Université de Bourgogne
Ecole Doctorale Environnement - Santé - STIC (E2S)

Mémoire pour l'obtention de
l'Habilitation à Diriger des Recherches (HDR)

PRODUCTION ET TRANSFERT DE CARBONE DANS LES HYDROSYSTEMES : APPROCHES SPATIO-TEMPORELLES MULTI-ECHELLES

Philippe AMIOTTE SUCHET

Présenté le 4 décembre 2009

devant le jury composé de :

Jean-François DECONINCK, Professeur à l' Université de Bourgogne,
Biogéosciences, Dijon - rapporteur

Jacques MUDRY, Professeur à l' Université de Franche Comté,
Chrono-environnement, Besançon - rapporteur

Michel MEYBECK, Directeur de Recherche au CNRS,
Sisyphe, Paris- rapporteur

Jean-Luc PROBST, Directeur de Recherche au CNRS,
Ecolab, Toulouse,- examinateur

Christian FRANCE-LANORD, Directeur de Recherche au CNRS,
CRPG, Nancy - examinateur

UMR Biogéosciences 5561, CNRS-Université de Bourgogne
Décembre 2009

Imagine *a science-based civilization far distant in the Galaxy that had built an interferometer of such resolving power that it could analyse the chemical composition of our atmosphere. Simply from this analysis, they could confidently conclude that Earth, alone among the planets of the Solar System, had a carbon-based life and an industrial civilization. They would have seen methane and oxygen coexisting in the upper atmosphere, and their chemists would have known that these gases are continually consumed and replaced. The odds of this happening by chance inorganic chemistry are very long indeed. Such persistent deep atmospheric disequilibrium reveals the low entropy characteristic of life. They would conclude that ours was a live planet — and the presence of CFCs in the atmosphere would suggest an industry unwise enough to have allowed their escape.*

James Lovelock
Gaia: The living Earth
Nature 426, 769-770, december 2003

Avant-propos

La recherche est une aventure, scientifique et collective. En septembre 1996, Michel Campy me souhaitait la bienvenue à l'UFR des Sciences de la Terre et Francis Andreux m'accueillait dans la toute petite équipe qu'il venait de créer. Elle s'appelait GéoSol – Géochimie des Interfaces Eau-Sol. Quel beau nom et surtout quelle bonne idée ! Débarquant d'une unité propre du CNRS à Strasbourg, grouillant de chercheurs, d'ingénieurs et de techniciens, il m'a fallut un (petit j'espère) temps d'adaptation à cette équipe, dont les contours extérieurs furent vite circonscrits, mais recelant d'insoupçonnables ressources à l'intérieur. Participer à la croissance et à la vie de GéoSol fut une aventure passionnante, enrichissante… et parfois épuisante.

J'avais débarqué donc, avec la ferme intention de poursuivre jusque dans ses derniers retranchements ce carbone, dont j'avais méticuleusement quantifié les apports fluviaux aux océans pendant 6 ans, en me demandant comment il était fabriqué. En fait de derniers retranchements, il s'agissait simplement (croyais-je) du sol et des matières organiques qu'il abrite. GéoSol, par les thèmes qu'elle abordait, était donc le bon endroit pour le faire. Je crois avoir avancé, et si cela a pu paraître laborieux, c'est que la chose est diablement complexe. J'en serais d'ailleurs resté au stade « zéro » sans des collègues compétents, impliqués et un peu obsédés par ces matières organiques informes et ingrates, résistantes à l'interrogatoire musclé, voire à la torture. Cela a été un réel plaisir de travailler avec Jean Lévèque (le maître bourreau), Marie-Jeanne Milloux (qui tient la hache), Catherine Hénault (le venoject® est son instrument préféré), Sylvie Dousset (et ses « cochonneries ») Fabrice Mona (qui nous a lâché, mais on ne lui en veut pas) et Olivier Mathieu (le rejeton). J'ai évolué avec l'équipe, aux grés des vents et des marées, contre lesquelles il a fallu parfois souquer ferme, d'un EPST (l'INRA) à l'autre (le CNRS).

Mais le principal était bien d'avancer dans cette quête passionnante de la connaissance des cycles biogéochimiques à l'échelle planétaire. Même si cette thématique n'apparaissait pas toujours prioritaire lorsque l'équipe était associée à l'INRA, j'ai toujours eu la liberté et les moyens de la poursuivre ; et puis l'INRA ouvrait d'autres perspectives du coté de la microbiologie. J'espère que ce mémoire démontrera la nécessité de constituer des équipes pluri-disciplinaire autour de la connaissance des cycles biogéochimiques. J'avouerai cependant me sentir plus à l'aise au sein de l'UMR Biogéosciences, et plus particulièrement de l'équipe SEDS, dont les objectifs scientifiques sont plus en phase avec les miens. Et puis j'ai enfin pu me laisser embarquer par Jeff (Buoncristiani) vers ses glaciers (enfin, ceux que l'on voit vraiment, pas les calottes Ordoviciennes).

Je tiens à rappeler ici que le métier d'enseignant-chercheur c'est aussi des missions de formation. Loin de me détourner de la recherche, l'enseignement est très souvent pour moi une ouverture que je trouve bénéfique au travail de recherche, et qui a le mérite de me maintenir un peu les pieds sur Terre. Mais si on pouvait juste en faire un petit peu moins… ? Et comme pour la recherche, il y a, derrière les filières d'enseignement une aventure collective enthousiasmante. J'en profite pour faire un petit coucou à Jean-Paul Loreau, auprès de qui j'ai beaucoup appris en trop peu de temps. Les autres, trop nombreux, me pardonneront de ne pas les citer ici. Sachez juste que les pauses café, les sorties labo (tiens ça fait longtemps) et… les séances de travail à VTT … je n'aurais pas pu faire sans.

Et puis on y est quand même ! La voici cette HDR, cette exception scientifique française que le monde entier nous envie. On peut se douter, vu la lenteur avec laquelle la chose s'est mise en place, que cela n'a pas forcément été une partie de plaisir. J'espère avoir pris soin cependant d'y mettre les formes pour que sa lecture soit aisée, pas trop rébarbative, et pas trop longue pour qui

laissera les publications de coté. Cette souffrance toute relative est très largement compensée par le très grand plaisir que j'éprouve à compter parmi les membres du jury cinq personnalités scientifiques dont j'admire les travaux et le parcours. Je les présenterai par « ordre d'entrée en scène ». Le premier est Jacques Mudry, que j'ai rencontré pour la première fois en 1987, alors que, étudiant en licence, j'assistais à la soutenance de sa thèse d'Etat à Besançon sur les «Apports du traçage physico- chimique naturel à la connaissance hydro- cinématique des aquifères carbonatés ». Ce fut mon premier vrai contact avec cette thématique que je n'ai plus quittée depuis. Un an plus tard, Jean-Luc Probst m'initiait concrètement à la recherche au cours de mon stage de Maîtrise, puis de DEA, puis encore en thèse de Doctorat. On comprendra que le personnage m'a marqué (et c'est un euphémisme), dans le bon sens du terme puisqu'il est encore là. C'est peu de dire qu'il m'a beaucoup appris. J'en profite pour rappeler que c'est à Strasbourg, dans l'équipe d'Yves Tardy, dont Jean-Luc fut le pilier, que la notion de « consommation de CO_2 par érosion chimique », passée aujourd'hui dans le langage courant du géologue, fut propagée en France. C'est au cours de mon année de DEA que j'ai fait la connaissance de Michel Meybeck, dont la thèse d'Etat trônait telle une bible (Jean-Luc l'avait fait reproduire et relier avec couverture cartonnée en 3 exemplaires à usage exclusif de l'équipe) sur le bureau des stagiaires. Autant dire que, lorsque j'ai raccompagné Michel à la gare à la suite du jury de thèse auquel il venait de participer à Strasbourg, j'étais un peu comme un « petit beur » des quartiers Nord de Marseille se retrouvant en tête à tête avec Zidane. La rencontre avec Christian France-Lanord est arrivée beaucoup plus tard, à l'occasion d'un colloque d'abord (mais je ne sais plus lequel) peu après ma thèse de Doctorat. J'apprécie sa vision planétaire des processus d'érosion et sa capacité à utiliser les outils géochimiques les plus fins à l'échelle continentale. Jean-François Deconinck est probablement le plus éloigné thématiquement de mes travaux. Ce fut son initiative que de proposer aux géologues évadés du coté de l'INRA, de rejoindre Biogéosciences et de rassembler au sein d'une même équipe, des sédimentologues intéressés par les paléo-environnements et des géochimistes travaillant sur l'environnement actuel. Les deux groupes se rencontrent sur le thème des transferts, et je crois que les pistes développées dans cette HDR ont la possibilité de consolider ces axes naissants.

Si il est une vertu à conférer à l'HDR, c'est bien d'amener le candidat à s'interroger, au cours d'une courte pause, sur les fondements de son activité scientifique et à vérifier qu'elle contribue, même modestement, à améliorer l'état de la Connaissance. J'espère que ce mémoire aura permis cela.

La recherche est une aventure scientifique, collective, et humaine donc. Mais elle ne vaut pas la vie. Merci à mes quatre Amours de partager tout cela et de me donner plus encore.

SOMMAIRE

DOSSIER SCIENTIFIQUE

1 Curriculum Vitae

Nationalité Française, Marié, 3 enfants

Coordonnées professionnelles :
UMR 6351 Biogéosciences – CNRS Université de Bourgogne
6 bd Gabriel, 21000 Dijon
tél. 33 3 80 39 39 71 – fax 33 3 80 39 63 87
philippe.amiotte-suchet@u-bourgogne.fr

1.1 Situation administrative

Maître de Conférence à l'Université de Bourgogne, UFR des Sciences de la Terre et de l'Environnement

Attaché à l'UMR 6351 Biogéosciences, CNRS-Université de Bourgogne

Bénéficiaire de la Prime d'Encadrement Doctoral et de Recherche (PEDR) depuis 1999

1.2 Diplômes et formation

1994 Doctorat de l'Université Louis Pasteur de Strasbourg, spécialité Géochimie, Mention très honorable avec félicitations du jury
Cycle du carbone, érosion chimique des continents et transferts vers les océans
soutenue le 8 avril 1994 à L'Université Louis Pasteur de Strasbourg devant le jury composé de MM. :
Larry FRAKES
Jean-Luc PROBST
Dominique RAYNAUD
Yves TARDY
Roland WOLLAST.
Directeur de thèse: Mr. Jean Luc PROBST (Chargé de Recherche au CNRS, UPR CNRS Centre de Géochimie de la Surface, Strasbourg)

1989 DEA de Géochimie de la Surface, Université Louis Pasteur, Strasbourg

1988 Maître ès Sciences de la Terre, spécialité Géologie Fondamentale et Appliquée, Université Louis Pasteur, Strasbourg

1.3 Carrière

2007 **Maître de conférences** à l'UFR des Sciences de la Terre et de l'Environnement, Université de Bourgogne – **UMR Biogéosciences**, (UMR 6351 CNRS-Université de Bourgogne, Direction P. Neige)

1999 – 2006 **Maître de conférences** à l'UFR des Sciences de la Terre et de l'Environnement, Université de Bourgogne – **UMR Microbiologie et Géochimie des Sols** (UMR INRA-Université de Bourgogne, A111 direction G. Catroux, puis 1229 direction P. Lemanceau)

1996 – 1998 **Maître de conférences** à l'UFR des Sciences de la Terre, Université de Bourgogne – **Equipe GéoSol – Géochimie des Interfaces Sol-Eau** (JE 470 du MENRT, direction F. Andreux).

1995 – 1996 **Post-doctorat**, contrat Projet Européen ESCOBA au Centre de Géochimie de la Surface, Strasbourg (UPR CNRS, direction B. Fritz)

1993 – 1995 **ATER** à l'Université de L. Pasteur de Strasbourg, Centre de Géochimie de la Surface, Strasbourg (UPR CNRS, direction B. Fritz)

1990 – 1994 **Allocataire-moniteur**, thèse de Doctorat à l'Université Louis Pasteur de Strasbourg

1.4 Fonctions administratives particulières

- décembre 2001 à mars 2004 **Directeur adjoint de l'UFR** des Sciences de la Terre et de l'Environnement, Université de Bourgogne

- mars 2003 à mars 2004 **Directeur par intérim de l'UFR** des Sciences de la Terre et de l'Environnement de, suite au congé pour longue maladie et au décès de Jean-Paul LOREAU, Directeur de l'UFR.

  Mes fonctions de Directeur par intérim m'ont notamment conduit à prendre en charge la mise en place finale de la mention de Master « Terre-Environnement » à l'Université de Bourgogne, dans le cadre du contrat 2004-2008 :

  - élaboration de la réponse à la navette Ministère de juin 2003;
  - mise en place des enseignements de 1ère année de Master (M1) pour octobre 2003 suite à l'avis favorable donné par le Ministère.

- 2000-2007 **Directeur des Etudes** du DESS puis Master spécialité Professionnelle « Espace Rural et Environnement - ERE» à l'Université de Bourgogne depuis octobre 2000 (responsable: Francis Andreux) :

  coordination pédagogique, responsable des stages en entreprise,

  élaboration de l'ensemble du dossier d'habilitation du Master PRO « Terre-Environnement », spécialité « Espace Rurale et Environnement – ERE » pour le contrat 2007-2010.

- depuis 2007 **Co-responsable** (avec P. Curmi, Pr ENSAD) du Master Pro « Espace Rural et Environnement - ERE».

1.5 Activités d'enseignement

Mes enseignements sont essentiellement dispensés dans les filières de Sciences de la Terre et de l'Environnement (y compris la préparation aux concours du Capes et de l'Agrégation de SVT), de la première à la cinquième année, et couvrent les domaines suivants :

Cartographie

Hydrologie, Hydrogéologie, Hydrogéochimie

Cycles biogéochimiques

Systèmes d'Information Géographique

Services annuels sur les 5 dernières années

	TP	TD	CM	Total	Total
	Heures réelles				Heures équivalent TD
2004-2005	73	81	47	201	200
2005-2006	82	64	49	195	193
2006-2007	57	82	49	188	194
2007-2008	144	76	41	261	234
2008-2009	108	75	42	225	211

1.6 Aide à l'insertion professionnelle des Docteurs

Correspondant de l'Association Bernard Gregory (ABG) et coordinateur de l'antenne ABG de l'Université de Bourgogne. « L'ABG a pour mission de favoriser l'insertion professionnelle en entreprise des jeunes titulaires d'un doctorat »

- Aide à la réflexion et conseils pour le projet professionnel, la rédaction de CV et la mise en ligne sur le serveur de l'ABG(http://www.abg.asso.fr/)

- Participation à des tables rondes (forum métier, Doctoriales©, Journées Biotechno,…)

- Animation sur les techniques de recherche d'emploi pour les Ecoles Doctorales de l'Université de Bourgogne et le CIES

1.7 Participation au fonctionnement des établissements d'enseignement supérieurs

Commissions de spécialistes

1998-2001 : 35-36ème section, Université de Bourgogne, membre titulaire élu, assesseur

2001-2004 : 35-36ème section, Université de Franche-Comté, membre titulaire nommé
23-24ème section, Université de Bourgogne, membre titulaire nommé

2004-2007 : 35-36ème section, Université de Franche-Comté, membre titulaire nommé
35-36ème section, Université de Bourgogne, membre suppléant élu.

2007-2010 : 35-36ème section, Université de Franche-Comté, membre titulaire nommé

Conseils et autres commissions

- Membre élu du Conseil d'UFR (UFR Des Sciences de la Terre et de l'Environnement)

  Activités particulières : Coordinateur informatique et communication, organisation des « Journées Portes Ouvertes » et des « Journées Grand Public » pour l'UFR

- Conseiller Environnement et Développement Durable auprès du Président de l'Université (J.C. Fortier puis S. Béjean) depuis 2004.

  Représentation du Président de l'Université auprès de différents organismes régionaux et notamment : Alterre (Agence Régional de l'Environnement et de Développement Soutenable), Atmosf'air (Agence Régional de surveillance de la Qualité de l'Air)

- Membre du Conseil d'Administration de la Maison de l'Environnement du Grand Dijon

- Membre du Conseil Scientifique du Parc Naturel Régional du Morvan

Expertises

Expert pour l'AERES – section des formations et des diplômes (2008)

1.8 Expertise scientifique

- Relecture pour des revues internationales à comité de lecture (par ordre de fréquence):

Chemical Geology
Journal of Hydrology
Geochimica et Cosmochimica Acta
Geoderma
Catena
Marine Chemistry
C.R. Geosciences
Canadian Journal of Fisheries and Aquatic Sciences

- Expert pour le Ministère de la Recherche (2005)

- Expert pour l'ANR (2006, 2007)

- Expert pour la NFS (USA, 2008)

- Jury de Thèse :

Thèse de Bruno Morel (février 2009), direction P. Durand (Sol-Agronomie Spatialisation, INRA-Agrocampus Rennes) et G. Gruau (Géosciences Rennes)

Transport de carbone organique dissous dans un bassin versant agricole à nappe superficielle. Université de Doctorat d'Agrocampus Ouest, Rennes

1.9 Participation à l'organisation de colloques

Membre du comité d'organisation du colloque "Analyse et Diversité des Substances Humiques Naturelles", novembre 1997, Dijon.

Membre du Comité Scientifique et du Comité d'organisation du « 2nd European Meeting on Environmental Chemistry », 12-15 décembre 2001, Dijon – responsable de la session poster (250 posters).

Membre du Comité d'organisation de la « 21ème Réunion des Sciences de la Terre, RST-2006 », 4-8 décembre 2006, Palais des Congrès, Dijon – responsable communication – informatique : mise en place et suivi du module web d'inscription et de paiement en ligne, coordination accès internet et vidéo-projection.

2 Animation de la recherche

Bénéficiaire de la Prime d'Encadrement Doctoral (1999-2007)

Coordinateur de plusieurs programmes de recherche

Encadrement et co-encadrement de 2 thèses de Doctorat et de stages de DEA/Master R

2.1 Coordination de projets scientifiques :

Elaboration et écriture des projets, recherche des co-financements, animation et coordination scientifique, rédaction des rapports de fin de contrat.

1996-2000 – 4 ans Contrat d'étude financé par le Conseil Régional de Bourgogne et l'Agence de l'Eau Seine-Normandie.	Relations entre occupation du sol, pratiques productives, qualité des eaux et paysage dans le Bas Morvan. Contrat d'étude en collaboration avec la Cellule d'Application en Ecologie (CAE) de l'Université de Bourgogne, le SESCPF INRA Orléans, en concertation avec la Parc Régional Naturel du Morvan et la DIREN Bourgogne.
1999-2002 – 3 ans Allocation de thèse financée par le Conseil Régional de Bourgogne et l'Agence de l'Eau Seine-Normandie	Evolution de la composition chimique des eaux de surface dans le Morvan granitique en réponse à la modification de l'occupation du sol: bilan et modélisation des transferts d'azote, de phosphore et de matières organiques.
2000-2002 – 2 ans Contrat d'Etude financé par le Conseil Régional de Bourgogne	Variations des stocks de matières organiques et des nutriments en fonction de l'occupation des sols dans le Massif du Morvan : vers la constitution d'un site atelier.
Depuis 2003	Responsable scientifique de l'Accord inter établissement Université de Bourgogne – INIDA Cap-Vert (Institut National de Recherche et de Développement Agricole). Mis en place à mon initiative en 2003 pour soutenir la coopération scientifique entre les deux établissements.
2006-2008 – 2 ans Contrat d'étude financé par le Conseil Régional de Bourgogne et l'Agence de l'Eau Seine-Normandie	Matières organiques dissoutes dans les eaux d'écoulement du Morvan granitique: dynamique de production et des transferts, relations avec les occupations du sol et la qualité des milieux aquatiques. Contrat d'étude en collaboration avec Unité Milieux Physiques et Environnement, Département Agriculture Environnement de l'ENESAD Dijon ; UR Biogéochimie des Ecosystèmes Forestiers (BEF) INRA Nancy ; UMR Biogéosciences, CNRS-Université de Bourgogne, Dijon ; UMR Microbiologie des Sols et de l'Environnement INRA- Université de Bourgogne, Dijon ; ONEMA - Ministère de l'Ecologie et de Développement Durable; Parc Naturel Régional du Morvan, Maison du Parc, Saint-Brisson.

