAPPORT D'ACTIVITÉ

1978

ANNEXE N° 12

Distribution of microbial metabolisms in natural environments  
displaying gradients of oxydo-reduction conditions

Colloque International CNRS  
 Biogéochimie de la Matière Organique  
 à l'Interface eau-sédiment marin.  
 Marseille 25-27 avril 1979.

*Distribution of microbial metabolisms in natural environments displaying gradients of oxidation-reduction conditions.*

55487

---

Gilles BILLEN and Suzanne VERBEUSTEL, Lab. d'Océanographie, University of Brussels, 50, av. F.-D. Roosevelt 1050 Brussels (Belgium).

Résumé : Distribution des métabolismes microbiens dans les milieux naturels présentant un gradient de conditions d'oxydo-réduction.

Du point de vue de l'écologie bactérienne, la présence d'un gradient de conditions d'oxydo-réduction dans les couches supérieures des sédiments marins constitue l'une des caractéristiques principales de cet habitat. Le potentiel d'oxydo-réduction peut être considéré à la fois comme le résultat de l'activité microbiologique, et comme un facteur déterminant quel type de métabolisme microbien se déroule dans un milieu donné. Ces deux points de vue sont adoptés successivement pour illustrer, par des exemples concrets choisis dans les sédiments marins et dans l'estuaire de l'Escaut, une théorie générale de la relation entre métabolisme bactérien et potentiel d'oxydo-réduction du milieu.

## I. INTRODUCTION.

The knowledge of the microbial metabolisms occurring in the upper layers of marine sediments is of prime importance for the understanding of the fate of organic material at the water-sediment interface.

From the point of view of microbial ecology, the presence of a sharp gradient of oxidation-reduction conditions in the upper layers of the sediments is one of the most striking characteristics of this habitat. Other environments, however, also displays such redox gradients : heavily polluted rivers are an exemple. In this paper we will compare results obtained in marine sediments on the one hand and in the Scheldt estuary

on the other hand, concerning the distribution of microbial metabolisms in the redox gradients exhibited by this two environments, as an illustration of a general theory on the relation between microbial metabolisms and redox potential of the medium.

In order to clarify the discussion, the basic classification of non photosynthetic microbial metabolisms is summarized in Table I, from the point of view of redox transformations.

Table I.:

(chemo)organotrophic (or heterotrophic) metabolisms	(chemo)lithotrophic metabolisms
<p><u>(organic)respiration:</u>            exoenergetic oxidation of a reduced substrate, S red</p> $\underline{S \text{ red} + O_x \rightarrow S_{ox} + Red;}$ <p>S red = organic</p>	<p><u>(mineral)respiration :</u>            exoenergetic oxidation of a reduced substrate, S red</p> $\underline{S \text{ red} + O_x \rightarrow S_{ox} + Red;}$ <p>S red = mineral</p> <p>eg : <math>Mn^{++}</math> ; manganioxidation  <math>NH_4^+</math>, <math>NO_2^-</math> ; nitrification  <math>Fe^{++}</math> ; ferrooxidation  <math>HS^-</math> ; sulfooxidation  <math>CH_4</math> ; methaneoxidation  <math>H_2</math> ; hydrogen oxidation</p> <p>at the expense of a mineral oxidant taken up from the external medium :</p> <p>eg : <math>O_2</math> : aerobic respiration  <math>MnO_2</math> : manganireduction )  <math>NO_3^-</math> : denitrification )  <math>Fe(OH)_3</math> : ferroreduction ) anaerobic  <math>SO_4^{--}</math> : sulfatoreduction ) respirations</p> <p><math>CO_2</math> : methane production</p>
<p><u>Fermentations :</u>            exoenergetic rearrangement of an organic substrate without intervention of an external oxidant(1)</p> $\underline{S \text{ red} \rightarrow S' \text{ red}}$	

(1) Excepted when molecular hydrogen is produced during the fermentation. This case present some, more than formal, analogy with respiratory metabolisms, of which it could represent a primitive form(Cray and Gest, 1965).

The concept and measurement of redox potential in natural environments have been discussed by several authors (Baas Becking et al, 1960; Stumm, 1966; Thorstenson, 1970; Billen, 1976). It has been stressed that a redox potential can be univocally defined in natural medium because an internal thermodynamic equilibrium is not far from being reached within the subsystem formed by the main mineral redox couples susceptible to be used in energy yielding metabolisms of microorganisms.