2.2 Encadrements de travaux de recherche

Co-encadrements de thèse de Doctorat

1999 -2003	LINGLOIS-DUSSERT Nathalie - Suivi interannuel et modélisation de la composition chimique des eaux d'écoulement en relation avec les occupations du sol. Thèse de Doctorat de l'Université de Bourgogne, soutenue le 13 juin 2003. Co-encadrement à 70%. Directeur de thèse : Francis ANDREUX, professeur à l'Université de Bourgogne.
2004 -	TAVARES Jacques – Bilan et modélisation de l'érosion des sols de l'Ile de Santiago (Cap Vert). Thèse de Doctorat de l'Université de Bourgogne, soutenance prévue en 2008. Co-encadrement à 80%. Directeur de thèse : Francis ANDREUX, professeur à l'Université de Bourgogne.
2006 – 2009 soutenance prévue le 23/10/09	GAUTHIER Anthony – Production et transfert de matières organiques dissoutes dans les hydro-systèmes sous couvert forestier. Thèse de Doctorat de l'Université de Bourgogne, soutenance prévue fin 2008. Co-encadrement à 50%. Directeur de Thèse : Catherine HENAULT, Chargée de Recherche HDR à l'INRA Dijon

Encadrement et co-encadrement de stages de DEA/Master 2 Recherche

1995	BERGER François - Utilisation des isotopes stables du carbone ($^{13}C/^{12}C$) pour tracer l'origine et le transfert de carbone inorganique dissous dans les eaux de surface: application au bassin versant du Strengbach (Vosges). DEA Physique et Chimie de la Terre, Université Louis Pasteur Strasbourg. Codirection avec J. L. PROBST (20 %) et F. GAUTHIER-LAFAYE (10 %) UPR CNRS-CGS Strasbourg.
1996	AUBERT Dominique. - Variations du $^{13}C/^{12}C$ dans les eaux de surface continentales en région tempérée. DEA Physique et Chimie de la Terre, Université Louis Pasteur Strasbourg. Co-direction avec Jean Luc PROBST (20 %) et F. GAUTHIER-LAFAYE (10%) UPR CNRS-CGS Strasbourg.
1997	VERREY Marie-Hélène. - Flux de CO_2 respirés par les sols à l'échelle globale: établissement d'une base de données et étude des variations spatio-temporelles. DSER Université de Bourgogne, Dijon Co-direction avec Francis Andreux (20%), UMR INRA MGS Dijon
1999	LINGLOIS Nathalie - Etude comparative des flux de nutriments (C, 13C, N, P) sur des petits bassins versants à végétation contrastée. DEA national de Science du Sol. Université de Nancy I.
2001	DELHAYE Frédéric – Hydrologie du bassin versant du Cousin (Morvan): bilan hydrique et modélisation de l'écoulement. DEA Géosystème-Evolution-Environnement (GEE), Université de Bourgogne, Dijon.
2002	MATTESCO Cédric - transfert de carbone organique dissous dans un sol forestier brun acide sous végétation contrastée : étude expérimentale en colonnes de sol non-perturbé. DEA Géosystème-Evolution-Environnement, Université de Bourgogne, Dijon. Co-direction avec Sylvie DOUSSET (10%), et Jean LEVEQUE (10%) UMR INRA MGS Dijon

2003	TAVARES Jacques - Cartographie de L'aléa érosion des sols dans l'île de Santiago (Cap Vert). DEA Géosystème-Evolution-Environnement (GEE), Université de Bourgogne, Dijon.
2005	SAIDY Halima – Modélisation du bilan hydrique sur les bassins versants de la Vouge, l'Ouche et la Tille. Master Recherche Climatologie – Environnement – Paléontologie – Sédimentologie (CEPS), Université de Bourgogne, Dijon.
2006	BAUJARD Elise – Etude de l'acquisition de la composition isotopique du carbone organique dissous dans un système « végétation-sol-solution ». Master Recherche Climatologie – Environnement – Paléontologie – Sédimentologie (CEPS), Université de Bourgogne, Dijon. Co-direction avec Jean LEVEQUE (20%) et Catherine HENAULT (10%), UMR INRA MGS Dijon
2007	CHAPUIS Anne – Bilan de l'érosion glaciaire à l'échelle du globe – impact de l'érosion chimique glaciaire sur les flux de carbone. Master Recherche Climatologie – Environnement – Paléontologie – Sédimentologie (CEPS), Université de Bourgogne, Dijon. Co-direction avec Jean-François BUONCRISTIANI (50%), UMR CNRS Biogéosciences, Dijon.
2008	CLERC Sylvain – Caractérisation physico-chimique de la fraction particulaire et dissoute des eaux de fonte glaciaires ; glacier des Bossons, Massif du Mont-Blanc, France. Master Recherche Géobiosphère, Université de Bourgogne, Dijon. Co-direction avec Jean-François BUONCRISTIANI (60%), UMR CNRS Biogéosciences, Dijon.

2.3 Participation à des programmes de recherche nationaux et internationaux

PIRAT et PEGI (Programme Environnement Géosphère Intertropicale) / opération GBF (Grands Bassins Fluviaux) de l'INSU-CNRS/ORSTOM. 1990-1992

DBT-I (*Dynamique et Bilan de la Terre*) / *Fleuves et Erosion* / *ONT Garonne* (Observatoire National de Terrain) de l'INSU-CNRS. 1990-1992

CO_2-PNEDC (Programme National d'Etude de la Dynamique du Climat) de l'INSU-CNRS. 1992-1994

ESCOBA I et II (European Study of Carbon in the Ocean, Biosphere and Atmosphere - Biosphere) du Programme Environnement de la CEE - 1992-1999

PEGI (*Programme Environnement Géosphère Intertropicale*) / Fonctionnement de Bassins Versants Intertropicaux, de l'INSU-CNRS/ORSTOM. 1994-1995

PRH (Programme de Recherches en Hydrologie) / Transferts et origines du carbone dans les écoulements de surface: traçage isotopique au ^{13}C de l'INSU-CNRS. 1995-1996

Biodiversité et Gestion Forestière" Effet des substitutions d'essence sur le fonctionnement organo-minéral de l'écosystème forestier et la diversité des communautés fongiques mycorhiziennes et saprophytes". Coordonnateur : J. RANGER, Biogéochimie des Ecosystèmes Forestiers, Centre de Recherches Forestières, INRA de Nancy-Champenoux. GIP ECOFOR 2000-2003.

Projet Européen SOURCE (Shifting Interfaces in the Soil-River-Groundwater System) – Work Package 2: Soil biophysical changes, water en sediment movements (micro/mesoscale). Coordonnateur: I. GRIEVE (Stirling University, UK). 6ème PCRDT. Projet retenu après

évaluation avec le score de 26/30 (score minimum pour un financement 24/30) - Classé 3ème à l'évaluation finale (pour un seul projet financé) - Projet non retenu.

ECLIPSE Les effets du climat sur la biodiversité et les transferts sédimentaires au Jurassique et Crétacé. Coordonnateur J.P. GARCIA (UMR CNRS Biogéosciences Dijon), INSU/CNRS 2002-2003

IGCP Project n° 404 *Terrestrial Carbon in the past 125 ka,* coordonateur: L. FRANCOIS (LGAP, Liège). UNESCO-IGCP 2000-2002.

IGCP Project 459 *Carbon Cycle and Hydrology in the Palaeo-Terrestrial Environments*). Coordonateur J.L. PROBST (LMTG Toulouse), UNESCO-IGCP 2002-2006

Système Eau-Ville-Territoire, programme DADP INRA-Région Bourgogne. Coordonnateurs J. LHERTS & P.M. COMBE (Laboratoire d'Economie et de Gestion, Université de Bourgogne. 2003-2005.

PAI FAST – Australie - Production et devenir des matières organiques dissoutes dans les écosystèmes faiblement anthropisés, coordonateurs C. Hénault (INRA Dijon) et P. Nelson (James Cook University, Cairns, Australia), 2007-2008.

ANR ERD ALPS - Erosion et Evolution du Relief dans les Alpes occidentales, coordinateur P. Van der Beek (Université Joseph Fourier, Grenoble). 2008-2012

2.4 Coordination de projets d'équipement de laboratoire

2000 - Acquisition d'un analyseur de carbone dans les eaux (Shimatzu TOC 5000), 194 KF

2006 – Acquisition d'une chromatographie ionique et rénovation d'une chromatographie ionique existante pour analyse des ions majeurs dans les eaux, 56 K€

2.5 Missions à l'étranger

Avril 2002 : République du Cap Vert – 15 jours
- repérage terrain île de Santiago
- mise en place de l'Accord Scientifique Inter-Etablissement Université de Bourgogne-INIDA

Septembre 2005 : République du Cap Vert – 15 jours
- terrain, bassin versant du Ribeira Secca, San Jorge, île de Santiago: échantillonnage, suivi de crue
- traitement des échantillons au laboratoire

Novembre 2007 : Australie – 15 jours
- repérage terrain forêt tropicale humide
- suivi de thèse en co-tutelle (A. Gauthier, PAI FAST)

2.6 Enseignements dans les filières recherche

DEA National de Sciences du Sol (Nancy, Rennes, Paris Grignon, Montpellier) de 1998 à 2005

- 3 heures d'enseignements : le rôle des sols et de l'érosion dans le cycle global du carbone

DEA Géosystèmes – Evolution-Environnement (GEE) puis M2 Recherche « Climatologie-Environnement-Paléontologie-Sédimentologie) de l'Université de Bourgogne, de 1999 à 2006.

- Responsable et coordinateur du module « Hydrochimie Superficielle » (20 heures d'enseignements)

- 8 à 10 heures d’enseignements chaque année: cycles biogéochimiques, isotopes stables du carbone inorganique dissous, transferts de matières en solution.

Master Géobiosphère / M2 Recherche, depuis 2007

- Coordinateur de l’option « EnviClim »

- 8 heures d’enseignements : cycle biogéochimique du carbone actuel et passé, isotopes stables du carbone inorganique dissous, approche bassin versant

3 Liste des Travaux

3.1 Publications

Les publications précédées d'une * sont issues des travaux de thèse de Doctorat

Articles dans des revues internationales à comité de lecture indexées au JCR

1. PROBST, J.L. and **AMIOTTE SUCHET, P.**, 1992. Fluvial suspended sediment transport and mechanical erosion in the Maghreb (North Africa). Hydrol. Sci. Journal, 37(6): 621-637.
2. PROBST, J.L. and **AMIOTTE SUCHET, P.**, 1993. Reply to the discussion by Fox H.R// Moore H.M. on " Fluvial suspended sediment transport and mechanical erosion in the Maghreb (North Africa)". Hydrol. Sci. Journal, 38(6): 560-562.
3. *** AMIOTTE SUCHET, P.** and PROBST, J.L., 1993a. Flux de CO_2 atmosphérique consommé par altération chimique continentale. Influence de la nature de la roche. C.R. Acad. Sci. Paris,, t. 317, Série II,: 615-622.
4. *** AMIOTTE SUCHET, P.** and PROBST, J.L., 1993b. Modelling of atmospheric CO_2 consumption by chemical weathering of rocks: Application to the Garonne, Congo and Amazon basins. Chemical Geology, 107: 205-210.
5. *** AMIOTTE SUCHET, P.** and PROBST, J.L., 1995. A global model for present day atmospheric/soil CO2 consumption by chemical erosion of continental rocks (GEM-CO2). Tellus, 47B: 273-280.
6. *** AMIOTTE SUCHET, P.**, PROBST, A. and PROBST, J.L., 1995. Influence of acid rain on CO_2 consumption by rock weathering: local and global scales. Water, Air and Soil Pollution, 85: 1563-1568.
7. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1996. River discharges of carbon to the world's oceans: determining local inputs of alkalinity and of dissolved and particulate organic carbon. C. R. Acad. Sci. Paris. t. 323, série IIa, 1007-1014.
8. LUDWIG, W., **AMIOTTE SUCHET, P.**, MUNHOVEN, G. and PROBST, J.L., 1998. Atmospheric CO_2 consumption by continental erosion: present-day control and implications for the Last Glacial Maximum. Global and Planetary Change, 16-17: 107-120.
9. **AMIOTTE SUCHET, P.**, AUBERT, D., PROBST, J.L., GAUTHIER-LAFAYE, F., PROBST, A., ANDREUX, F. and VIVILLE, D., 1999. $\delta^{13}C$ pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges mountains, France). Chemical Geology, 159: 129-145.
10. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.-L., 1999. Enhanced chemical weathering of rocks during the last glacial maximum: a sink of atmospheric CO_2? Chem. Geol, 159: 147-151.
11. SEMHI, K., **AMIOTTE SUCHET, P.**, CLAUER, N. and PROBST, J.L., 2000. Impact of the nitrogen fertilizers on the natural weathering erosion processes and fluvial transport in the Garonne basin. Applied Geochemistry, 15: 865-878.
12. SEMHI, K., **AMIOTTE SUCHET, P.**, CLAUER, N. and PROBST, J.L., 2000. Dissolved silica in the Garonne river waters: changes in the weathering dynamics. Environmental Geology, 40: 19-26.

13. AUMONT, O., ORR, J.C., MONFRAY, P., LUDWIG, W., **AMIOTTE SUCHET, P.**, and PROBST, J-L, 2001. Riverine-driven interhemispheric transport of carbon. Global Biogeochemical Cycles, 15: 393-405.

14. **AMIOTTE SUCHET, P.**, PROBST, J.L. and Ludwig, W., 2003. Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. Global Biogeochem. Cycles, 17((2)): 1038, doi : 10.1029/2002GB001891..

15. **AMIOTTE-SUCHET, P**., LINGLOIS, N., LEVEQUE, J. and ANDREUX, F., 2007. ^{13}C composition of dissolved organic carbon in upland forested catchments of the Morvan Mountains (France): Influence of coniferous and deciduous vegetation. Journal of Hydrology, 335(3-4): 354-363.

16. COPARD, Y., **AMIOTTE-SUCHET, P**. and DI-GIOVANNI, C., 2007. Storage and release of fossil organic carbon related to weathering of sedimentary rocks. Earth and Planetary Science Letters, 258(1-2): 345-357.

Articles expertisés dans des revues non indexées au JCR

17. *** AMIOTTE SUCHET, P.** and PROBST, J.L., 1996. Origines du carbone inorganique dissous dans les eaux de la Garonne - variations saisonnières et interannuelles. Sci. Géol. Bull, 49: 101-126.

18. * PROBST, J.L., LUDWIG, W. and **AMIOTTE SUCHET, P.**, 1997. Global modelling of CO_2 uptake by continental erosion and of carbon river transport to the oceans. Sci. Geol. Bull., 50(1-4): 131-156.

19. AMIOTTE SUCHET P., LINGLOIS N., CHAUVIN C., GENIN B., ANDREUX F. 2007. Influence du changement d'occupation des sols sur la composition chimique des eaux de surface dans le Bas-Morvan granitique. Bourgogne Nature, numéro spécial n°3 La Forêt Morvandelle. Sous presse.

Thèse, Chapitres d'ouvrages:

20. PROBST, J.L., **AMIOTTE SUCHET, P.** and TARDY, Y., 1992. Global continental erosion and fluctuations of atmospheric CO2 consumed during the last 100 years. In: Y.K. Kharaka and A.S. Maest (Editors), Water Rock Interactions. Balkema, Rotterdam, pp. 483-486.

21. * PROBST, J.L., **AMIOTTE SUCHET, P.** and LUDWIG, W., 1994. Continental erosion and river transports of carbon to oceans. In: S.G. PANDALAI (Editor), Trends in Hydrology. Research Trends, Council of Scientifique Information, TRIVANDRUM, pp. 453-468.

22. * **AMIOTTE SUCHET, P.**, 1995. Cycle du carbone, érosion chimique des continents et transferts vers les océans. Sciences Géologiques, Mémoires, 97, Strasbourg, 156 pp.

23. * **AMIOTTE SUCHET, P.** and PROBST, J.L., 1995. Erosion chimique du bassin versant du Congo: variabilité spatio-temporelle des flux de CO_2 consommé par altération de la croute continentale. In: J.C. Olivry and J. Boulègue (Editors), Grands Bassins Fluviaux Periatlantiques: Congo, Niger, Amazone. ORSTOM, "Colloques et Séminaires", Paris, pp. 51-68.

24. ANDREUX, F., ROUX, F., LINGLOIS, N., NGUYEN, T.K.N., **AMIOTTE SUCHET, P.** and LÉVÊQUE, J., 2002. Impact of changing forest management on soil organic matter in low mountain acid media. In: A. Violante, P.M. Huang, J.-M. Bollag and L. Gianfreda (Editors), Soil Mineral-Organic Matter-Microorganism Interactions and Ecosystem Health. Elsevier, Amsterdam, pp. 383-407.

Publication en révision

25. GAUTHIER, A., **AMIOTTE SUCHET, P.**, NELSON, P., LEVEQUE, J., ZELLER, B., HENAULT, C., Dynamics of the water extractable organic carbon pool during mineralisation in soils from Douglas fir plantation and oak-beech forests – an incubation experiment. En révision pour Plant and Soil.

3.2 Communications dans des congrès (orales et posters)

26. *__AMIOTTE SUCHET, P.__ and PROBST, J.L., 1992. Flux de bicarbonates et variations hydroclimatiques sur le bassin de la Garonne (ONT Garonne), Dynamique et Bilans de la Terre, résultats des travaux 1988-1992. CNRS, Institut National des Sciences de l'Univers.

27. *__AMIOTTE SUCHET, P.__ and PROBST, J.L., 1992. Flux de CO_2 atmosphérique consommé par érosion chimique des continents et transfert de carbone du réservoir biosphère-sol vers les océans. Résumé. 14e R.S.T, Toulouse, 13-15 avril 1992. Soc. Géol. Fr. édit. Paris.

28. *__AMIOTTE SUCHET, P.__ and PROBST, J.L., 1993. Atmospheric CO_2 consumption by chemical weathering of continental rocks: influences of drainage and lithology, Proceedings of the 4th. International CO2 conference Carqueiranne, 13-17 septembre 1993,. World Meteorological Organization, pp. 224-227.

29. *__AMIOTTE SUCHET, P.__ and PROBST, J.L., 1994. Variations saisonnières et interannuelles de la consommation de CO2 par érosion chimique sur le bassin de la Garonne. Résumé, 5e RST, Nancy 26-28 avril 1994. Soc. Géol. Fr. Paris, pp. 21.

30. *__AMIOTTE SUCHET, P.__, PROBST, A., PROBST, J.L., FRITZ, B., VIVILLE, D. and AMBROISE, B., 1995. Influence of acid rain on the carbon cycle: local and global scale, Proceedings of Acid Reign'95, 5th International Conference on Acidic Deposition, 26-30 june 1995, Gothenburg, Sweden.

31. LUDWIG, W., **AMIOTTE SUCHET, P.**, MUNHOVEN, G., PROBST, J.L. and KEMPE, S., 1995. Modelling the consumption of atmospheric CO_2 by continental erosion, IGBP/GAIM First Science Conference, Garmisch-Partenkirchen, Germany.

32. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1995. Modelling the consumption of atmospheric CO2 by continental erosion, Proceedings XIV International Union for Quaternary Research Congress, 3-10 august 1995, Berlin, Germany. Terra Nostra, Abstracts, pp. 170.

33. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1996. Consommation de CO_2 par érosion continentale et transports fluviaux de carbone vers les océans. poster, Programme International Geosphère Biosphère - France, INSU/CNRS - MENESRIP, Paris, France.

34. PROBST, J.L., LUDWIG, W. and **AMIOTTE SUCHET, P.**, 1996. Erosion des continents et transports fluviaux de carbone vers les océans: influence sur la teneur en CO_2 de l'atmosphère au cours du dernier maximum glaciaire, Séance spécialisée de la Société Géologique de France, du Comité français de Stratigraphie et du Comité français du PICG, 4 et 5 novembre 1996, Paris.

35. **AMIOTTE SUCHET, P.**, AUBERT, D., GAUTHIER-LAFAYE, F., PROBST, A., VIVILLE, D., ANDREUX, F. and PROBST, J.L., 1997. Variabilté spatio-temporelle de la composition isotopique du carbone inorganique dissous sur le bassin versant du Strengbach (Vosges), 15e RST. Soc. Géol. Fr. édit. Paris, 10-12 avril 1996, Orléans, pp. 107.

36. **AMIOTTE SUCHET, P.**, AUBERT, D., GAUTHIER-LAFAYE, F., PROBST, A., VIVILLE, D., ANDREUX, F. and PROBST, J.L., 1997. Seasonal variations of the stable isotope composition of dissolved inorganic carbon in surface water of a small granitic catchment: the Strengbach case study (Vosges). EUG 9. abstract supplement n°1, Terra Nova Volume 9,, 23-27 March 1997, pp. 249.

37. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1997. Continental erosion: a sink of atmospheric CO_2 during the last glacial maximum? Oral, EUG 9, 23-27 March 1997. . Terra Nova, abstract supplement n°1, Volume 9, pp. 248.

38. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1997. Continental erosion: a sink of atmospheric CO_2 during the last glacial maximum?, Proceedings 5th International Carbon Dioxide Conference. Extended Abstract,, 8-12 septembre 1997, Cairns (Australie),, pp. 207-208.

39. SEMHI, K., PROBST, J.L. and **AMIOTTE SUCHET, P.**, 1997. Effects of N-fertilizers on weathering processes in the Garonne basin, EUG 9. abstract supplement n°1, Terra Nova Volume 9, Strasbourg, 23-27 March 1997, pp. 588.

40. **AMIOTTE SUCHET, P.**, VERREY, M.H., ANDREUX, F., LEVEQUE, J. and PROBST, J.L., 1998. Carbon dioxide released to the atmosphere by soil respiration: a global scale approach, 16e World Congress of Soil Science, Montpellier (France) 20-26 August 1998, pp. 8.

41. LUDWIG, W., **AMIOTTE SUCHET, P.** and PROBST, J.L., 1998. Modelling the atmospheric CO_2 consumption and river carbon inputs to the oceans by continental erosion., Goldschmidt Conference 1998. Mineralogical Magazine, Vol. 62a, Part 2, Toulouse, pp. 919-920.

42. PROBST, J.L., **AMIOTTE SUCHET, P.**, BOEGLIN, J.L., MORTATTI, J. and LUDWIG, W., 1998. Silicate rock weathering and atmospheric/soil CO_2 consumed by major world river basins, Goldschmidt Conference 1998. Mineralogical Magazine, Toulouse, pp. 1216-1217.

43. **AMIOTTE SUCHET, P.**, CHAUVIN, C., GENIN, B., CHRETIEN, J., LEVEQUE, J. and ANDREUX, F., 1999. Spatial and Temporal Variability of Nitrogen and Phosphorus Fluxes in a Rural Catchment: the Cousin Case Study (Morvan, France), J. Conf. Abs. 4, EUG 10, Strasbourg, March 28 - April 1 1999, pp. 560.

44. PROBST, J.L., **AMIOTTE SUCHET, P.**, BOEGLIN, J.L., MORTATTI, J. and LUDWIG, W., 1999. silicate rock weathering and atmospheric/soil CO_2 uptake estimated from river transport of alkalinity, cations and silica, Hydrological and Geochemical Processes in Large Scale River Basins, Manaus, November 16-19 1999.

45. PROBST, J.L., **AMIOTTE SUCHET, P.** and LUDWIG, W., 1999. Climatic control of silicate weathering, silica river transports and atmospheric/soil CO_2 uptake: the major role of runoff, EUG 10. J. Conf. Abstr., 4, Strasbourg, March 28 - April 1 1999, pp. 230.

46. PROBST, J.L., LUDWIG, W. and **AMIOTTE SUCHET, P.**, 1999. Silicate rock weathering and atmospheric/soil CO_2 uptake during the Last Glacial Maximum., J. Conf. Abs. 4, EUG 10, Strasbourg, March 28 - April 1 1999, pp. 18.

47. ANDREUX, F., LINGLOIS, N., ROUX, F., **AMIOTTE SUCHET, P.** and LEVEQUE, J., 2000. Impact of changing forest management on organic matter and organic-mineral interactions in soils and streams of selected low mountain acid media., 3rd ISMOM, Naples-Capri (Italy) May 22-26.

48. ANDREUX, F. and **AMIOTTE SUCHET, P.**, 2000. L'acidification des sols et des eaux : inventaire des causes et évaluation des risques, 5ème colloque transfrontalier CLUSE

"Risques Majeurs: perceptions, globalisation et Management", Université de Genève, 21 et 22 septembre 2000.

49. FRANCOIS, L., PROBST, J.L., DEPETRIS, J., SCHOTT, J., POKROVSKY, O., MUNHOVEN, G., GODDERIS, Y. and **AMIOTTE SUCHET, P.**, 2000. A process-oriented model to calculate weathering rates and CO_2 consumption over large river basins: application to the Parana river basin, 31st International Geological Congress, Rio de Janeiro, August 06-17 2000.

50. LINGLOIS, N., **AMIOTTE SUCHET, P.**, LEVEQUE, J. and ANDREUX, F., 2000. Dissolved organic carbon content and $\delta^{13}C$ variations in streams of small catchment with contrasted vegetation. (Morvan, France), 10th International Meeting of the International Humic Substances Society (IHSS 10). proceedings vol. 2, 24-28 july 2000, Toulouse (France), pp. 735-738.

51. LINGLOIS, N., **AMIOTTE SUCHET, P.**, LEVEQUE, J. and ANDREUX, F., 2000. Natural isotopic tracing of dissolved organic carbon in small catchments of Morvan, 1ères Journées Françaises de Chimie Environnementale, Nancy, France.

52. PROBST, J.L., **AMIOTTE SUCHET, P.**, BOEGLIN, J.L., MORTATTI, J. and LUDWIG, W., 2000. Silicate rock weathering and atmospheric soil/CO_2 uptake in tropical lateritic regions, 31st International Geological Congress, Rio de Janeiro, August 06-17 2000.

53. **AMIOTTE SUCHET, P.**, MATTESCO, C., DOUSSET, S., LEVEQUE, J., LINGLOIS, N. and ANDREUX, F., 2002. Transferts de carbone organique dissous dans un sol forestier brun acide sous végétation contrastée : étude expérimentale en colonnes de sol non perturbe, Journées Nationales d'Etude des Sols, Orléans, 22-24 octobre 2002.

54. **AMIOTTE SUCHET, P.**, PROBST, J.L. and LUDWIG, W., 2003. Distribution spatiale des principaux types de roche affleurant a la surface des continents : implications pour les flux de co2 consommés par érosion chimique et les apports de carbone inorganique aux oceans, Colloque TectoClim, Lille, 10-11 décembre 2003.

55. DI-GIOVANNI, C. and **AMIOTTE SUCHET, P.**, 2003. Organic carbon released from carbonates and shales by chemical weathering: implications for the global organic carbon cycle understanding, 16 ème congrès I.N.Q.U.A., Reno, 23- 31 juillet 2003, pp. 118.

56. DI-GIOVANNI, C. and **AMIOTTE SUCHET, P.**, 2003. Altération chimique des roches carbonatées et libération de matières organiques fossiles., Colloque Tecto-Clim, Lille, France.

57. FOURNIER, A.L., GARCIA, J.P., **AMIOTTE SUCHET, P.** and BUONCRISTIANI, J.F., 2003. estimation de la production Sédimentaire et des flux de carbone a long terme d'un géosystème continental du crétacé inférieur, Colloque TectoClim, Lille, France.

58. PROBST, J.L., **AMIOTTE SUCHET, P.** and LUDWIG, W., 2003. The major role of the different continental rockoutcrop abundance on the global carbon cycle: implication for atmospheric/soil CO2 uptake by continental weathering and alkalinity river transport to the oceans, Proceedings of the XVI INQUA Congress, 23-30 July 2003, Reno, Nevada, USA, pp. 131.

59. **AMIOTTE SUCHET, P**., BAUJARD, E., HENAULT, C., GAUTHIER, A., LEVEQUE, J., RANGER, J., 2006. Influence de la dégradation des matières organiques et du couvert végétal sur la composition isotopique du carbone organique dissous : le cas des alocrisols forestiers du morvan, Les Matières Organiques en France: Etat de l'Art et Prospectives, 22-24 janvier 2006, Carqueiranne, France.

60. **AMIOTTE SUCHET, P**., LEVEQUE, J., HENAULT, C., GAUTHIER, A., ANDREUX, F., 2006. ^{13}C differentiation between dissolved and solid organic carbon in soils as induced by

substitution of a native deciduous forest by a coniferous forest., 18th World Congress of Soil Science, Philadephia.

61. GAUTHIER, A., **AMIOTTE-SUCHET, P.,** HÉNAULT, C., LÉVÈQUE, J., NELSON, P. and RANGER, J., 2007. ^{13}C differentiation of the dissolved organic carbon pool during carbon mineralization in soil from a native deciduous forest and a coniferous plantation, International Symposium on Forest Soils and Ecosystem Health, Noosa, Australia.

62. **AMIOTTE SUCHET, P**., CHAPUIS, A., BUONCRISTIANI, J.-F., (2008) Impact de l'érosion glaciaire sur les bilans mondiaux des apports de matières aux océans et de la consommation de CO2 par érosion chimique. In: *Réunion des Sciences de la Terre, RST-2008*, Nancy, 21-24 avril 2008.

63. GAUTHIER, A., **AMIOTTE-SUCHET, P.**, HENAULT, C., NELSON, P., LÉVÈQUE, J., RANGER, J., (2008) Isotopic differentiation (^{13}C) of dissolved organic carbon and CO_2 during organic matter degradation in forest soils: influence of vegetation. In: *2008 Western Pacific Geophysics Meeting, AGU*, Cairns, Australia, 29 July - 1 August 2008.

64. HÉNAULT, C., GAUTHIER, A., BIZOUARD, F., NELSON, P., LEVEQUE, J., ZELLER, B., **AMIOTTE-SUCHET, P.**, (2008) Effect of temperature on soil microbial structure and fractionation during C mineralization. In: *12th International Symposium on Microbial Ecology – ISME-12*, Cairns, Australia, August 17 - 22, 2008

3.3 Conférences invitées

65. **AMIOTTE SUCHET, P.**, 1996. Le rôle de l'érosion chimique dans le cycle géochimique du carbone., Séminaire "Climatologie et Géosciences de Surface", Centre des Sciences de la Terre, Dijon, novembre 1996.

66. **AMIOTTE SUCHET, P.**, 1999. Soil CO2, rock weathering and river transport of carbon to the oceans., "Biological participation in the global carbonate cycle", organisé par Peter WESTBROOK, Fondation des Treilles (France), 12-17 septembre 1999.

67. **AMIOTTE SUCHET, P.**, LINGLOIS, N., ANDREUX, F., CHAUVIN, C. and GENIN, B., 2000. Impact de l'évolution de l'occupation des sols sur la qualité des eaux du cousin (bas Morvan granitique). . Journée "Eau et Arbre", Agence de l'Eau Seine-Normandie Direction Seine Amont, 27 octobre.

68. **AMIOTTE SUCHET, P.** and ANDREUX, F., 2001. Contribution du CO_2 respirés par les sols au cycle global du carbone: une approche par modélisation. Journée AFES "Sols et Gaz impliqués dans l'Effet de Serre", organisée par Jean-Claude GERMON,, INA-PG, Paris, 30 novembre 2000.

3.4 Banques de données numériques

69. **AMIOTTE SUCHET P.** and PROBST J.L. (1995) - A global 1 degre by 1 degre distribution of atmospheric soil CO_2 consumption by continental weathering and of riverine HCO_3^- yield. CDIAC Database DB1012, CDIAC (Carbon Dioxide Information Analysis Center), Oak Ridge National Laboratory, P.O. Box 2008, TN 37831-6335, USA, available on internet: http://cdiac.esd.ornl.gov.

70. LUDWIG W., **AMIOTTE-SUCHET P**. and PROBST J.L. Global river fluxes of carbon and sediments to the oceans:. gridded estimates for the riverine export of carbon and of sediments in a spatial resolution of 0.5 x 0.5 degree longitude/ latitude. 10 datasets and 11 figures, Goddard Space Flying Center, NASA, The International Satellite Land-Surface Climatology Project (ISLSCP),

http://islscp2.sesda.com/ISLSCP2_1/html_pages/groups/carbon/river_carbon_flux_xdeg.html

71. **AMIOTTE SUCHET, P**., PROBST, J.L., LUDWIG, W. (2003) - Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans, http://www.omp.obs-mip.fr/omp/umr5563/4equ/hg/IGCP459/litho.html

3.5 Rapports scientifiques et autres publications

72. **AMIOTTE SUCHET, P.,** CHAUVIN, C. and CHRETIEN, J., 1998. Relations entre occupation du sol, pratiques productives, qualité des eaux et paysage dans le Bas Morvan. Rapport intermédiaire n°1, Université de Bourgogne, Centre des Sciences de la Terre, Dijon.

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MEMOIRE

Ce mémoire a pour ambition de présenter les principales approches que j'ai utilisées depuis la fin de ma thèse de Doctorat dans le but d'améliorer notre connaissance de l'influence des transferts fluviaux de carbone continents-océans. Les résultats rassemblés ci-après ont tous été publiés (ou sont en cours de publication pour les plus récents travaux) dans des revues internationales à comité de lecture. J'ai choisi de rassembler ces publications à la fin, plutôt que de les insérer dans le texte du mémoire. Ce dernier aura, auparavant, tenté de faire le point sur mes 15 années de recherche, puis d'esquisser les contours de la prochaine décennie.

Dans un premier temps, je replacerai les transferts de nutriments continents-océans dans la connaissance du fonctionnement des cycles biogéochimiques globaux. Puis, les transferts de carbone à l'échelle globale seront plus particulièrement abordés à travers un modèle d'érosion. Dans un troisième temps, je réduirai l'échelle d'approche pour examiner la dynamique spatio-temporelle des transferts à l'échelle du bassin fluvial. L'échelle plus fine du bassin versant, voir du profil de sol, permettra ensuite de s'interroger sur la possibilité d'utiliser les isotopes stables en abondance naturelle pour tracer les transferts de carbone. Je tenterai alors, sur la base de ces acquis, de présenter les principaux axes à suivre dans les années à venir.

1 Les transferts de matières continents-océans et les cycles biogéochimiques globaux

1.1 Les enjeux de la connaissance des cycles biogéochimiques globaux

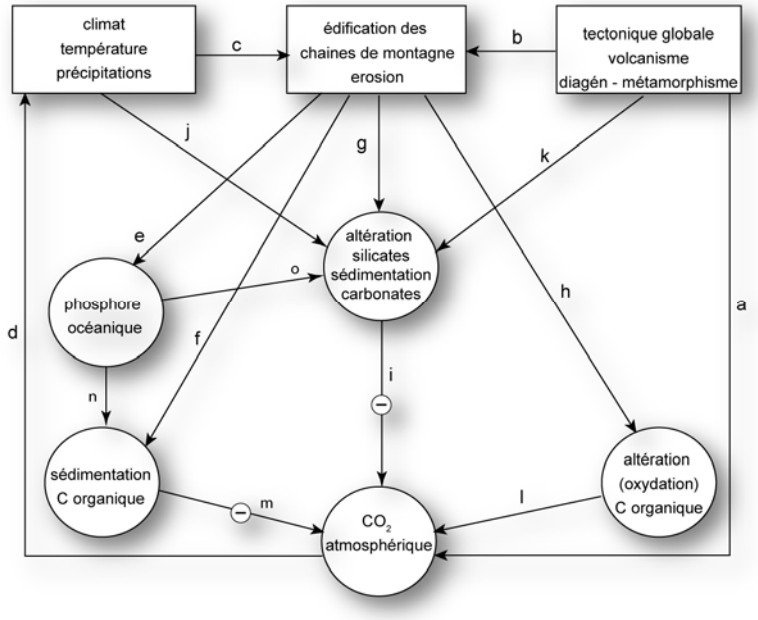
La connaissance des cycles biogéochimiques globaux, de leurs interactions entre eux et des liens très forts les unissant au système climatique, constituent la clef incontournable de la compréhension du fonctionnement du système Terre. Les grands cycles biogéochimiques sont l'élément essentiel de la régulation des climats tout comme ils se trouvent fortement influencés par l'évolution de ces derniers. Cette double interaction a été mise en évidence aussi bien dans le fonctionnement actuelle et holocène de la machine climatique (Augustin *et al.*, 2004; Falkowski *et al.*, 2000; IPCC, 2007; Ruddiman, 2008; Siegenthaler *et al.*, 2005) qu'à l'échelle des temps géologiques (Berner, 2003; Fletcher *et al.*, 2008; Royer, 2006; Royer *et al.*, 2007).

En raison de l'augmentation historique de la concentration en CO_2 dans l'atmosphère et du réchauffement climatique induit, le cycle du carbone a été au cœur de très nombreuses recherches au cours des 30 dernières années. Les cycles de l'oxygène, de l'azote et du phosphore, fortement liés à la vie sur Terre, n'ont pas bénéficiés de la même attention, notamment dans le fonctionnement des cycles à court terme. A l'échelle des temps géologiques, le couplage des cycles entre eux est devenu une nécessité et l'amélioration des modèles de cycle géologiques du carbone nécessite d'intégrer les cycles de l'oxygène, du phosphore, de l'azote et du soufre. Les enjeux des recherches dans ce domaine sont extrêmement forts tant en ce qui concerne notre capacité à comprendre le fonctionnement des climats, passés et futurs, qu'en ce qui concerne l'évolution physique, chimique et biologique de la Terre et des organismes qu'elle abrite.

Le premier modèle de Berner (BLAG Model) il y a 25 ans était relativement simple: il comportait 3 réservoirs de carbone inorganique et ne prenaient explicitement en compte que les processus abiotiques (Berner *et al.*, 1983). Il a ensuite évolué vers des versions plus complexes (GEOCARB) incluant les formes inorganiques et organiques du carbone (Berner, 1991; Berner & Canfield, 1989; Berner, 2003). Enfin, récemment le modèle GEOCARBSULF (Berner, 2006) a couplé les cycles du soufre, de l'oxygène et du carbone permettant de simuler l'évolution des teneurs atmosphériques en CO_2 et en O_2. D'autres modèles récents de cycle géologique du carbone

intègrent les couplages entre cycles du carbone, de l'oxygène, du soufre et du phosphore (Godderis & Joachimski, 2004; Simon *et al.*, 2007; Zachos & Kump, 2005). Pour une synthèse complète des couplages et processus connus entre les différents cycles on se reportera aux travaux de Berner (2003) sur l'évolution des teneurs en oxygène dans l'atmosphère terrestre au cours du Phanérozoïque.

Les mécanismes clefs du fonctionnement des cycles biogéochimiques sont les boucles de rétroactions. Elles correspondent à un enchainement de processus conduisant soit à stabiliser le système (rétroaction négative ou régulation), soit à emballer le système (rétroaction positive ou effet boule de neige). Dans le cycle géologique du carbone par exemple, une augmentation de la concentration de CO_2 dans l'atmosphère provoque, par effet de serre, l'augmentation de la température et des précipitations, ce qui favorise l'érosion chimique des silicates sur les continents et de la sédimentation des carbonates dans les océans. Cela a pour conséquence finale de diminuer la concentration de CO_2 dans l'atmosphère. Cet enchainement (d – j – i sur la figure 1) constitue une boucle de régulation majeure dans le cycle géologique du carbone. L'enchainement d – c – f – m (figure 1) constitue une autre boucle de régulation, similaire à la précédente, mais impliquant le carbone organique.

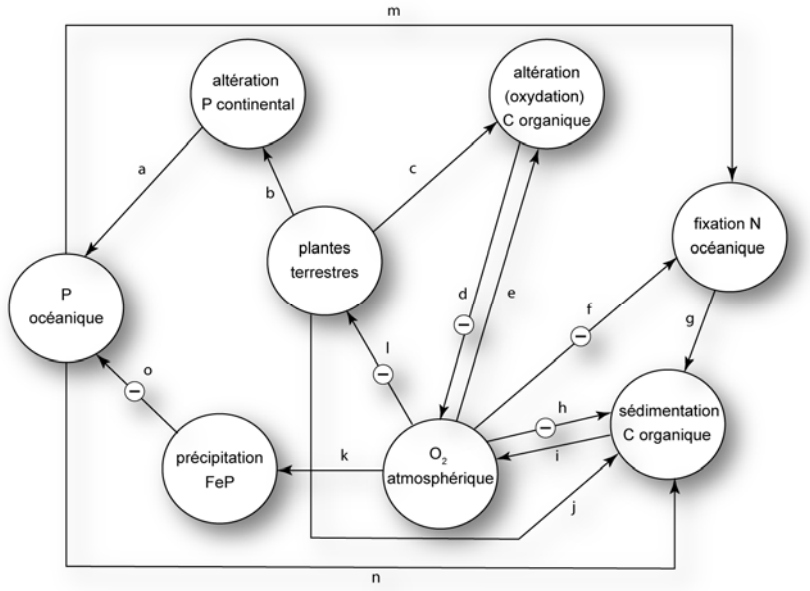


a : émission de CO2 dans l'atmosphère par l'activité tectonique (volcanisme, décarbonatation et oxydation des matières organique au cours du métamorphisme et de la diagénèse ; b : contrôle des orogénèses et de l'érosion des continents par l'activité tectonique globale ; c : contrôle de l'érosion des continents par les climats (précipitation et température) ; d : effet de serre ; e : érosion des sols et des roches continentales et transfert de P vers les océans ; f : érosion des sols et des roches continentales, transfert et sédimentation de matières organiques dans les océans ; g et i : érosion chimique des roches silicatées continentales, transfert vers les océans, sédimentation des roches carbonatées dans les océans ; h et l : mise à l'affleurement des roches sédimentaires et oxydation de leurs matières organiques ; j : contrôle de l'altération des roches silicatées et de la sédimentation des roches carbonatées par les climats ; k : contrôle de l'altération des roches silicatées et de la sédimentation des roches carbonatées par l'activité tectonique globale ; m : sédimentation et enfouissement des matières organiques ; n et o : contrôle de la production primaire océanique par le phosphore (P élément bio-limitant)

figure 1 : Forçages climatique et géologique des relations et rétroactions entre les principaux processus du cycle géologique du carbone.

Les flèches simples représentent des relations positives (l'accroissement de la cause amplifie l'effet) ; les flèches avec un signe négatif représentent une relation négative (l'accroissement de la cause diminue l'effet). Une boucle qui compte un nombre impaire de « flèches négatives » est une boucle de rétroaction négative (*negative feedback*) ou boucle de régulation ; une boucle qui compte un nombre paire de flèche négative (y compris zéro) est une boucle de rétroaction positive (*positive feedback*) ou « effet boule de neige ».

La teneur atmosphérique en oxygène est, elle aussi, régulée par plusieurs rétroactions (figure 2). Les plus simples sont les processus d'oxydation des matières organiques à la surface des continents (boucle e – d) et dans les océans (boucle h – j). Ces boucles matérialisent également les couplages entre cycle de l'oxygène et cycle du carbone. D'autres enchainements, impliquant l'azote (boucle f – g – i) ou le phosphore (l – b – a – n – i et k – o – n – i), viennent compléter les dispositifs de régulation de la teneur en oxygène dans l'atmosphère au cours des temps géologiques. Cependant, un certain nombre de ces boucles sont encore discutées. Ainsi, la boucle impliquant la fixation de N_2 par les organismes planctoniques (boucle f – g – i) mise en évidence par Falkowski (1997) aurait une influence fortement limitée à cause de réactions gourmandes en énergie et parce que le phosphore resterait l'élément bio-limitant dans l'océan (Berner *et al.*, 2003). Un autre exemple d'interrogation est l'influence réelle de la végétation terrestre sur l'érosion chimique des roches et la libération de phosphates en solution ou l'oxydation des matières organiques des roches sédimentaires.



a : érosion des sols et des roches continentales et transfert vers les océans ; b et c : stimulation de l'altération chimique par les plantes terrestres (actions de la rhizosphère, libérations d'acides organiques, accroissement de la pCO_2 des sols ; d et e :oxydation des matières organiques à la surface des continents (sols, roches) ; f : inhibition de la fixation de N2 par les le phytoplancton ; g et n: production primaire nette océanique et sédimentation ; h et i : oxydation des matières organiques dans l'océan profond ; j : production primaire nette terrestre, transfert et sédimentation ; k et l : précipitation d'oxydes de fer dans les océans avec adsorption de P ; m : contrôle de la productivité primaire océanique par le phosphore (P élément bio-limitant)

figure 2 : diagramme des principales relations et les rétroactions biogéochimiques entre l'oxygène atmosphérique et les nutriments C, N, P (d'après Berner, 2003; Berner *et al.*, 2003). Les flèches simples représentent des relations positives (l'accroissement de la cause amplifie l'effet) ; les flèches avec un signe négatif représentent une relation négative (l'accroissement de la cause diminue l'effet). Une boucle qui compte un nombre impaire de « flèches négatives » est une boucle de rétroaction négative (*negative feedback*) ou boucle de régulation ; une boucle qui compte un nombre paire de flèche négative (y compris zéro) est une boucle de rétroaction positive (*positive feedback*) ou « effet boule de neige ».

Ces représentations (figure 1 et figure 2) préfigurent les couplages entre les cycles de l'oxygène, du carbone, de l'azote, du phosphore et du soufre. Leurs simplifications, leur vision partielle et les nombreuses incertitudes montrent bien l'étendue de la tache à accomplir pour une meilleure compréhension des cycles biogéochimiques. Un des points à améliorer concerne les mécanismes d'apport aux océans de ces éléments clefs par le drainage des surfaces continentales.