So defined, the value of the redox potential can be viewed either as the result of microbial activity, as far as respiratory metabolisms consume oxidants from the medium, or as a factor determining which kind of microbial metabolisms can occur.

These two points of view will be successively adopted in the following presentation.

## II. Bacterial activity as the cause of redox gradients in sediments and in rivers.

When the sum of all respiratory metabolisms in a given medium - expressed as a rate of oxidant consumption - is higher than the rate of import of oxidant to this medium, the redox potential decreases. The process resemble a redox titration of the oxidants of the medium by the organic matter initially present, conducted at the rate of overall respiratory activity. The opposite occurs when the rate of oxidants import exceed the rate of respirations.

This idea has been applied for relating total heterotrophic activity, its geographical and seasonal variations, to redox profiles in marine sediments (Wollast & Billen, unpublished) and in the Scheldt estuary (Billen et al, 1976). Using the assumption that an internal redox equilibrium exists for the mineral redox couples, the distribution of all redox species have been calculated by this model.

## III. Redox conditions as determinant of bacterial metabolisms.

The free energy change associated with the oxidation of a particular reduced substrate by an oxidant depends on the availability of this oxidant, in the medium, ie on the Eh (Billen, 1976).

In the case of mineral substrates, this dependance determines a critical value of the Eh under which the oxidation of these substrates is not more exoenergetic, and thus the corresponding chemolithotrophic metabolisms are

impossible. This limitation will be illustrated by observations concerning the zones of occurrence of nitrification in marine sediments and in the Scheldt estuary.

In situ rate of nitrification as been determined by aid of dark C<sup>14</sup> bicarbonate incorporation with and without addition of a specific inhibitor of nitrification (Billen, 1976; Somville, 1978).

In both environments, nitrification is shown only to occur above a certain Eh limit. Moreover, the predictable seasonal variations of the redox gradient results in variations in the distribution of the nitrifying activity.

Oxidation of organic compounds, on the other hand, is exoenergetic in the whole range of Eh encountered in natural media so that chemoorganotrophic metabolisms are always possible. Their energy yield, however, is lower at lower Eh. (This last point can be illustrated by data about the growth yield of heterotrophic bacteria obtained by measurement of incorporation and respiration of several organic substrates in various environments).

Fermentative metabolisms, having for only result a reorganization of the organic substrate, without modification of its gross redox level, are, from a thermodynamic point of view, quite insensitive to redox conditions. It is generally thought, however, that oxygen toxicity toward most fermentative bacteria, or competition between fermentative and respiratory metabolisms, result in the quasi-complete absence of fermentative metabolisms in aerobic conditions.

Data, collected both in marine sediments and in the Scheldt estuary, about concentration and rate of microbial utilization of fermentation products (lactate, acetate, ethanol ...), show that this is not necessarily true. For understanding the pathways of organic matter degradation in various oxidation-reduction conditions, these data can offer a promising approach.

#### IV. References :

- BAAS BECKING, LGM, KAPLAN, IR & MOORE, D, 1960 - Limits of the natural environment interm of pH and Eh. J. Geol. 68, 243-284.
- G. BILLEN - A method for evaluating nitrifying activity in sediments by dark C<sup>14</sup> bicarbonate incorporation. Water Research. 10, 51-57 (1976).
- G. BILLEN - The dependance of the various kinds of microbial metabolisms on the redox state of the medium. Communication

présentée au SCOR/UNESCO workshop on the biogeochemistry of estuarine sediments. Melreux, 29 nov.-3 déc. 1976.

- G.BILLEN, J. SMITZ, M. SOMVILLE & R. WOLLAST - Dégénération de la matière organique et processus d'oxydo-réduction dans l'estuaire de l'Escaut. Rapport de synthèse, projet "Mer". Vol. 10. J.C. NIHOUL et R. WOLLAST, éd. pp. 102-152. (1976).
- M. SOMVILLE, 1978 - A method for the measurement of nitrification rates in water. Water Research 12, 843-848.
- W. STUMM, 1966 - Redox potential as an environmental parameter : conceptual significance and operational limitation. Proc. Int. Water Pollution Res. Conf. (3rd, Munich) 1, 283-308.
- D.C. THORSTENSON, 1970 - Equilibrium distribution of small organic molecules in natural waters. Geochim. Cosmochim. Acta 34, 745-770.