1.2 Les apports de nutriment aux océans

Leur rôle dans le fonctionnement des cycles biogéochimiques

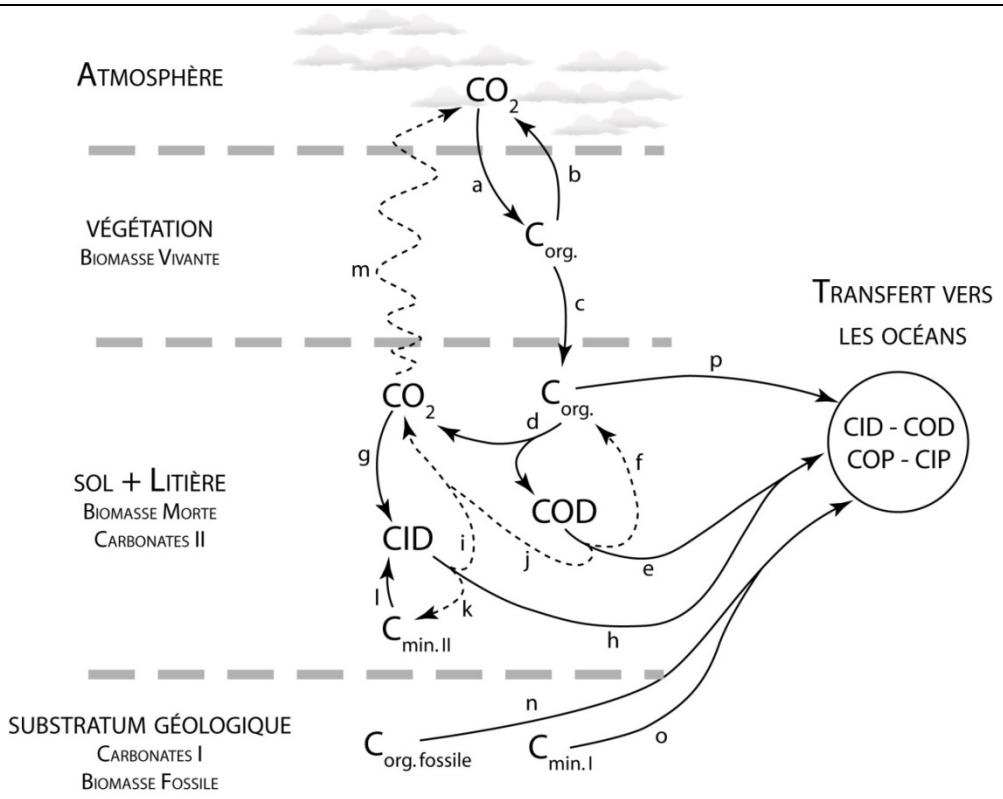
L'examen des interactions entre la composition de l'atmosphère (CO_2 et O_2), la disponibilité des nutriments (C, N, P) et les forçages radiatif ou tectonique (figure 1et figure 2) montre que l'érosion des continents et le transfert des matériaux vers les océans jouent un rôle de premier ordre dans le fonctionnement des grands cycles biogéochimiques à l'échelle des temps géologiques. On rappellera tout d'abord que l'érosion des surfaces continentales (roche + sol + couverture végétale) constitue le principal transfert entre les continents et les océans. Elle est contrôlée par des facteurs aussi bien géologiques, climatiques que biologiques. Par ailleurs, l'érosion continentale occupe une place prépondérante dans les rétroactions cycles biogéochimiques – climat. Ainsi, l'érosion chimique des silicates sur les continents, combinée à la précipitation des carbonates dans les océans est reconnue depuis longtemps comme le premier processus régulateur de la concentration en CO_2 dans l'atmosphère au cours des temps géologiques (Amiotte Suchet *et al.*, 2003; Berner, 1991; Berner *et al.*, 1983; Berner, 2006; Chamberlain, 1899; François & Walker, 1992; Garrels & Mackenzie, 1971). La prise en compte du rôle de la biosphère dans les cycles a encore renforcé le rôle de l'érosion continentale à travers deux chaines de processus. Premièrement, le carbone organique enfouis dans les sédiments après avoir été fixé dans la biomasse terrestre et océanique, est redonné au système océan-atmosphère par l'érosion des roches continentales (Berner, 1991), seul moyen de « boucler » le cycle avec une rétroaction possible via les relations végétation – érosion. Deuxièmement, l'érosion des minéraux phosphatés des roches continentales contrôle l'apport de phosphore aux écosystèmes marins et intervient de se fait directement sur la « pompe biologique océanique » (Godderis & Joachimski, 2004), accentuant ainsi la boucle de régulation CO_2 atmosphérique – climat – érosion – CO_2 atmosphérique.

L'influence des transferts continents-océans est plus marginale à l'échelle humaine ou historique, notamment parce que la rapidité des processus et la taille des flux en jeu à cette échelle (photosynthèse – respiration notamment) sont sans commune mesure : chaque année la biomasse terrestre fixe environ 120 Gt de carbone pendant que les fleuves apportent environ 1 Gt de carbone aux océans (Amiotte Suchet, 1995). Cependant, plusieurs auteurs ont souligné que ces transferts de matières (et pas uniquement de carbone) continents-océans ne devaient pas être négligés, parce qu'ils constituaient un flux net entre les continents et les océans (Sarmiento & Sundquist, 1992) et pouvaient affecter les échanges océan-atmosphère (Aumont *et al.*, 2001). En outre, Falkowski et al. (2000) rappellent que la séquestration durable de CO_2 anthropogénique dans les océans est liée aux apports fluviaux de cations nécessaires à la précipitation des minéraux carbonatés.

Les apports fluviaux de carbone aux océans : sources, production, transfert

Le carbone est au centre des interactions entre cycles biogéochimiques et climat, et les rétroactions impliquent fortement les transferts de carbone entre continent et océans. La compréhension et la quantification des processus conduisant à ces transferts de carbone par les fleuves est donc un point clef de la connaissance de l'évolution du climat au cours des temps géologiques.

La question est cependant complexe car les apports fluviaux de carbone aux océans revêtent des formes multiples et proviennent de plusieurs sources. La figure 3 représente de façon exhaustive les sources et les processus de transfert possible des différentes formes de carbone dans les hydro-systèmes. Elle est complétée par la figure 4 qui schématise la production et les transferts de carbone inorganique dissous.



CO_2 : dioxyde de carbone gazeux de l'atmosphère et des sols - C_{org} : carbone organique de la biomasse – COP : carbone organique particulaire dans les eaux d'écoulement – CIP : carbone inorganique particulaire dans les eaux d'écoulement - COD : carbone organique dissous composé de molécules organiques en solution - CID : carbone inorganique dissous composé de CO_2(aq), H_2CO_3, HCO_3^- et CO_3^{2-} - $C_{min\ II}$: carbone minéral des minéraux carbonatés de précipitation secondaires dans le sol - $C_{min\ I}$: carbone minéral des minéraux carbonatés primaire du substratum géologique – $C_{org.\ fossile}$: carbone organique fossile des roches du substratum géologique

a : photosynthèse ; b : respiration autotrophique ; c : production de litière et incorporation dans le sol ; d : dégradation des matières organiques par l'activité microbiologique et production de matières organiques dégradées, de COD et de CO_2 ; e : transfert de COD vers l'hydro-système avec éventuellement re-précipitation (f) ou oxydation (j) pendant le transfert ; g : passage de CO_2 en solution (CO_2(aq) + H_2CO_3) et utilisation du CO_2 dissous dans l'hydrolyse acide des minéraux avec conversion en ions HCO_3^- et CO_3^{2-} ; h : transfert de CID vers l'hydro-système avec éventuellement précipitation de minéraux carbonatés (k) et dégazage de CO_2 (i) pendant le transfert ; l : hydrolyse des minéraux carbonatés ; m : dégazage de CO_2 vers l'atmosphère ; n : désagrégation mécanique des matières organiques et transfert de COP vers l'hydro-système ; o : désagrégation mécanique des minéraux carbonatés et transfert de CIP vers l'hydrosystème.

figure 3 : Sources et transferts de carbone dans le système végétation – sol – eau

Dans les environnements continentaux on distingue deux sources majeures de carbone : i) la biomasse de la végétation et des sols et ii) les roches du substratum géologique. La première source est essentiellement composée de carbone organique (500 Gt + 1500 Gt de $C_{org.}$ pour la végétation et les sols respectivement ; Batjes, 1996 ; Denman, 2007) en interaction rapide avec le CO_2 atmosphérique via la photosynthèse et la respiration autotrophique et hétérotrophique. Elle est complétée par du carbone minéral sous forme de minéraux carbonatés de précipitation secondaire ($C_{min.II}$), notamment dans les sols sous climats arides et semi-arides (750 Gt de C environ ; Batjes, 1996). On considérera que l'ensemble de ce carbone est d'origine atmosphérique et, qu'à l'échelle des temps géologiques, il reste stocké très temporairement dans ce réservoir. La seconde source est majoritairement composée de carbone minéral des minéraux carbonatés ($C_{min.I}$, 120 10^6 Gt de C) et, dans une moindre mesure, de carbone organique des kérogènes et des combustibles fossiles (respectivement 23 10^6 et 5000 Gt de $C_{org.\ fossile}$, Amiotte Suchet, 1995). L'érosion chimique et mécanique de ces matériaux (végétation, sol et subtratum géologique) aboutit au transfert de

carbone vers les océans sous forme de carbone organique particulaire (COP), de carbone organique dissous (COD), de carbone inorganique particulaire (CIP) et de carbone inorganique dissous (CID). La dégradation de la matière organique par les microorganismes joue un rôle important : elle produit à la fois du COD et du CO_2. Ce dernier, après dissolution dans les eaux de percolation, forme l'acide carbonique impliqué dans les réactions d'hydrolyse acide des minéraux (figure 4). Il est alors transformé en ions HCO_3^-, plus stables, qui constituent en moyenne 2/3 du CID apporté aux océans.

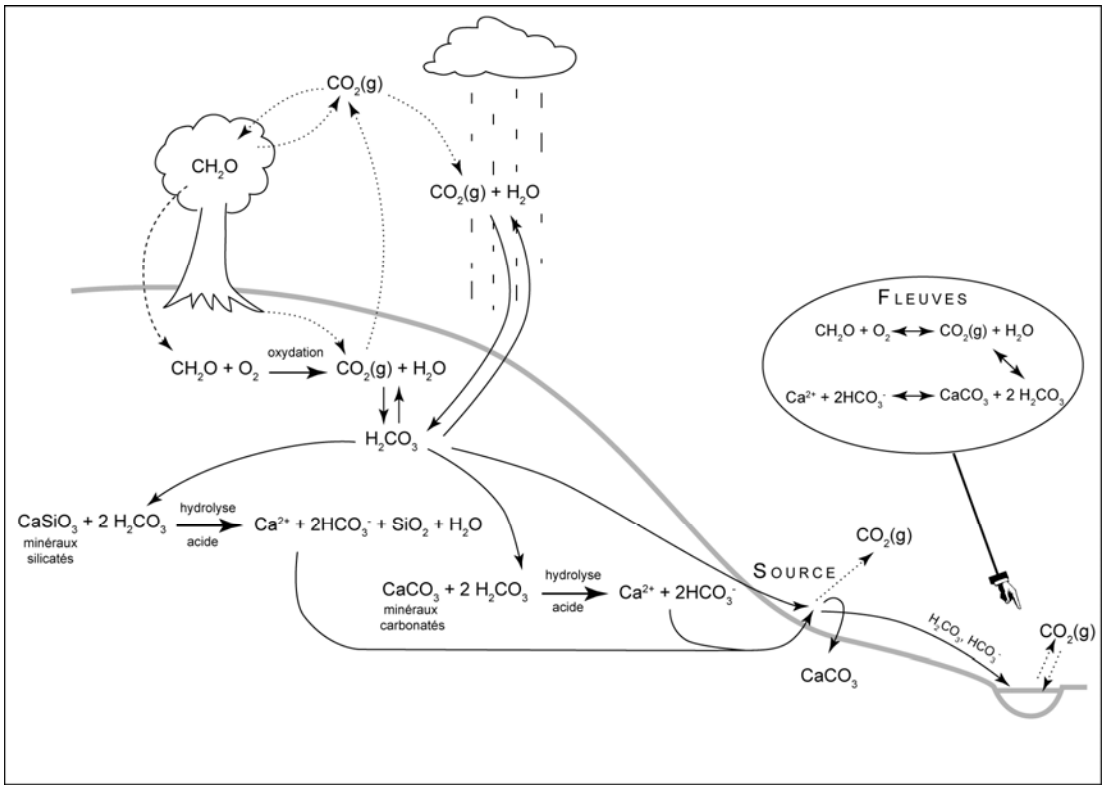


figure 4 : érosion chimique des roches, production et consommation de carbone inorganique dissous dans un hydro-système.

La question essentielle est alors de déterminer l'origine (substratum géologique ou sol-végétation) de ces différentes formes de carbone. En effet, le transfert de carbone d'origine atmosphérique (sol + végétation) puis sa sédimentation dans les bassins sédimentaires est un puits de CO_2 atmosphérique. Par contre, si le carbone transféré est d'origine géologique il n'y a aucun transfert entre réservoirs (de l'atmosphère vers un réservoir géologique) et l'effet sur la quantité de CO_2 dans l'atmosphère est nul (figure 5). Autrement dit, seul le premier cas permet une rétroaction climat-cycle du carbone à l'échelle des temps géologiques. Or, ces différentes formes de carbone ne sont pas clairement marquées (chimiquement ou physiquement) par leurs origines, ce qui rend particulièrement difficile la reconnaissance de leurs sources. De plus, un même processus peut produire du carbone ayant une double origine : par exemple l'hydrolyse acide des minéraux carbonatés par l'acide carbonique produit en solution des ions HCO_3^- dont la moitié est d'origine atmosphérique (figure 4). Enfin, ces différentes formes de carbone peuvent évoluer (précipitation, hydrolyse, dégradation, oxydation) à tout moment au cours de leur transfert (figure 3 et figure 4).

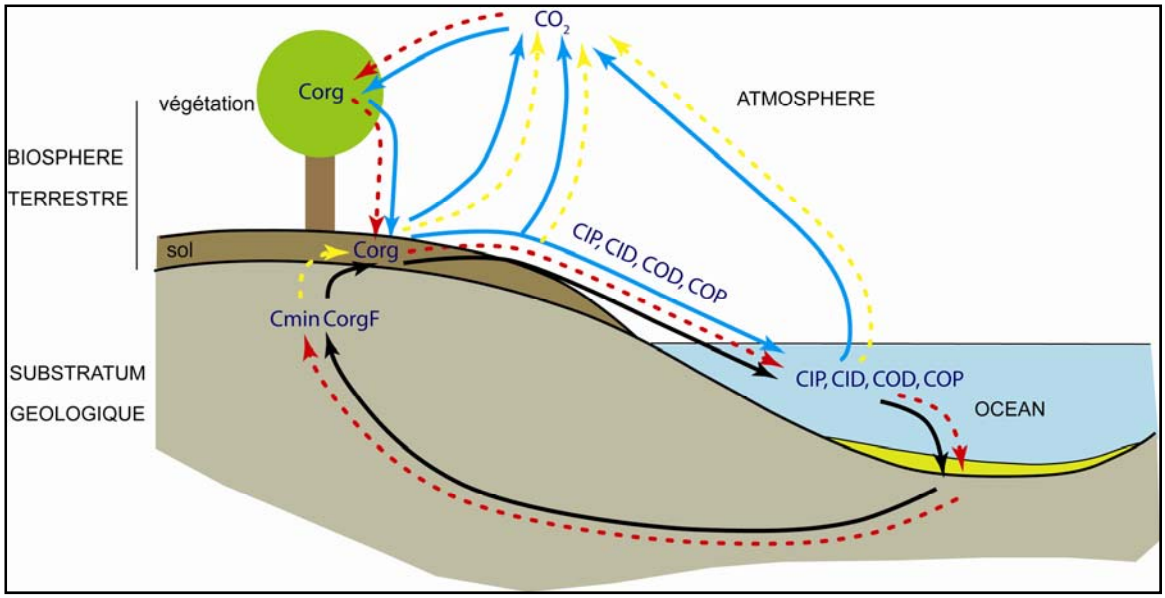


figure 5 : Le piégeage du CO_2 atmosphérique par l'érosion des sols sur les continents et sédimentation dans les océans. Les boucles bleue et noire n'ont pas d'effet sur la taille des réservoirs: le carbone retourne au réservoir d'où il vient. Le trajet rouge prélève du CO_2 dans l'atmosphère et le piège dans la lithosphère pour un temps long ; il est complété par le trajet jaune qui transfert du carbone fossile à l'atmosphère. Corg : carbone organique d'origine atmosphérique, CorgF : carbone organique de la lithosphère ou fossile, Cmin : carbone minéral de la lithosphère. Dans les eaux : CIP et CID : carbone inorganique particulaire et dissous, COP et COD : carbone organique particulaire et dissous.

L'ensemble de mes recherches, depuis le début de ma thèse de Doctorat, visent à améliorer notre connaissance des transferts de matières continents-océans, plus particulièrement en ce qui concerne le carbone. Quels sont les facteurs de ces transferts ? Comment ces transferts varient-ils dans l'espace et dans le temps ? Quelles quantités sont apportées chaque année aux océans ? Comment évoluent-elles avec le changement climatique ?

Au début des années 90, l'état des lieux sur la question était limité à la connaissance des processus et à l'établissement de bilans d'apports de carbone par les fleuves à l'océan mondial (Berner *et al.*, 1983; Holland, 1978; Kempe, 1979; Meybeck, 1979; Meybeck, 1987; Meybeck, 1992; Probst, 1992; Wollast & Mackenzie, 1983). En outre, les chercheurs travaillant sur la thématique de la séquestration de CO_2 atmosphérique au cours des temps géologiques étaient peu nombreux, notamment en France. D'ailleurs, l'expression « consommation de CO_2 par érosion chimique » restait obscure pour la plupart des géologues. Il s'agissait donc d'aller au-delà du simple bilan et de mieux définir quels étaient les principaux facteurs de ces transferts pour ensuite mieux cerner leur dynamique spatiale et temporelle.

Ma thèse de Doctorat, réalisée au Centre de Géochimie de la Surface à Strasbourg sous la direction de Jean-Luc Probst, a porté sur les transferts de carbone inorganique par les fleuves à l'échelle continentale (Amiotte Suchet, 1994; Amiotte Suchet & Probst, 1993a; 1993b; Amiotte Suchet & Probst, 1995a; 1995b). Cette étude à conduit au développement d'un modèle diagnostique (MEGA) permettant de reconstituer l'origine des flux d'éléments majeurs (dont le carbone inorganique) en solution dans les eaux d'écoulement ainsi que d'un modèle permettant de simuler la consommation de CO_2 par érosion chimique des roches continentales (GEM-CO_2). Parallèlement, les transferts de carbone organique furent traités grâce aux travaux de thèse de Wolfgang Ludwig (Ludwig, 1996) effectués dans le même laboratoire et sous la même direction scientifique. L'ensemble de ces travaux a notamment abouti à la mise au point du modèle GEM-C permettant de simuler la variabilité spatiale et temporelle des transports fluviaux de carbone pour

l'ensemble des surfaces continentales (Ludwig *et al.*, 1996a). Les bilans globaux des transferts estimés par ces travaux sont présentés dans le tableau 1.

Cependant, GEM-C ne prenait pas clairement en compte le sol, les processus de production de carbone organique et inorganique qui s'y tenaient et leurs facteurs de contrôle climatiques et biologiques. D'autre part, il ne différenciait pas le carbone organique fossile du carbone organique des sols. A la suite de ma thèse de Doctorat, mes travaux de recherche se sont donc tournés vers ces questions. Pour y répondre, il était nécessaire de retourner vers l'acquisition de nouvelles données sur le terrain, en explorant notamment de nouvelles méthodes permettant de tracer les transferts de carbone et de les relier au fonctionnement des sols. Parallèlement, GEM-C et MEGA ouvraient un vaste champ d'applications dans le domaine de l'érosion des continents et des apports fluviaux aux océans.

tableau 1 : apports fluviaux de carbone aux océans : sources, formes, quantités (d'après Amiotte Suchet & Probst, 1995b; Ludwig *et al.*, 1996a)

Origine	Forme	Apport moyen annuel aux océans (109 t/an)
CO_2 des sols et de l'atmosphère	CID	0,23
Carbone organique des sols	COD	0,20
	COP	0,19
Carbone minéral des sols (minéraux carbonatés secondaires)	CID	??
	CIP	??
Carbone inorganique géologique (minéraux carbonatés primaires)	CID	0,10
	CIP	0,17
Carbone organique fossile	COD	??
	COP	??

CID : carbone inorganique dissous ; CIP : carbone inorganique particulaire ; COD : carbone organique dissous ; COP : carbone organique particulaire

1.3 Pour une approche intégrée multi-échelle

Dans le domaine des transferts fluviaux continents-océans, les travaux se trouvent systématiquement confrontés aux difficultés de l'analyse des processus à des échelles spatiales et temporelles extrêmement variables : de l'échelle microscopique à l'échelle planétaire, de l'échelle des temps géologiques à l'échelle journalière.

Les échelles multiples nécessitent des approches multiples elles aussi, mais surtout complémentaires. En effet, les modèles globaux se nourrissent des processus mis en évidence et quantifiés à des échelles fines et permettent en retour de définir quels processus sont les plus pertinents à large échelle. Les approches utilisées dans mes travaux de recherche font aussi bien appel à la modélisation qu'à l'observation et à la mesure à l'échelle des bassins versants comme à l'échelle de dispositifs expérimentaux au laboratoire.

La modélisation : quantification des transferts à large échelle

Deux modèles ont été développés en thèse de doctorat (Amiotte Suchet, 1994; Amiotte Suchet & Probst, 1993a; 1993b; Amiotte Suchet & Probst, 1995a; 1995b) : GEM-CO2 (Global Erosion Model – CO2) et MEGA (Major Element Geochemical Approach). Ils ont ensuite été améliorés et appliqués à différentes questions dans mes travaux post-thèse dans le cadre de collaborations (Amiotte Suchet *et al.*, 2003; Aumont *et al.*, 2001; Copard *et al.*, 2007; Ludwig *et al.*, 1998; Ludwig *et al.*, 1996a; Ludwig *et al.*, 1999; Semhi *et al.*, 2000a; Semhi *et al.*, 2000b).

GEM-CO2 est un modèle paramétrique simple permettant de simuler la distribution spatiale et temporelle des apports de CID aux océans en tenant compte de leurs origines. Il est basé sur les relations lithologie - drainage - flux de CID quantifiées à l'échelle de petits bassins versants monolithologiques.

MEGA est un modèle diagnostique qui reconstitue l'origine minéralogique des ions majeurs (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, HCO_3^{-}) mesurés en solution dans les eaux d'écoulement. Il s'applique à la composition des matières en solution mesurées dans les eaux des bassins fluviaux et détermine, par exemple, quelles sont les différentes proportions de Ca^{2+} provenant des apports atmosphériques, de l'altération des silicates, des carbonates ou du gypse.

Ces deux modèles, par des approches complètement différentes, visent à déterminer quelle part prend le CO_2 des sols et de l'atmosphère dans les apports de CID aux océans.

Utilisation des isotopes stables du carbone à l'échelle des bassins versants

Dans toute recherche visant à déterminer et quantifier la production et le transfert d'élément chimique dans l'environnement, l'utilisation des isotopes stables a toujours été un outil pertinent. La composition isotopique de l'élément est marquée soit directement par le réservoir source, soit par les processus ayant affecté l'élément tout au long de son parcours (production, changement de forme ou d'état notamment). Deux types d'approches sont alors possibles : i) définir l'origine de l'élément dont la composition isotopique a gardé la mémoire du réservoir source ; ii) retrouver la chaine des processus (et des paramètres les contrôlant) ayant isotopiquement marqué l'élément chimique.

Une part conséquente de mes travaux post-thèse ont été consacrés à l'utilisation des isotopes stables du carbone pour tracer les transferts de CID et COD dans les hydro-systèmes. Il s'agissait tout d'abord de comprendre comment le carbone en solution dans les eaux d'écoulement (CID et COD) acquérait sa composition isotopique en travaillant à l'échelle de petits bassins versants. Cette approche, a permis en outre d'explorer à l'échelle des bassins versants, les mécanismes de production de carbone inorganique et organique dissous directement liés au fonctionnement du sol et totalement absents des modèles GEM-C et MEGA.

On rappellera ici tout l'intérêt de « l'approche bassin versant » pour l'étude de processus liés au fonctionnement des sols. En effet, la signature géochimique portée par les eaux d'écoulement à l'exutoire de l'hydro-système résulte de l'ensemble des processus physiques, chimiques et biologiques présents dans cet hydro-système, notamment dans ses sols. L'analyse de cette signature permet donc en théorie d'identifier ces processus et parfois de les quantifier. A titre d'exemple, une telle approche a été d'un grand bénéfice dans l'étude de l'acidification des écosystèmes forestiers.

Approches expérimentales au laboratoire

L'approche à l'échelle des bassins versants, même très homogènes et de faible dimension, souffre de certaines lacunes. Si la fonction intégratrice gomme les hétérogénéités et permet de dégager des tendances, elle occulte également souvent la réalité des mécanismes. Le bassin versant est trop souvent une « boite noire » dont on observe et quantifie les flux entrant et sortants. Par ailleurs, le non contrôle de certains paramètres, notamment climatiques, rend les interprétations plus complexes et limite la généralisation des résultats. Les approches expérimentales au laboratoire viennent avantageusement compléter les dispositifs bassin versant, en focalisant les recherches sur des mécanismes précis et en permettant de contrôler le maximum de facteurs. La quantification des processus est alors plus précise et complète. La question de la réalité de ces processus sur le terrain peut ensuite être levée en travaillant à nouveau à l'échelle du bassin versant.

2 Le rôle de l'érosion dans le cycle biogéochimique du carbone : apports du modèle GEM-C

Cette approche a été initiée en thèse de Doctorat puis affinée et appliquée dans des travaux post-thèse. Elle concerne plus particulièrement les transferts de carbone inorganique dissous (CID essentiellement constitué d'ions HCO_3^-) à l'échelle globale. Pour plus d'information sur le développement et la validation du modèle GEM-CO2 (transferts de CID uniquement), qui évolua avec les travaux de W. Ludwig en GEM-C (transfert de CID, de COD et de COP), on se référera aux publications suivantes : Amiotte Suchet and Probst (1993a; 1993b; 1995b), Amiotte Suchet et al. (Amiotte Suchet *et al.*, 1995) et Ludwig et al. (1996a).

Le résultat essentiel de ces travaux a été de proposer, pour la première fois, une distribution spatiale des apports de carbone par les fleuves aux océans avec une bonne fiabilité et une résolution de 5° x 5° autorisant le couplage avec les modèles de cycle du carbone. L'influence des apports fluviaux aux océans sur le fonctionnement actuel du cycle géochimique du carbone était alors inconnue, bien que certains auteurs (Sarmiento & Sundquist, 1992) reconnaissaient depuis quelques années que ces apports ne pouvaient être négligés même à courte échelle de temps. Une collaboration initiée par J.L. Probst et W. Ludwig avec J. Orr et O. Aumont (LSCE, Gif/Yvette) a permis de coupler GEM-C avec un modèle 3D de cycle du carbone océanique, montrant clairement que la distribution spatiale des apports fluviaux de carbone influençait les transferts inter-hémisphériques de carbone dans l'océan (Aumont *et al.*, 2001).

A des échelles de temps plus longues, de nombreuses autres questions restaient en suspens. Je présenterai ici trois exemples d'application de GEM-CO2 ou de GEM-C permettant d'apporter des éléments de réponse quant au rôle joué par l'érosion et les transferts fluviaux dans le cycle géochimique du carbone. La nature des roches affleurant à la surface des continents et exposée à l'érosion est au cœur de ce questionnement :

quelle est l'influence de la distribution spatiale des roches affleurant à la surface des continents sur l'érosion chimique des roches et donc sur les apports de CID aux océans ?

la modification de l'état de surface des continents par des évènements climatiques globaux comme les glaciations quaternaires (accroissement des surfaces continentales englacées, baisse du niveau marin) engendre-t-elle une variation significative de la consommation de CO2 atmosphérique par érosion ?

Quelle est la part de carbone organique fossile libéré par l'érosion des roches continentales dans les apports fluviaux de carbone aux océans ?

2.1 Distribution spatiale des roches continentales et consommation de CO_2 par érosion chimique.

GEM-CO_2 a clairement montré que la nature des roches altérées à la surface des continents constitue, avec l'intensité du drainage, la clef des variations de la consommation de CO_2 atmosphérique. On rappellera en outre que seule l'altération des roches silicatées affecte à long terme la concentration de CO_2 dans l'atmosphère et que ces roches silicatées s'altèrent à des vitesses différentes. En résumé, les roches carbonatées n'ont aucune influence et, parmi les roches silicatées, l'altération des basaltes consomme 4 fois plus que celle des granites et 2 fois plus que celle des roches volcaniques acides (Amiotte Suchet & Probst, 1993a).

Plusieurs aspects doivent alors être examinés :

- Quel est le poids de chacun des grands types de roche affleurant à la surface des continents dans les apports de CID aux océans et dans la consommation de CO_2 par érosion chimique ?
- La quantification des apports aux océans par l'estimation des flux de CID transporté par les grands fleuves mondiaux, représentant moins de la moitié des surfaces

continentales, est-elle pertinente? Autrement dit, la géologie du substratum des grands bassins fluviaux est-elle représentative de l'ensemble des surfaces continentales ?

Il était donc nécessaire dans un premier temps de construire une carte mondiale des différents types de roche affleurant à la surface des continents et prenant en compte la nature minéralogique des roches (figure **6**). Dans un second temps, GEM-CO_2 a permis de déterminer les quantités de CID (ou d'alcalinité) mis en solution et de CO_2 consommé pour chaque type de roche et pour chaque grand bassin fluvial.

tableau 2 : bilan global des apports de CID aux océans et de la consommation de CO_2 par érosion chimique des roches continentales par classe lithologique

	Sables et grès (a)	Shales (b)	Roches carbonatées (c)	Roches de bouclier (d)	Roches volcaniques acides (e)	Basaltes (f)	Total*
CID transporté par les fleuves, Ft	1,1	8,57	17,26	1,5	0,21	1,49	30,1
CID transporté par les fleuves, Fs	30,92	250,84	956,53	40,36	64,31	215,04	223,4
CO_2 consommé, Ft	1,1	8,57	8,63	1,5	0,21	1,49	21,5
CO_2 consommé, Fs	30,92	250,84	478,26	40,36	64,31	215,04	159,4
Surface (10^6 km_2)	35,42	34,16	18,03	37,13	3,05	6,94	134,7
Drainage ($mm.an^{-1}$)	195,73	400,06	301,55	424,85	303,18	448,94	340,3
pourcentage du CID total (%)	3,7	28,4	57,3	5,0	0,7	4,9	100,0
pourcentage du CO_2 total (%)	5,1	39,9	40,1	7,0	1,0	6,9	100,0
pourcentage du CO_2 consommé par altération des silicates (%)	8,5	66,6		11,7	1,6	11,6	100,0
Proportion d'affleurement (%)	26,3	25,4	13,4	27,6	2,3	5,2	100,0

F_T : flux total en 10^{12} $moles.an^{-1}$; F_S : flux spécifique en 10^3 $moles.km^{-2}.an^{-1}$

* Somme des colonnes a-f ou moyenne pondérée par les surfaces des colonnes a-f pour les flux spécifiques et le drainage

Le bilan présenté dans le tableau 2 montre tout d'abord que, malgré une faible proportion d'affleurement (13,4%) l'altération des carbonates contribue à plus de 57% des apports de CID aux océans et implique 40% de la totalité du CO_2 consommé par érosion chimique des roches. Sur ce dernier point, on se focalisera sur l'altération des silicates, seul véritable puits de CO_2 à long terme. Les shales semblent être les roches silicatées les plus influentes : leur altération contribue à 28,4 % des apports de CID aux océans ce qui correspond à près de 40% de la totalité du CO_2 consommé (les 2/3 du CO_2 consommé par l'altération des silicates). Par comparaison, l'altération des roches de bouclier (roches plutoniques et métamorphiques) ne consomme que 7 % du CO_2 total pour la même surface d'affleurement. La question de la présence de minéraux carbonatés dans les shales reste posée. Elle constituerait environ 6% de la totalité des minéraux des shales en moyenne mais cette proportion reste fortement variable à l'intérieur de cette classe lithologique très hétérogène (Garrels & Mackenzie, 1971).

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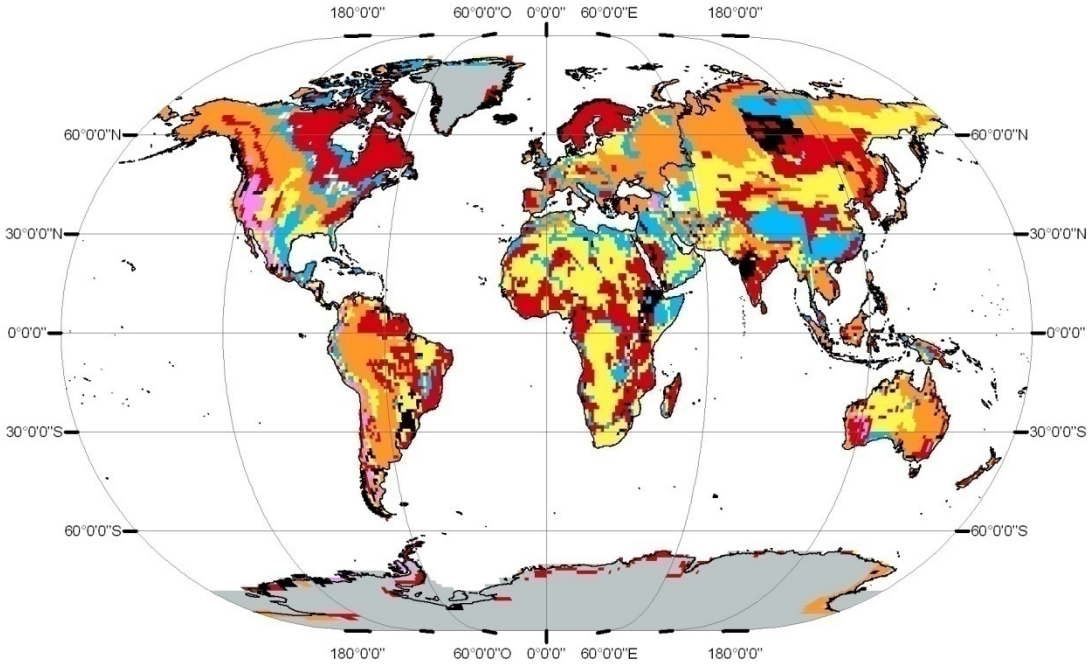

figure **6** : Distribution spatiale des différents types de roche affleurant à la surface des continents

Le poids des basaltes doit être considéré avec attention (7 % du CO_2 total pour seulement 5% des affleurements): non seulement il arrive en deuxième position des roches silicatées mais leur présence à la surface des continents est directement liée à l'avènement des grands évènements volcaniques qui ont probablement très fortement perturbés le fonctionnement du système Terre au cours de son histoire géologique. De tels évènements (Trapp du Deccan, Trapp du Parana) peuvent en quelques centaines de milliers d'années doubler la superficie des affleurements et accentuer la régulation de CO_2 atmosphérique par érosion chimique (Dessert *et al.*, 2003).

tableau 3 : composition lithologique relative des 39 plus grands bassins fluviaux (en % de la surface totale S_T).

	Sables et grès	Shales	Roches carbonatées	Roches de bouclier	Roches volcaniques acides	Basaltes	Total*
39 grands bassins fluviaux S_T = 49,11 10^6 km^2	22,3	32,2	11,8	27,1	1,6	5,0	100
Surfaces continentales non glacées S_T = 134,74 10^6 km^2	26,3	25,4	13,4	27,6	2,3	5,2	100

La distribution des grands types de roche par grand bassin fluvial (tableau 3) montre une relativement bonne représentativité des proportions observées pour l'ensemble des surfaces continentales. On notera cependant que les shales sont plutôt surreprésentées au détriment des sables et des grès. L'extrapolation des bilans d'altération réalisés sur les grands bassins fluviaux à

l'ensemble des surfaces continentales pourrait donc conduire à une légère surestimation puisque les shales sont 4 fois plus altérables que les sables et les grès (Amiotte Suchet & Probst, 1993a; Amiotte Suchet & Probst, 1993b)

GEM-CO_2 montre ici clairement que les apports de CID à l'océan sont avant tout le fait de l'altération des roches carbonatées et des shales (plus de 80% des apports) alors que surfaces affleurantes constituent moins de 40% des surfaces continentales. En ce qui concerne la régulation du CO_2 atmosphérique à long terme par l'altération des silicates, les shales et les basaltes sont à considérer avec attention, les premières pour leur influence sur les flux totaux, les seconds pour leur lien direct avec les cycles tectoniques globaux.

Ce travail montre également l'importance du facteur lithologie et la nécessité d'en avoir une bonne représentation. Il ne faut pas négliger les efforts à poursuivre pour améliorer notre connaissance de la typologie des surfaces continentales. Sur ce point en particulier, on se référera aux récents travaux de Durr et al. (2005) et Meybeck et al. (2006) notamment.

Publication:

Amiotte Suchet, P., Probst, J.L., Ludwig, W., (2003) Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochem. Cycles*, 17((2)), 1038, doi : 10.1029/2002GB001891.

2.2 L'Erosion des surfaces continentales: un puits de CO_2 atmosphérique au dernier maximum glaciaire ?

La sensibilité de la consommation de CO_2 à la physionomie géologique des surfaces continentales débouche sur de nombreuses questions, notamment celle de l'influence des glaciations. En effet, d'un coté la mise en place des calottes soustrait de larges surfaces de roche à l'érosion chimique pendant que, d'un autre coté, de nouvelles surfaces continentales sont exposées par la baisse du niveau des océans. Il s'agit alors de savoir si une telle perturbation augmente la consommation de CO_2 par érosion chimique ou bien la diminue. Autrement dit, le refroidissement climatique est-il renforcé ou limité par cette modification de l'état des surfaces continentales (Ludwig *et al.*, 1998) ?

Une collaboration entre le CGS Strasbourg (J.L. Probst, W. Ludwig), où j'étais en contrat post-doctoral, et le LGAT de Liège (L. François, G. Munhoven) a permis d'apporter des éléments de réponse à cette question. Ma contribution à ce travail portait essentiellement sur la prise en compte du changement d'état de surface des continents. Les résultats ont été publié dans *Chemical Geology* en 1999 (Ludwig *et al.*, 1999).

Nous avons choisi d'appliquer GEM-CO2 aux conditions du dernier maximum glaciaire (18000 ans b.p.). L'utilisation de GEM-CO2 dans le cadre de ce travail nous a rapidement confronté à une difficulté majeure : le manque d'informations fiables concernant 1) la distribution spatiale des variables climatiques, notamment du drainage, et 2) la nature des roches nouvellement mises à l'affleurement par la baisse du niveau marin. La démarche a donc consisté à tester différentes configurations lithologiques des surfaces continentales nouvellement exposées dans le contexte climatique du dernier maximum glaciaire. Ce dernier a été reconstruit dans le cadre de cette étude sur la base des sorties du modèle de circulation générale (GCM) ECHAM2 (Lautenschlager & Herterich, 1990) simulant le climat global du dernier maximum glaciaire.

Dans un premier temps, considérant que le drainage continental est le premier facteur de l'érosion des continents, la lithologie des marges océaniques découvertes au dernier maximum glaciaire n'a pas été prise en compte. Le bilan de la consommation de CO_2 a été réalisé en

extrapolant les flux de CO_2 consommé simulés pour les surfaces continentales actuelles aux surfaces continentales du dernier maximum glaciaire. Les variables prises en compte sont le changement de superficie continentale et le changement de drainage. Les résultats (Ludwig *et al.*, 1999) montrent que, les surfaces continentales exposées à l'érosion ayant peu changé en superficie (la perte de superficie par englacement est grossièrement compensée par le gain de nouvelles surfaces par baisse du niveau marin), c'est la variation de drainage continental qui contrôle l'évolution des flux de CO_2 consommé. En conséquence, le drainage étant globalement plus faible au dernier maximum glaciaire qu'aujourd'hui (diminution de 9%), le flux de CO_2 consommé était inférieur d'environ 5% par rapport à celui simulé pour les temps actuels. Par ailleurs il n'y a aucune différence en termes de consommation de CO_2 par l'altération des silicates.

Dans un second temps, un test de sensibilité a été réalisé pour évaluer le rôle potentiel des changements de lithologie sur les marges continentales découvertes au dernier maximum glaciaire. Les résultats des simulations sont synthétisés dans le tableau 4. Le flux total pour l'ensemble des surfaces continentales serait augmenté de 15 à 30% lorsque ce sont des carbonates qui affleurent au moins partiellement sur les marges continentales. Par contre, le flux consommé par l'altération des silicates ne change pas ou même diminue dans la plupart des cas (jusqu'à -20%). Dans le cas de la configuration la plus réaliste, dans laquelle les marges sont composées de carbonates aux latitudes inter-tropicales et de shales aux autres latitudes, le modèle montre une augmentation de 22% du flux total et une diminution de 5% du flux consommé par l'altération des silicates.

tableau 4 : consommation de CO_2 atmosphérique sur les marges continentales découvertes au dernier maximum glaciaire pour différentes lithologies

Nature lithologique des marges océaniques découvertes au dernier maximum glaciaires	*F*CO2 total				*F*CO2 consommé par altération des silicates	
	Surface ancienne (Tg C.a^{-1}) (1)	Surface découverte (TgC.an^{-1}) (2)	Total (Tg C.an^{-1})	Variations (% du flux actuel) (3)	(Tg C.an^{-1})	Variations (% du flux actuel) (3)
sable/grès	175.69	15.40	191.09	83.1	125.10	89.4
carbonates	175.69	128.90	304.59	132.4	112.60	80.5
shales	175.69	56.30	231.99	100.9	166.10	118.7
carbonates 30°S–30°N (shales ailleurs)	175.69	105.80	281.49	122.4	132.20	94.5
carbonates 30°S–30°N (sables/grès ailleurs)	175.69	89.30	264.99	115.2	115.70	82.7

(1) Surfaces continentales actuelles exposées à l'érosion au dernier maximum glaciaire
(2) Surfaces continentales nouvellement exposées (marges continentales)
(3) Ratio dernier maximum glaciaire/actuel exprimé en %

En conclusion, les résultats de ce travail montrent que la consommation de CO_2 par érosion chimique des silicates ne change pas, voir tendrait à diminuer dans les conditions géologiques et climatiques du dernier maximum glaciaire. Le refroidissement ne serait donc pas amplifié par la mise en place d'une boucle de rétro-action positive via l'altération des continents.

Reste que ces simulations sont avant tout indicatives car le modèle souffre d'un certain nombre de lacunes : i) les processus d'érosion chimique en environnement glaciaire ne sont pas pris en compte et sont supposés être les mêmes qu'en contexte non glaciaire ; ii) l'érosion chimique des surfaces continentales englacées est supposée nulle car non exposés aux

précipitations ; iii) la climatologie reconstruite d'après le GCM reste très approximative, notamment en ce qui concerne le drainage continental.

Publications:

Ludwig, W., Amiotte Suchet, P., Munhoven, G., Probst, J.L., (1998) Atmospheric CO2 consumption by continental erosion: present-day control and implications for the Last Glacial Maximum. Global and Planetary Change, 16-17, 107-120.

Ludwig, W., Amiotte Suchet, P., Probst, J.-L., (1999) Enhanced chemical weathering of rocks during the last glacial maximum: a sink of atmospheric CO2? *Chem. Geol*, 159, 147-151.

2.3 Libération de carbone organique fossile dans les environnements continentaux superficiels

Les précédents travaux sur la modélisation des transferts de carbone continents-océans ont été récemment complétés par une étude, basée sur GEM-CO2, qui estime les quantités de carbone organique fossile remises dans le cycle supergène par altération des roches (Copard *et al.*, 2007). Là encore, la régulation de la concentration de CO_2 dans l'atmosphère par enfouissement ou minéralisation de carbone organique fossile est au cœur de la problématique des rétroactions climat-cycle du carbone. L'oxydation de matières organiques à la surface de la Terre (dans le sol, au cours du transfert continent-océan ou dans les océans) n'a pas d'incidence sur la taille des réservoirs si ces matières organiques ont été récemment produites à partir de CO_2 atmosphérique par les organismes photosynthétiques. En revanche, si ces matières organiques sont « fossiles », leur oxydation constitue un transfert du substratum géologique vers l'atmosphère, modifiant la taille des réservoirs (figure 5). De la même façon, le transfert continent-océan puis l'enfouissement de matières organiques ne constitue un puits de CO_2 atmosphérique que si ces matières organiques sont produites à court terme par photosynthèse de CO_2 de l'atmosphère.

La question de la proportion de carbone organique fossile (COF) dans les quantités de COD et de COP transportées par les fleuves est posée depuis plusieurs décennies sans qu'aucune réponse n'ait clairement été apportée, notamment en raison de la difficulté que les chercheurs ont à distinguer les matières organiques récentes des matières organiques fossiles (voir l'analyse bibliographique dans Copard *et al.*, 2007). Cette difficulté conduit à privilégier d'autres approches visant à estimer les flux de COF à partir des processus producteurs plutôt qu'à tenter de les observer et les identifier dans les milieux naturels. Ainsi, l'approche proposée dans ce travail comporte deux étapes. Elle consiste, dans un premier temps, à évaluer les quantités de COF présentes dans le premier mètre du substratum géologique, sur la base de la distribution mondiale des types de roche (Amiotte Suchet *et al.*, 2003) et de leurs caractéristiques présentées dans le tableau 5.

tableau 5 : proportion à la surface des continents (d'après Amiotte Suchet *et al.*, 2003), densité (calculé d'après Berton & Le Berre, 1995) et teneur en carbone organique (calculé d'après Ronov & Yaroshevskiy, 1976) des principales catégories de roches sédimentaires (Copard *et al.*, 2007).

	proportions on continental surface (%)	density	OC content (weight %)	lithological description
Shales	25.4	2.2	1.00	clastic and argilaceous sediments (poorly carbonated)
Carbonates	13.4	2.5	0.28	all rocks with more >50% of carbonates minerals
sand and sandstones	26.2	2.1	0.24	all sandy sediments

Dans un second temps, les quantités de COF potentiellement libérées par l'altération de ce premier mètre de roche sont estimées en adaptant GEM-CO2 (Amiotte Suchet & Probst, 1995b) pour qu'il calcule des flux d'érosion chimique (et plus seulement des flux de carbone inorganique dissous). GEM-CO2 est alors modifié pour calculer la totalité des matières mises en solution par érosion des roches sédimentaires, notamment en tenant compte du résidu insoluble de ces roches.

Les résultats peuvent paraître assez surprenants, particulièrement pour ce qui concerne le stock de carbone organique fossile dans le premier mètre du substrat géologique. Il est en effet estimé à 1100 Gt de carbone, ce qui est comparable au 1500 Gt de carbone organique présent dans le premier mètre de sol (Eswaran *et al.*, 1993). On notera cependant qu'il n'est pas réparti de façon homogène à la surface des continents puisqu'uniquement présent dans les roches sédimentaires. Ainsi, parmi les 40 plus grands bassins fluviaux, cinq bassins (Amazone, Ob, Mississipi, Parana, Lena) renfermeraient près de 40% du stock de carbone organique fossile pour moins de 30 % de la surface des bassins fluviaux. Par contre, le bassin du Congo, deuxième plus grand bassin en surface, renferme moins de 2% du stock de COF (près de 10 fois moins que celui de l'Amazone).

La quantité de COF libérée annuellement par l'altération des roches présente logiquement une distribution hétérogène à la surface des continents (figure 7) et reflète la distribution des shales (riches en COF) et du drainage (qui favorise l'érosion chimique). Le bilan des quantités de COF libérée par érosion chimique sur chaque bassin fluvial place l'Amazone largement en tête avec près de 11 millions de tonnes de carbone par an, soit près de ¼ de la production mondiale annuelle ($43\ 10^6$ $tC.an^{-1}$). Ceci n'est pas surprenant car l'Amazone est bien le plus grand, le plus arrosé et le plus riche en shales de tous les grands bassins fluviaux. Reste que les autres bassins les plus producteurs de COF comme le Ganges-Brahmapoutre, l'Ob, le Mississipi ou la Paraná présentent des flux au minimum 10 fois plus petits ($1{,}17$ à $0{,}32\ 10^6$ $t.C.an^{-1}$) que celui de l'Amazone.

Ces estimations doivent être replacées puis discutée en considérant l'équation bilan suivante :

$$COF_{fleuve} = COF_{sol} + COF_{roche} + COF_{alluvion} - COF_{sed} - COF_{min} \qquad \text{(Équation 1)}$$

Où :

$COF_{océan}$: COF total apporté aux océans par les fleuves

COF_{sol} : COF libéré par l'érosion chimique des roches et stocké dans les formations superficielles

COF_{roche} :COF issu de l'érosion mécanique des roches

$COF_{alluvion}$: COF issu de l'érosion mécanique des dépôts des plaines d'inondation

COF_{sed} : COF déposé dans le bassin versant

COFmin : COF minéralisé au cours de sont transport dans le bassin versant

L'estimation de $43\ 10^6$ $tC.an^{-1}$ réalisée dans ce travail correspond au terme COF_{sol} de l'équation 1. Si on considère que le flux total de COF exporté par les fleuves vers les océans (COF_{fleuve}) est d'environ $80\ 10^6$t. C/an (Meybeck, 1993) et que le flux de COF issu de l'érosion mécanique des roches (COF_{roche}) est d'environ $40\ 10^6$t. C/an (Blair *et al.*, 2003), on en déduit que les autres termes de l'équation 1 sont négligeables ou se compensent. Cela ne paraît pas aberrant et met bien en évidence l'intérêt de notre démarche.

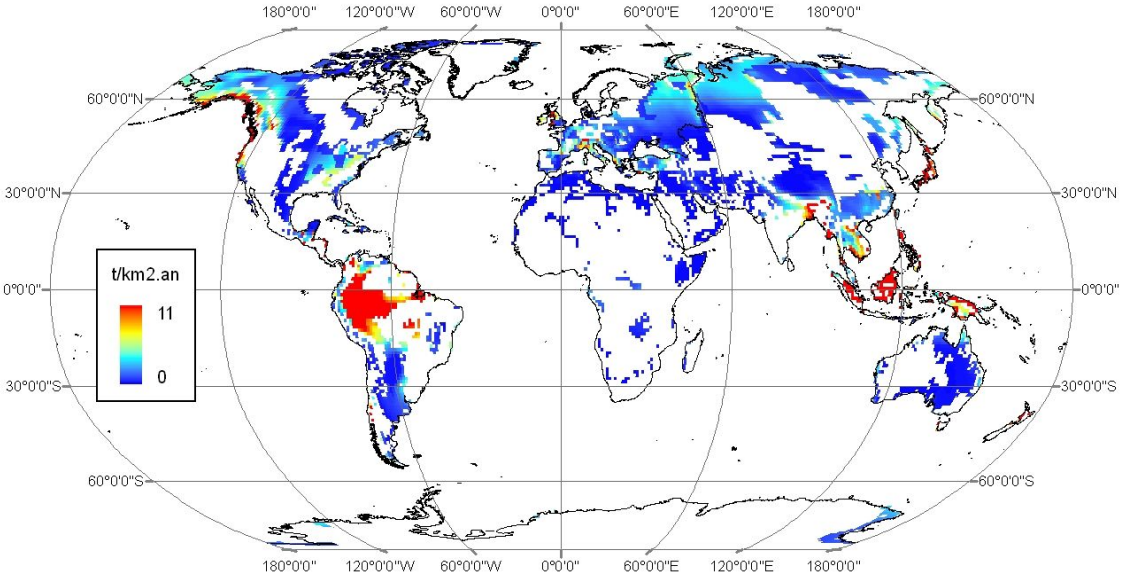

figure 7 : Quantités de carbone organique fossile (COF, en $t.km^{-2}.an^{-1}$) libérée par l'altération du premier mètre de roches sédimentaires affleurant à la surface des continents

Cependant, l'examen particulier du bassin de l'amazone met bien en évidence les nombreuses zones d'ombre. Ainsi, si l'on compare les 11 10^6 $t.C.an^{-1}$ de COF produit par l'érosion chimique des roches sur le bassin versant de l'Amazone aux 17 10^6 $t.C.an^{-1}$ de carbone organique particulaire (COP) transporté par l'Amazone, on peut supposer que la part du COF dans le COP apporté par l'Amazone à l'océan atlantique ne devrait pas être négligeable. Ceci est pourtant en contradiction avec plusieurs travaux montrant que ce COP a une origine récente (Hedges *et al.*, 1986; Mayorga *et al.*, 2005). On peut faire le même constat concernant le Ganges-Brahmapoutre : le bassin versant est le second plus grand producteur de COF (1,17 10^6 $t.C.an^{-1}$), mais qu'il délivre au Golf du Bengale serait d'origine moderne à plus de 70% (Galy *et al.*, 2007). Les explications à ces contradictions sont multiples : quelle est la stabilité du COF une fois libéré dans les environnements superficiels ? Est-il largement minéralisé, transformé en composés plus évolués, éventuellement dissous ? Comment est-il incorporé aux matières organiques fraiches dans les sols ? Est-il clairement distinguable du carbone moderne ? Garde t-il son identité fossile ?

Les questions à élucider restent donc nombreuses, mais ce travail de modélisation à l'échelle globale, similaire à l'approche GEM-C et basée sur une évolution de GEM-CO2, a permis de mettre en évidence que le premier mètre de roche sédimentaire pouvait contenir quasiment autant de carbone que les sols (1100 et 1500 Gt.C respectivement) et que ce carbone fossile pouvait être libéré en surface à raison de 43 10^6 $t.C.an^{-1}$. On peut donc soupçonner la présence d'une part non négligeable de COF dans les apports de carbone fluviaux aux océans et les prochains travaux doivent s'atteler à détecter ce COF et à examiner son devenir dans les environnements supergènes.

Publication:

Copard, Y., Amiotte-Suchet, P., Di-Giovanni, C., (2007) Storage and release of fossil organic carbon related to weathering of sedimentary rocks. *Earth and Planetary Science Letters*, 258(1-2), 345-357.

3 Dynamique des transferts continents-océans : approche diagnostique MEGA

On vient de le voir, les approches globales sont pertinentes pour évaluer l'impact des processus d'érosion à l'échelle planétaire et leur rôle dans le fonctionnement des cycles biogéochimiques. Elles restent cependant « statiques » et ne permettent pas d'aborder la dynamique même de ces processus. Une autre approche consiste à *déconvoluer* les signaux géochimiques observés à l'exutoire des bassins versants. Cette approche n'est pas seulement une interprétation des variations spatio-temporelles des flux hydro-chimiques ; elle consiste surtout en un diagnostique du fonctionnement de l'hydro-système et des processus qu'il abrite. Là encore, l'élaboration d'un modèle s'avère nécessaire. Ce dernier ne permet alors pas de simuler mais plutôt d'identifier et de caractériser les processus pour mieux comprendre leur dynamique.

Le modèle MEGA a été développé en thèse de doctorat et permet de reconstituer l'origine (minéraux, CO_2 du sol) des éléments transportés en solution par les grands fleuves mondiaux. Il avait alors montré par une approche indépendante la validité des résultats de GEM-CO2 mais n'avait pas fait l'objet de publications. Le modèle à été par la suite utilisé dans le cadre des travaux de thèse de Khadija Sehmi sur le bassin de la Garonne, sous la direction de Jean-Luc Probst au Centre de Géochimie de la Surface à Strasbourg.

MEGA (figure 8) fonctionne selon une procédure dite « en cascade », familière aux pétrographes déterminant des compositions minéralogiques virtuelles de roches (la Norme) à partir de leur composition chimique. Il est construit sur la base de différentes hypothèses et procédures issues des travaux de Garrels et Mackenzie (1971), Holland (1978), Meybeck (1979), Stallard (1980), et Berner et al. (1983). Il est décrit en détail dans Amiotte Suchet et Probst (1996) et Semhi et al (2000b).

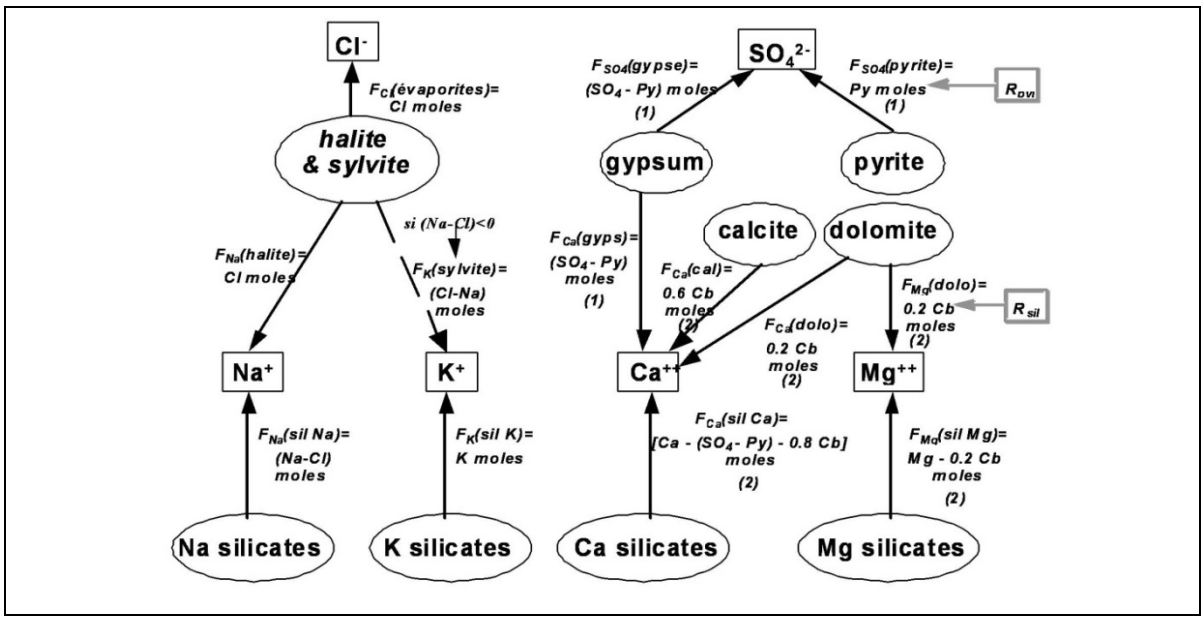

figure 8 : Représentation schématique du modèle MEGA (Major Element Geochemical Approach) reconstituant l'origine minéralogique des éléments majeurs en solution issu de l'érosion chimique des roches. La procédure MEGA s'applique à la composition en éléments majeurs des eaux continentales après correction des apports atmosphériques. Voir Amiotte Suchet et Probst (1996) et Semhi et al (2000b) pour plus de détails.

Appliqué au bassin versant de la Garonne, il a tout d'abord permis de mettre en évidence l'influence de l'acidité générée par les engrais azotés sur la dynamique des transferts de carbone inorganique dissous (Semhi *et al.*, 2000b). En effet, la nitrification des engrais azotés produit des protons d'acide fort (ions H^+) qui prennent la place des protons d'acide carbonique dans les réactions d'altération des minéraux silicatés et carbonatés, diminuant de ce fait la consommation de CO_2 par érosion chimique. On détermine ainsi que sur le bassin versant de la Garonne, 12 à 26% de la dissolution des carbonates sont attribués à la nitrification des engrais azotés avec pour conséquence une diminution d'environ 13% de la consommation de CO_2 par érosion chimique.

L'un des points clefs de la procédure MEGA réside dans sa capacité à différencier les éléments provenant des minéraux silicatés de ceux provenant des minéraux carbonatés. Il est alors possible, sur la base de la décomposition assurée par MEGA d'examiner assez finement la mobilité de la silice à l'échelle du bassin versant. L'hydrolyse des minéraux silicatés s'accompagne, la plupart du temps, de la formation de minéraux secondaires : argiles et oxy-hydroxydes de fer et d'aluminium. La nature de ces minéraux secondaires dépend fortement de la quantité de silice restée sur place. Le rapport molaire silice/alumine (SiO_2/Al_2O_3) présent dans les minéraux secondaires permet alors d'évaluer l'intensité de l'évacuation de silice (Pedro, 1966). Tardy (1969) propose de calculer ce rapport (Re) sur la base de la composition des chimique des eaux drainant les roches silicatées (sil):

$$\mathrm{Re} = \frac{\mathrm{SiO_2}}{\mathrm{Al_2O_3}} = \frac{(3\mathrm{Na} + 3\mathrm{K} + \mathrm{Ca} + \mathrm{Mg} + \mathrm{SiO_2})}{(0{,}5\mathrm{Na} + 0{,}5\mathrm{K} + \mathrm{Ca} + \mathrm{Mg})} \qquad \text{Équation 2}$$

Un rapport Re égale à 2 signifie que le principal minéral secondaire formé par altération des minéraux silicatés est la kaolinite (monosiallitisation), typique d'environnements à forte altération. Au dessus ou en dessous de cette valeur, l'altération tendra vers la bisiallitisation ou l'allitisation respectivement. Les valeurs données par MEGA sont introduites dans l'équation 2 et permet le calcul de Re à l'échelle des bassins versants, même s'ils sont en partie occupés par des roches carbonatées.

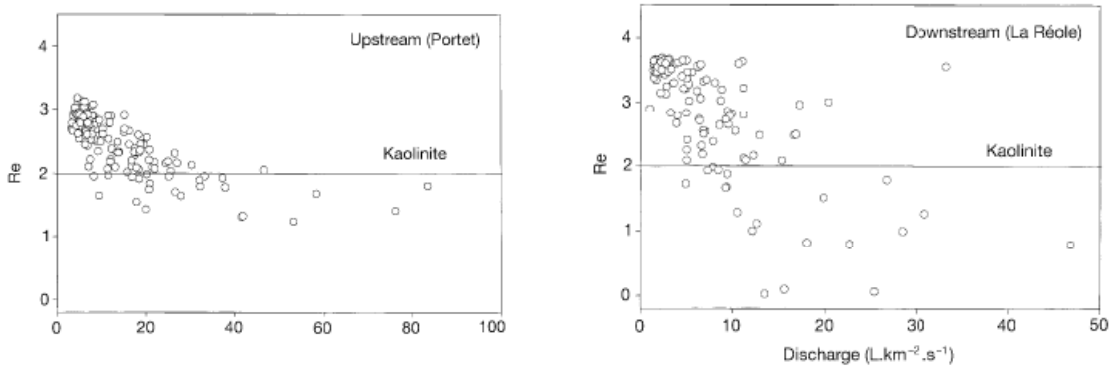

figure 9 : Relation entre le rapport Re (rapport Al_2O_3/SiO_2 des minéraux secondaires formés lors des processus d'altération) et le débit de la Garonne amont (Portet) et aval (La Réole). Re est calculé sur la base de l'origine des éléments majeurs en solution dans les eaux de la Garonne déterminée par le modèle MEGA.

Le calcul est conduit sur le bassin de la Garonne à partir des analyses des échantillons d'eau hebdomadaires du programme DBT-ONT Garonne (INSU-CNRS) de 1989 à 1992. La valeur moyenne de Re sur ces trois années est de 3, ce qui signifie que la bisiallitisation est dominante sur le bassin de la Garonne. Plus surprenant, cette valeur moyenne est plus élevée à l'aval qu'à l'amont du bassin, montrant que la mobilité de la silice est plus grande à l'amont. Il semble que,

malgré des températures plus fraîches à l'amont, l'altération des minéraux y est favorisée grâce à des flux d'eau plus forts et un renouvellement plus rapide des solutions. Cette influence du drainage sur la mobilité de la silice est particulièrement bien illustrée par la relation négative entre Re et le débit de la Garonne (figure 9).

L'approche MEGA est avant tout un outil permettant de porter un diagnostique sur le fonctionnement de l'altération chimique à l'échelle d'un bassin versant, quelque soit sa superficie. Sa puissance, son intérêt, comme ses défauts, sont ceux de l'approche « bassin versant » : la composition chimique de l'eau s'écoulant à l'exutoire du bassin versant intègre l'ensemble des processus de mise en solution des matériaux présents sur le bassin. L'enregistrement de ces signaux géochimiques puis leur déconvolution permet alors d'apprécier assez finement la dynamique du système. Ainsi, il semblerait que sur le bassin de la Garonne la mobilité de la silice soit avant tout favorisée par les flux d'eau plutôt que par la température, ce qui implique qu'une plus grande quantité de silice est évacuée depuis la partie amont du bassin par rapport à la partie aval.

Publications :

Semhi, K., Amiotte Suchet, P., Clauer, N., Probst, J.L., (2000a) Dissolved silica in the Garonne river waters: changes in the weathering dynamics. *Environmental Geology*, 40, 19-26.

Semhi, K., Amiotte Suchet, P., Clauer, N., Probst, J.L., (2000b) Impact of the nitrogen fertilizers on the natural weathering erosion processes and fluvial transport in the Garonne basin. *Applied Geochemistry*, 15, 865-878.

4 Utilisation des isotopes stables du carbone en abondance naturelle comme traceur et marqueur des processus de production et de transfert

4.1 Composition isotopique du carbone dans l'environnement

L'utilisation des isotopes stables du carbone en abondance naturelle est une approche qui apparait comme prometteuse pour remonter aux sources du carbone transporté en solution (CID, COD) par les cours d'eau ainsi qu'aux processus producteurs de ce carbone. Cependant, l'acquisition de la composition isotopique du carbone et son évolution au cours des processus de mise en solution puis de transfert dans les hydro-systèmes restait mal connue. En effet, seuls les processus de fractionnement isotopique entre les différents composants du système carbonaté ($CaCO_3$, H_2CO_3, CO_3^{2-}, HCO_3^- CO_2) ont été bien étudiés, (Deines *et al.*, 1974; Faure, 1986; Mook & JC, 1974; Zhang *et al.*, 1995). Pour le reste, de nombreuses interrogations subsistent sur d'éventuelles différentiations isotopiques au cours des processus producteurs de CO_2 comme de carbone organique dissous dans les sols (figure 10). Ainsi, si de nombreuses études se sont attachées à observer et mesurer les variations de la composition isotopique du carbone du CO_2 dans les sols (par exemple Cerling *et al.*, 1991; Dorr & Munnich, 1980; Galimov, 1966; Rightmire, 1978), très peu se sont focalisées sur les fractionnements éventuels au cours de la minéralisation des matières organiques (Andrews *et al.*, 2000; Crow *et al.*, 2006). En ce qui concerne le carbone organique dissous (COD), les éventuels fractionnements ayant lieu au cours de la décomposition des matières organiques n'ont pas fait l'objet de travaux jusqu'à récemment.

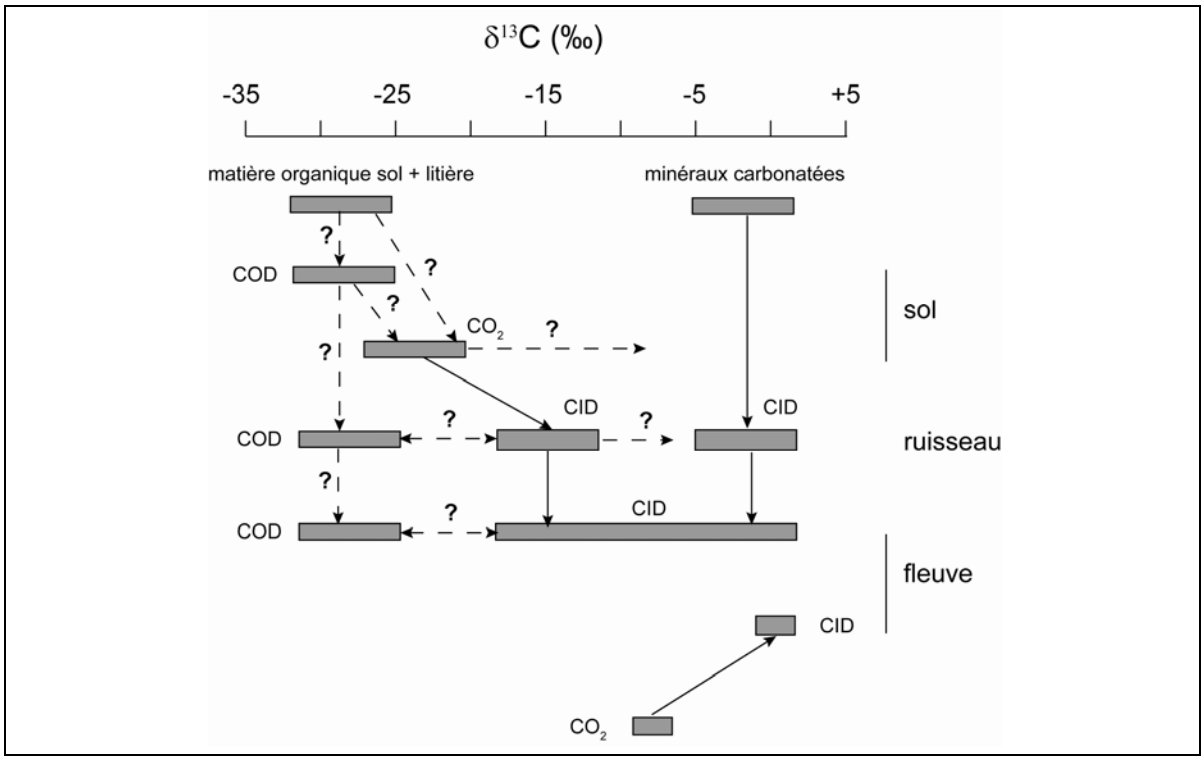

figure 10 : composition en isotopes stables du carbone ($\delta^{13}C$) dans les principaux compartiments des hydro-systèmes ; les flèches représentent les processus de fractionnement isotopique bien documentés (trait plein) ou encore mal connus (tiretés)

Il s'agissait donc en premier lieu d'identifier et de caractériser les processus de marquage dans des hydro-systèmes de petite taille où la signature isotopique est contrôlée par un faible nombre de facteurs, de façon à relier plus clairement les signatures isotopiques aux sources. Une première étude (Amiotte Suchet *et al.*, 1999) s'est focalisée sur les variations spatio-temporelles de la composition en isotopes stable ($\delta^{13}C$) du carbone inorganique dissous (CID) des eaux d'écoulement sur le bassin versant de recherche expérimental du Strengbach dans les Vosges alsaciennes (commune d'Aubure). Par la suite une seconde étude (Amiotte-suchet *et al.*, 2007) a eu pour objet la composition en isotopes stables du COD dans les eaux d'écoulement de quatre petits bassins versant à végétation contrastée dans le Morvan. Cette dernière étude a été récemment complétée par une approche expérimentale au laboratoire visant à observer l'acquisition de la composition isotopique du COD et du CO_2 produit au cours de l'incubation d'échantillons de sols forestiers (Gauthier *et al.*, en révision).

4.2 Marquage isotopique du carbone inorganique dissous (CID)

A l'issu des travaux de thèse, une question évidente restait posée : est-il possible d'identifier les origines du CID autrement que par modélisation ? Un outil n'avait encore jamais été utilisé dans ce cadre : la composition en isotopes stables du carbone. La bibliographie indiquait clairement qu'en théorie le carbone inorganique dissous devait porter une signature isotopique très différente selon sa provenance (minéraux carbonatés des roches ou CO_2 du sol). Cependant, les résultats des rares travaux sur la composition isotopique du CID des eaux fluviales restaient complexes à interpréter, notamment parce qu'on ne connaissait pas concrètement quelles étaient les signatures isotopiques délivrées à l'amont des bassins fluviaux.

Au cours des années 90, plusieurs études montraient que la composition isotopique du CID dans les eaux des fleuves variait dans le temps et dans l'espace. L'interprétation de ces résultats restait cependant délicate, notamment parce que le marquage isotopique du CID provenant du CO_2 des sols (67 % du CID des fleuves en moyenne) restait méconnu.

L'étude (Amiotte Suchet *et al.*, 1999) que nous avons menée sur le bassin versant expérimental du Strengbach (Haut-Rhin, Aubure) visait à comprendre comment, dans un hydro-système simple sur substrat silicaté où la seule source de carbone est le CO_2 du sol et de l'atmosphère, le carbone inorganique dissous acquérait sa composition isotopique et comment celle-ci variait dans le temps. En d'autres termes, dans le cadre de l'altération chimique des minéraux silicatés, les ions hydrogénocarbonates sont-ils clairement marqués par le CO_2 du sol ? Pendant un cycle hydrologique complet (novembre 1994 à décembre 1995) les eaux d'écoulement ont été échantillonnées une fois par semaine à l'exutoire du bassin versant et 17 autres points (affluents, sources, nappe) ont été échantillonnés 5 fois, pour détermination du $\delta^{13}C$ du CID. Dans le même temps, une ligne d'extraction cryogénique a été construite et mise au point dans les laboratoires du Centre de Géochimie de la Surface à Strasbourg pour l'extraction du carbone inorganique dissous en vue de l'analyse de sa composition isotopique.

Les résultats obtenus nous on paru plutôt surprenant dans un premier temps. Tout d'abord, les variations temporelles de la composition isotopique du carbone inorganique dissous ($\delta^{13}C_{CID}$) dans les eaux souterraines (sources, nappe) mettent en évidence une évolution saisonnière de la composition isotopique du CO_2 respiré dans les sols du bassin. En effet, en hiver les eaux souterraines ($\delta^{13}C_{CID}$ de -20 à -25 ‰) sont à l'équilibre isotopique avec du CO_2 du sol ayant un $\delta^{13}C$ d'environ -26 ‰ proche de celui de la matière organique des sols. Par contre, en été, les valeurs de $\delta^{13}C_{CID}$ augmentent (-15 à -20 ‰), signifiant que le $\delta^{13}C$ du CO_2 du sol serait d'environ -20 ‰ en raison du fractionnement induit par la diffusion moléculaire du CO_2 dans les pores du sol. Ce résultat original a été complété par un second concernant la signature isotopique du CID

dans les eaux du ruisseau. Rapidement, le CID perd la signature isotopique qu'il a acquise dans les sols pour se stabiliser à un $\delta^{13}C$ d'environ -12‰. En confrontant la composition isotopique du CID mesurée à celle calculée à l'équilibre, on a pu mettre en évidence que seule la partie CO_2 aqueux du CID perdait sa signature par équilibrage avec l'atmosphère. Les ions HCO_3^- par contre, semblaient conserver leur signature originelle.

Ce travail a permis pour la première fois de montrer que, dans le cadre d'un petit bassin versant sur substrat non-carbonaté, la composition isotopique du CID dépendait de la proportion de CO_2 aqueux par rapport aux ions HCO_3^- : la composition isotopique du CO_2 aqueux est en équilibre avec celle du CO_2 atmosphérique alors que celle des ions HCO_3^- est héritée du CO_2 des sols. Enfin, dans les eaux souterraines, le CID serait à l'équilibre isotopique avec le CO_2 du sol, enregistrant de ce fait des processus de fractionnement isotopique affectant le CO_2 respiré par le sol. Ces résultats permettent de progresser aussi bien dans l'interprétation de la composition isotopique du CID dans les fleuves (Brunet et al., 2005), que dans l'utilisation du $\delta^{13}C_{CID}$ pour tracer les écoulements dans la zone non saturée des hydro-systèmes ((Emblanch et al., 2003).

Publication:

Amiotte Suchet, P., Aubert, D., Probst, J.L., Gauthier-Lafaye, F., Probst, A., Andreux, F., Viville, D., (1999) d13C pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges mountains, France). *Chemical Geology*, 159, 129-145.

4.3 Marquage isotopique du carbone organique dissous (COD)

Les matières organiques dissoutes (MOD) des cours d'eau sont en très grande partie produites dans les sols lors de la dégradation des matières organiques. L'influence du « bio-fonctionnement » des sols sur la production de MOD en quantité comme en qualité, bien que souvent évoquée, reste méconnue. Pourtant il s'agit là d'un enjeu fort, pour trois raisons principales : 1) les MOD constituent un paramètre important de qualité des eaux continentales (Piccolo, 1994; Zsolnay, 1996) tout en étant 2) un substrat et une source d'énergie pour les micro-organismes (Marschner & Kalbitz, 2003; Maurice *et al.*, 2002) et 3) en assurant ¼ des apports de carbone par les fleuves aux océans (Ludwig *et al.*, 1996a; Ludwig *et al.*, 1996b).

Dans les écosystèmes forestiers tempérés, la substitution de la forêt native de feuillus par des essences résineuses modifie le « bio-fonctionnement » du sol. Il s'agit alors de savoir si cette importante modification affecte la production et le transfert des matières organiques dissoutes dans les hydro-systèmes aussi bien sur le plan de la qualité que sur celui de la quantité. Si la quantité peut facilement être déterminée à partir des concentrations en carbone organique dissous (COD), la nature des MOD reste une question complexe, notamment en raison de difficultés à identifier de façon suffisamment complète ses constituants. La composition isotopique du carbone organique dissous ($\delta^{13}C_{DOC}$) s'avère dès lors un outil très intéressant parce qu'il est plus facilement accessible en routine et parce qu'il caractérise par une seule valeur l'ensemble de la composition chimique des MOD.

Nous avons utilisé deux approches complémentaires pour apporter des éléments de réponse à la question posée : une approche à l'échelle de petits bassins versants et une approche expérimentale au laboratoire

Observation sur le terrain à l'échelle des bassins versants

Dans un premier temps, nous avons à nouveau utilisé l'approche « bassin versant » en examinant la variabilité spatio-temporelle des signaux chimiques (concentrations et flux de COD)

et isotopiques ($\delta^{13}C_{DOC}$) dans les eaux drainant des petits bassins versants les plus simples possibles. Le Morvan granitique, au centre de la Bourgogne, est une région naturelle où la pression anthropique est faible et les conversions de forêts de feuillus traditionnelles (chênaie-hêtraie) en plantations de résineux sont courantes. Elle nous apparaissait comme un lieu d'étude à la fois accessible et intéressant par rapport aux questions posées. Dans le cadre du travail de thèse de Nathalie Linglois-Dussert (Linglois, 2003), le choix s'est porté sur 4 petits bassins versants forestiers, proches les uns des autres (maximum 10 km) soumis aux mêmes conditions climatiques, de taille similaire et drainant le même substratum granitique. Le seul paramètre variant réellement était le couvert végétal : 2 bassins versants étaient couvert majoritairement par des résineux, 1 par de la chênaie-hêtraie et 1 par une forêt mixte composée à la fois de feuillus et de résineux.

L'analyse de la variabilité spatiale et temporelle des concentrations en COD et de leur signature isotopique associée ($\delta^{13}C_{DOC}$) dans les eaux de ruisseau et dans les solutions de sol des bassins versant de 1999 à 2001 a permis d'apporté les premières réponses à la question du marquage isotopique du COD (Amiotte-suchet *et al.*, 2007). Premièrement, nous avons montré que la composition isotopique du COD est systématiquement appauvrie de 1 à 2 ‰ en ^{13}C par rapport à la matière organique de la litière et des sols dont il est issu. La composition isotopique du COD de la litière n'explique que les valeurs les moins négatives de $\delta^{13}C_{DOC}$ observées dans les ruisseaux (figure 11). Cela impliquerait soit une évolution biochimique du COD au cours de son transfert dans le ruisseau, soit la présence d'un milieu producteur de COD appauvri en ^{13}C sur le bassin versant. Deuxièmement, cet appauvrissement en ^{13}C du COD des ruisseaux est plus accentué dans le bassin versant sous végétation de feuillus par rapport aux bassins sous végétation résineuse, probablement en liaison avec la dynamique de dégradation des matières organiques de la litière et des sols.

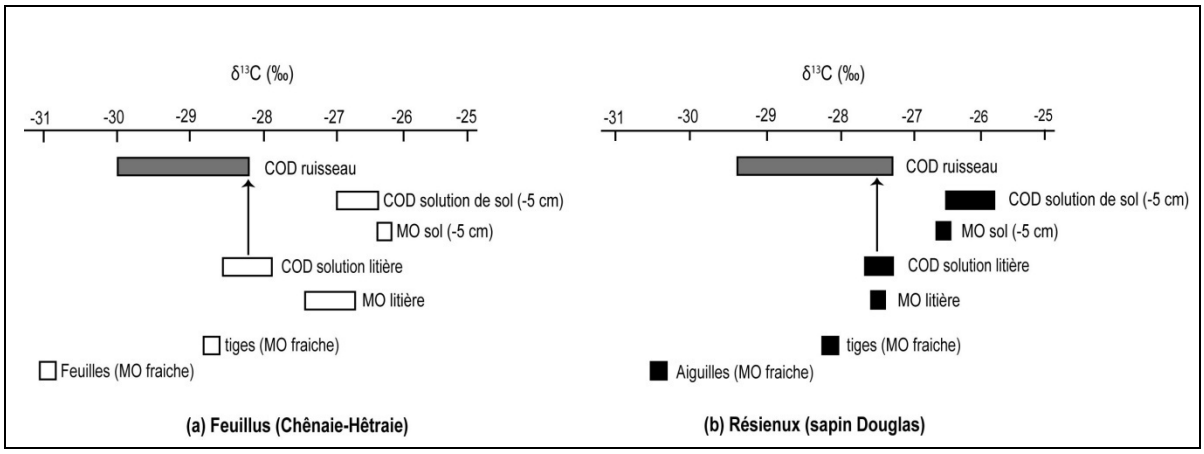

figure 11 : composition isotopique ($\delta^{13}C$) du carbone des matières organiques solides (MO) et du carbone organique dissous (COD) dans les différents compartiments d'un bassin versant en fonction de la végétation (modifié d'après Amiotte-suchet *et al.*, 2007).

En résumé, l'étude permet de préciser deux points en particulier. Tout d'abord, le COD n'a pas tout à fait la même composition isotopique que les matières organiques dont il est issu avec un appauvrissement en ^{13}C de -1 à -2 ‰. Ensuite, le couvert végétal, bien qu'il ne marque pas de façon différente les litières qu'il produit, influence la composition isotopique du COD des ruisseaux qui serait plus pauvre en ^{13}C dans le bassin versant sous feuillus par rapport à ceux sous résineux. Ces résultats sont évidemment trop partiels et concernent trop peu de cas d'étude pour être généralisés, d'autant plus que les mécanismes reliant la nature du couvert végétal avec la production de COD dans les sols et la composition isotopique du COD des ruisseaux restent obscures.

Ceci pose donc d'autres questions, concernant notamment les facteurs contrôlant la production en quantité et en qualité du COD dans les sols. En effet, si la végétation influence bien les quantités et la composition du COD du sol, les processus supportant cette relation ne sont pas clairement identifiés. Trois facteurs, tributaires du couvert végétal peuvent en fait jouer un rôle : i) la composition des matières organiques originelles, ii) la dégradation (cinétique, taux) des matières organiques, iii) la nature des populations microbiennes dégradant les matières organiques.

Une approche à l'échelle des bassins versants ne peut aborder ces processus. Nous avons alors mis en place une étude expérimentale nous permettant d'observer les mécanismes en jeu lors de la production de carbone organique dissous à partir de matières organiques de sols prélevés sous différents couverts forestiers.

Approche expérimentale

Il s'agit donc d'analyser la composition isotopique du COD au moment où il est produit dans les sols et mettre ainsi en évidence un éventuel fractionnement entre la phase solide et la phase dissoute. L'extraction de solutions à partir d'échantillons de sols incubés permettait d'avoir accès à des matières organiques dissoutes produites en conditions contrôlées donc simplifiées. De façon à mettre en évidence les facteurs de contrôle supposés, nous avons fait varier l'origine des matières organiques (sols sous feuillus et sous résineux), leur maturation (horizons superficiel et plus profond), leur vitesse de dégradation (incubation à des températures différentes). Le choix des sols à prélever s'est tout naturellement porté sur les alocrisols du site expérimental de la forêt de Breuil-Chenue dans le Morvan. Il s'agit de l'un des 9 sites ateliers du réseau des *Observatoires de Recherche en Environnement* sur le fonctionnement des écosystèmes forestiers (F-ORE-T) du GIP Ecofor. Ce site, géré par l'Unité de *Biogéochimie des Ecosystèmes Fortestiers* de l'INRA de Nancy-Champenoux, a pour objectif l'étude de l'influence des substitutions d'espèces forestières sur le fonctionnement des écosystèmes forestiers. Il comprend 8 parcelles expérimentales plantées d'essences feuillues et résineuses, plus une parcelle ayant conservé la chênaie-hêtraie originelle (Ranger, 2004). Cet atelier offrait le gros avantage de pouvoir travailler sur des prélèvements dans des conditions homogènes, bien connues et largement documentées, de bénéficier de la logistique de l'INRA de Nancy, enfin de pouvoir comparer les solutions extraites des sols incubés à celles échantillonnées sur le terrain par bougies poreuses.

En fin d'hiver 2007, nous avons échantillonné les sols en quatre points différents, sur deux profondeurs (0-5 cm et 5-10 cm), dans la parcelle de chênes (*Quercus sessiliflora* Smith) et de hêtre (*Fagus sylvatica* L) en taillis-sous-futaie (TSF) d'une part, et dans la parcelle de sapin Douglas (*Pseudotsuga menziesii* Franco) d'autre part. A partir de chaque échantillon, 70g de sol ont été incubés sous atmosphère sans CO_2 pendant 98 jours à 4 températures différentes (8, 12, 20 et 28 °C). Au cours de l'incubation, 5 séries de 64 échantillons (4 points de prélèvement x 2 profondeurs x 2 parcelles x 4 températures) ont été sacrifiés (à 7, 21, 42, 63 et 98 jours) pour extraction des matières organiques hydrosolubles selon un protocole d'extraction à l'eau froide standard (Jones & Willett, 2006) et mesure des concentrations en carbone organique dissous extractible et de sa composition isotopique associée. Enfin, au tout au long de l'incubation, le CO_2 émis par minéralisation des matières organiques des échantillons de sol est prélevé pour évaluer l'activité microbienne (évolution des concentrations en CO_2 au cours du temps) et mesurer sa composition en isotopes stables du carbone.

Ce travail, réalisé dans le cadre de la thèse d'Anthony Gauthier [(Gauthier, 2009) soutenance prévue le 23 octobre 2009] est en cours de publication. Il a déjà fait l'objet de deux communications dans des congrès internationaux (Gauthier *et al.*, 2008; Hénault *et al.*, 2008) et d'une publication en révision pour *Plant and Soil* (Gauthier *et al.*, en révision).

Les premiers résultats montrent que les quantités de carbone organique extractibles (WEOC, pour *Water Extractable Organic Carbon*) produites au cours de l'incubation sont supérieures pour les sols échantillonnés sous TSF par rapport à ceux de la parcelle de Douglas, quelle que soit la température. La figure 12a montre par exemple à 28°C, que si les quantités initialement présentes dans les sols (à 0 jours d'incubation) sont similaires, les quantités produites ensuite sont plus élevées sous feuillus (TSF) et pour les sols de l'horizon de surface (0-5 cm). On notera en outre que la production de WEOC est plus forte dans les échantillons prélevés à 5-10 cm sous feuillus par rapport à ceux de l'horizon 0-5 cm sous Douglas, alors que ces derniers sont caractérisés par une plus forte activité microbienne (figure 12b). Ceci montre clairement que la production de carbone organique dissous extractible dans les sols est d'abord contrôlée par la nature des matières organiques dégradées plutôt que par leur quantité et leur taux de dégradation.

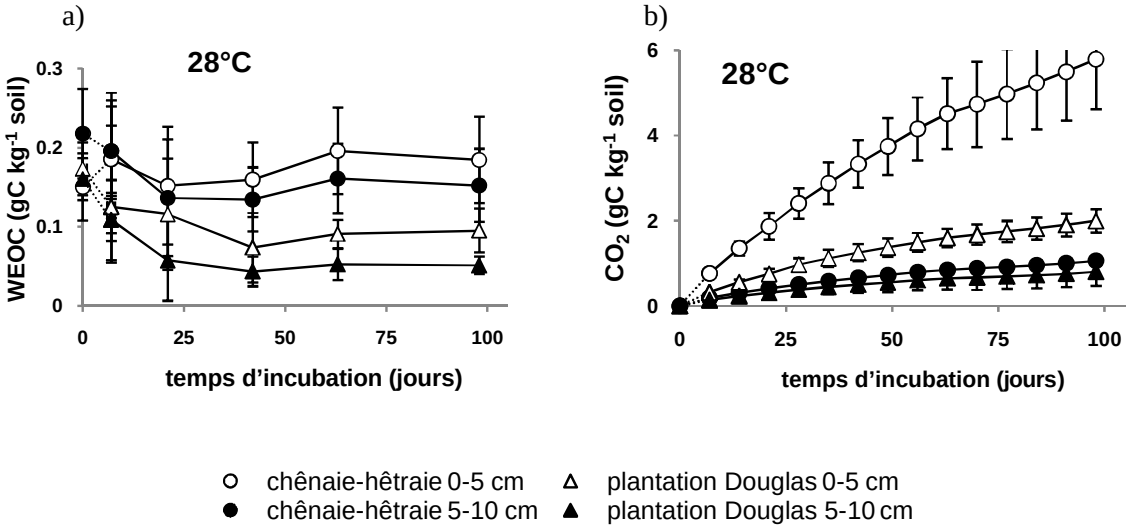

figure 12 : évolution a) de la quantité de carbone organique dissous extractible (WEOC) et b) des quantités de CO_2 émis par l'activité microbienne pour les sols incubés pendant 96 jours à 28°C (d'après Gauthier *et al.*, en révision).

En ce qui concerne la composition isotopique du carbone organique dissous extractible (δ^{13}C-WEOC), les résultats de l'expérience sont plus confus. On constate tout d'abord que le δ^{13}C-WEOC est systématiquement enrichi en ^{13}C (de 0,5 à 1,2 ‰) par rapport à la phase solide dont il est issu (Gauthier *et al.*, en révision). Ensuite, il ne semble pas affecté ni par la durée de l'incubation, ni par la température, ni même de façon claire par la végétation. On remarquera cependant, comme par exemple à 28°C (figure 13), que les valeurs de δ^{13}C-WEOC sont plus négatives pour les échantillons de l'horizon 0-5 cm de la parcelle sous TSF.

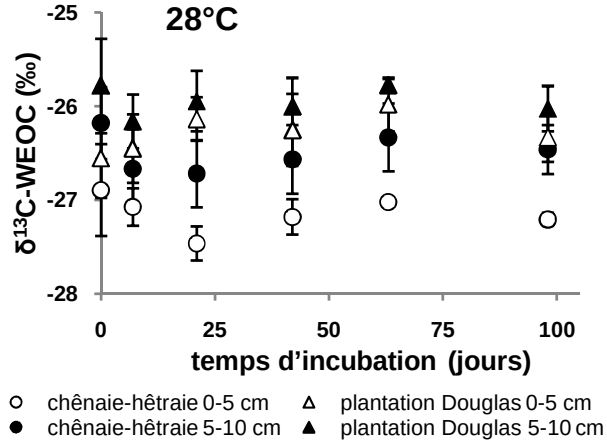

figure 13 : évolution du $\delta^{13}C$ du carbone organique extractible ($\delta^{13}C$-WEOC) dans les sols incubés pendant 96 jours à 28°C (d'après Gauthier *et al.*, en révision).

Le $\delta^{13}C$ du CO_2 ($\delta^{13}C$-CO_2) émis par l'activité microbienne montre des valeurs plus contrastées et ses variations semblent dépendre à la fois du temps d'incubation, de la température et de la nature de la matière organique source. Nous avons notamment observé (Gauthier *et al.*, en révision) que les valeurs de $\delta^{13}C$-CO_2 augmentent brusquement dans la deuxième partie de l'incubation, traduisant probablement un changement dans le pool de matière organique dégradée par l'activité microbienne. En complément, on notera que cette brusque augmentation des valeurs de $\delta^{13}C$-CO_2 est plus accentuée à basse qu'à haute température. En conséquence, la composition isotopique moyenne du CO_2 émis en fin d'incubation est dépendante de la température (figure 14).

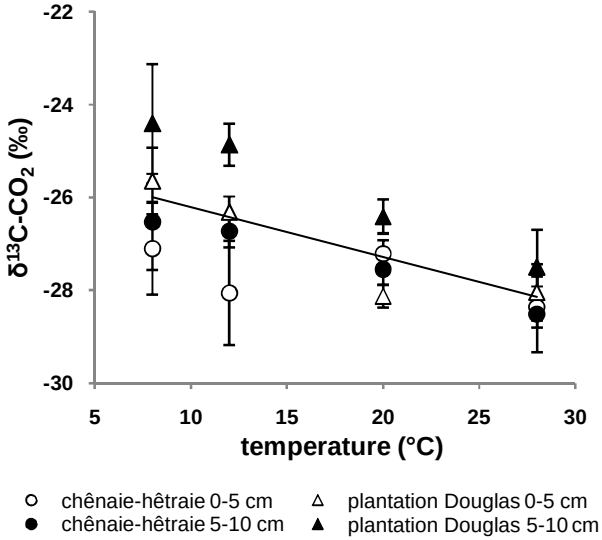

figure 14 : évolution du $\delta^{13}C$ du CO_2 émis ($\delta^{13}C$-WEOC) en fonction de la température pour les sols en fin d'incubation (d'après Gauthier *et al.*, en révision).

Ces résultats apportent un éclairage nouveau sur notre compréhension des mécanismes de production de matières organiques dissoutes dans les sols. Si la production est effectivement plus élevée sous feuillus, c'est plus en raison de la composition des matières organiques fraiches originelles, plus riches en composés labiles (Cote *et al.*, 2000; Priha *et al.*, 2001), que lié au taux de dégradation de celles-ci : la température, comme l'intensité de l'activité microbienne ne

seraient pas des facteurs de premier plan. Les signatures isotopiques ($\delta^{13}C$) de ces matières organiques dissoutes semblent par contre moins bien contraintes. Il apparaît cependant que les échantillons issus de l'horizon 0-5 cm sous feuillus (TSF) produisent un carbone organique dissous extractible plus pauvre en ^{13}C (jusqu'à -1,5 ‰) que tous les autres échantillons, et sont en même temps ceux où l'activité microbienne est la plus intense.

Les différentiations isotopiques entre phases solides et solubles, en début (après 7 jours d'incubation) et en fin d'incubation, peuvent être synthétisées sur la figure 15. En début d'incubation, le CO_2 émis est fortement appauvri en ^{13}C (de 2 à 3 ‰) par rapport au carbone organique du sol alors que le carbone organique dissous extractible est lui légèrement enrichi en ^{13}C. Le même schéma général est conservé en fin d'incubation, mais avec un plus faible fractionnement entre phase solide et phase gazeuse.

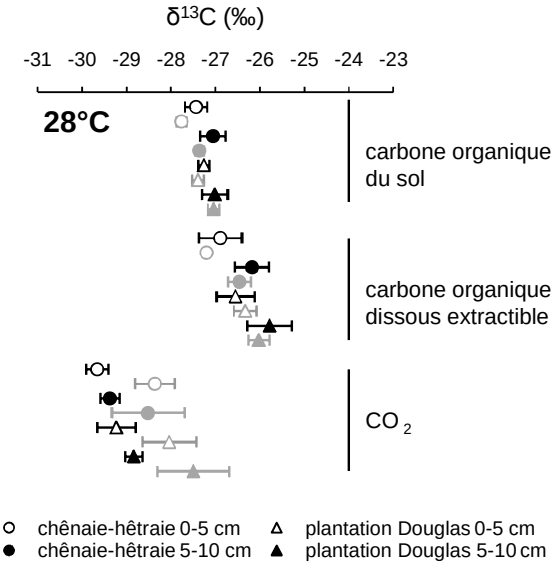

figure 15 : composition isotopique ($\delta^{13}C$) des différents compartiments de carbone, avant (en noir) et après (en gris) incubation à 28°C

Même si ces résultats apparaissent comme plutôt cohérents, ils sont cependant partiellement contradictoires avec les observations généralement effectuées sur le terrain. Ainsi, la composition isotopique du CO_2 du sol, telle qu'elle est observée (figure 10), est plus riche en ^{13}C, alors que le CO_2 produit lors des incubations est appauvri en ^{13}C. Inversement, le carbone organique dissous (COD) transporté par les ruisseaux (figure 11) est appauvri en ^{13}C, alors que le COD extractible produit serait plutôt enrichi. Certes, dans les deux cas, on admettra que les composés ne sont pas tout à fait comparables : Le CO_2 produit subit un transfert avant d'être du CO_2 du sol et le COD extractible est différent du COD des solutions gravitaires qui se retrouvera ensuite dans les écoulements. Ces incohérences mettent en évidence les difficultés méthodologiques liées à la multiplicité des approches et au changement d'échelle. D'un coté, l'approche à l'échelle du bassin versant permet une vision globale et réelle du fonctionnement de l'hydro-système, mais n'a pas la « résolution » nécessaire pour aborder les mécanismes. De l'autre, l'approche expérimentale à l'échelle du profil de sol permet de mieux identifier les processus et leurs facteurs, mais reste trop déconnectée de la réalité du terrain. La coïncidence des deux approches nécessite de généraliser les résultats de la seconde à l'échelle de la première, ce qui passe par la modélisation et la prise en compte des processus de transfert d'une dimension à l'autre.

Publications :

Amiotte-suchet, P., Linglois, N., Leveque, J., Andreux, F., (2007) 13C composition of dissolved organic carbon in upland forested catchments of the Morvan Mountains (France): Influence of coniferous and deciduous vegetation. *Journal of Hydrology*, 335(3-4), 354-363.

Gauthier, A., Amiotte Suchet, P., Nelson, P., Lévèque, J., Zeller, B., Hénault, C., (en révision) Dynamics of the water extractable organic carbon pool during mineralisation in soils from Douglas fir plantation and oak-beech forests - an incubation experiment. *Plant and Soil*.

Gauthier, A., Amiotte-Suchet, P., Henault, C., Nelson, P., Lévèque, J., Ranger, J., (2008) Isotopic differentiation (13C) of dissolved organic carbon and CO2 during organic matter degradation in forest soils: influence of vegetation. In: *2008 Western Pacific Geophysics Meeting, AGU*, Cairns, Australia, 29 July - 1 August 2008.

5 Changements globaux, apports de matières aux océans et cycles biogéochimiques (Perspectives de recherche)

Je ne reviendrai pas ici sur les enjeux de la compréhension du fonctionnement des cycles biogéochimiques développée au début du mémoire. Cette dernière partie développe plusieurs pistes de recherche ayant toutes pour objectif d'améliorer notre connaissance des apports de nutriments (C, N, S, P) aux océans. Identifier les sources et quantifier l'influence des facteurs des variations spatio-temporelles de ces apports reste une cible de choix.

Il subsiste plusieurs zones d'ombre, parmi lesquelles j'en privilégierais deux :

- Le rôle des fluctuations climatiques, et plus particulièrement des glaciations, sur la consommation de CO_2 par érosion chimique
- L'influence de la végétation et des sols sur les transferts de nutriments continents-océans.

Ces deux points se focalisent essentiellement sur les transferts, un troisième vient les compléter en examinant plus spécifiquement les processus de production de ces éléments dans les sols.

Ces trois aspects ont bien pour objectifs de contribuer à la connaissance du fonctionnement des grands cycles biogéochimiques, à l'échelle planétaire et/ou au cours des temps géologiques. Ils devraient cependant apporter des réponses à des questionnements très actuels, appliqués à des échelles plus restreintes comme par exemple la qualité des eaux et des sols, l'eutrophisation ou le transfert de polluants.

Pour ce qui est des outils, comme on l'a déjà vu dans la première partie du mémoire (paragraphe 1.3), je plaide pour des approches multi-échelles, du sol au bassin versant, et multi-outils, de la modélisation aux démarches expérimentales de terrain et de laboratoire.

Les pistes de travail présentées ci-dessous sont présentées par ordre de « faisabilité ». La première est complètement opérationnelle, la dernière plus spéculative et imprécise, s'agissant notamment des outils et des approches.

5.1 Le rôle des fluctuations climatiques : érosion en contexte glaciaire

La question de l'érosion chimique en contexte de refroidissement global a été maintes fois posée (Lerman *et al.*, 2007; Ludwig *et al.*, 1999; Munhoven, 2002; Raymo & Ruddiman, 1992), mais n'a toujours pas trouvé de réponse satisfaisante. La raison principale est le manque de données fiables sur la question. Deux hypothèses de travail s'opposent : la première (voir la synthèse de Lerman *et al.*, 2007) prédit une diminution de l'érosion chimique en liaison avec des températures plus basses et un drainage continental diminué en période de glaciation. Cela correspond à la boucle de rétro-action négative, désormais classique, du cycle des carbonates-silicates (voir boucle d-j-i figure 1). La seconde oppose, qu'à l'échelle locale, l'érosion chimique augmente en contexte glaciaire du fait de l'action mécanique des glaciers broyant les roches et favorisant le contact minéraux-solutions altérantes (Anderson *et al.*, 2000; Gislason *et al.*, 1996).

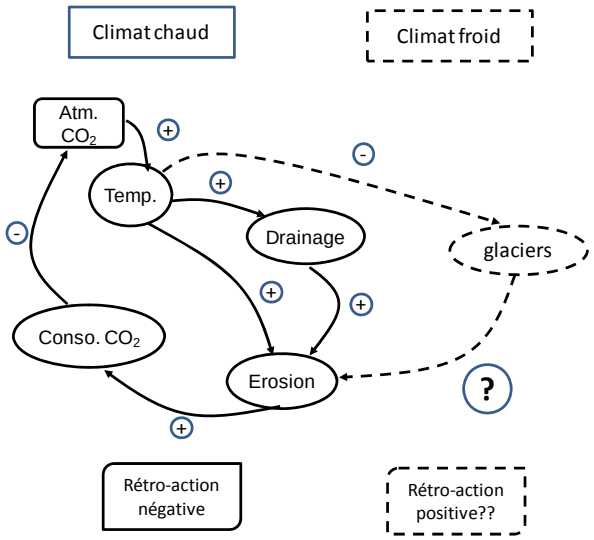

figure 16 : schéma synthétique des rétroactions climat-érosion en climat chaud (trait plein) et froid (pointillés). Si les glaciers favorisent l'érosion à l'échelle globale (flèche soulignée d'un point d'interrogation), l'érosion en contexte glaciaire forme une rétroaction positive.

Cette question mérite attention car si l'érosion augmente effectivement à l'échelle globale en contexte glaciaire, cela aurait pour effet d'inclure une rétroaction positive dans les interactions climat-érosion (figure 16) : moins de CO_2 dans l'atmosphère conduit à plus de glaciers qui favorisent l'érosion chimique des roches silicatées, elles-mêmes consommant du CO_2 atmosphérique. En outre, une étude préliminaire sur la base de la composition chimique moyenne de 112 torrents pro-glaciaires (Amiotte Suchet *et al.*, 2008) met en évidence des concentrations plus fortes pour la plupart des éléments dans les torrents pro-glaciaires par rapport aux ruisseaux sur les mêmes substratum (figure 17). Cette base de données est en cours d'exploitation (collaboration J.F. Buoncristiani, Biogéosciences Dijon ; A. Chapuis, University of Life Science, Norvège) et devrait nous aider à établir un premier bilan de la consommation de CO_2 par érosion chimique en contexte glaciaire à l'échelle globale.

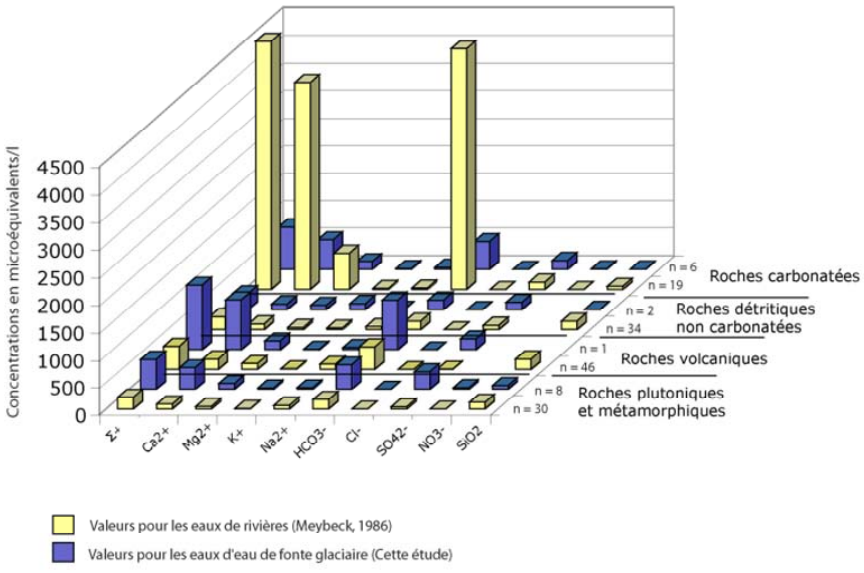

figure 17 : comparaison des composition chimiques moyenne des eaux de fonte glaciaire et des ruisseaux en contexte non glaciaire pour différents substratum géologiques.

Pour apporter quelques éléments de réponse, des travaux ont été entrepris en 2008 dans le cadre de l'ANR ERD Alps (coordinateur : Peter Van Der Beek, Grenoble) en collaboration avec J.F Buoncristiani (UMR Biogéosciences, Dijon) pour établir des bilans d'érosion en contexte glaciaire à l'échelle du massif du Mont-Blanc.

Le dispositif consiste en un suivi temporel des eaux du torrent pro-glaciaire des Bossons (Chamonix), complété par des mesures régulières sur l'Arve à Chamonix. Le glacier des Bossons draine un bassin versant majoritairement englacé (90% de sa surface) dont le substratum géologique est constitué de granites et de roches métamorphiques. Le site du torrent des Bossons a été équipé de systèmes d'acquisition en continu de la turbidité, de la conductivité et des hauteurs d'eau. Des campagnes de terrain, appuyées par des préleveurs automatiques, permettent en outre de prélever pour analyse de la composition chimique jusqu'à un échantillon par heure en été. En plus de l'établissement de bilans d'érosion, le projet doit également permettre en 4 ans d'observation, de mieux cerner l'origine des éléments et leur dynamique d'évacuation en fonction de la saison et des fluctuations des flux hydro-glaciaires du système.

5.2 Le rôle des changements de végétation

Les travaux visant à estimer, à l'échelle continentale, les apports de nutriments aux océans sont peu nombreux. Le bilan réalisé par Meybeck (1982; 1992) à l'échelle globale n'a jamais été revu ; il a été récemment complété par des bilans régionaux pour la Méditerranée (Ludwig *et al.*, 2009) ou pour la Mer du Nord (Brion *et al.*, 2004). Ces approches, si elles permettent de chiffrer de façon fiable les apports aux océans, souffrent de deux inconvénients. Premièrement, le bilan résulte du fonctionnement du bassin versant à l'époque actuelle, lequel est fortement affecté, s'agissant des flux de nutriments, par les activités humaines. En conséquence, il devient difficile d'accéder au fonctionnement naturel des hydro-systèmes, ce qui empêche i) l'évaluation de l'impact des activités humaines sur ces flux, ii) l'utilisation des flux et de leur dynamique pour documenter les transferts continents-océans dans les modèles de cycles biogéochimiques. Deuxièmement, ces approches ne prennent que très peu en compte les sources des composés, ainsi que les facteurs de contrôle des processus de production et de transfert ; ces éléments sont essentiels à la mise au point de modèles paramétriques simples, comme GEM-C, simulant les transferts à large échelle.

Il me semble que l'approche utilisée dans le développement de GEM-C (Amiotte Suchet & Probst, 1995b; Ludwig *et al.*, 1996a), déjà présente dans le « Temperate Stream Model » de Meybeck (1987), a montré son intérêt. Il s'agit de mettre en évidence et de quantifier les relations qui relient les flux hydro-chimiques à leurs principaux facteurs, sur la base d'observations effectuées à des échelles suffisamment fines pour que ces facteurs puissent être identifiés et caractérisés. Cette échelle est clairement celle du petit bassin versant, dans un contexte où la pression anthropique est suffisamment faible pour ne pas affecter les signaux hydro-géochimiques.

Grâce à ce type d'approche, le rôle de la lithologie et du climat sur l'érosion des roches et les transferts de carbone inorganique aux océans semble relativement bien cerné aujourd'hui. En revanche, l'influence de la végétation sur les transferts de nutriment (C, N, P) l'est beaucoup moins, alors qu'elle est à la fois source et un facteur de contrôle de ces transferts, comme nous l'avons récemment montré (Amiotte-suchet *et al.*, 2007; Gauthier *et al.*, en révision). D'une part, le couvert végétal intervient à différents niveaux du cycle de ces éléments (prélèvements, libération par dégradation des matières organiques). D'autre part, elle est sensible aux changements climatiques. La figure 18 montre par exemple que, dans le même contexte hydro-climatique et géomorphologique, les concentrations moyennes en phosphore dans les eaux de bassins versant forestiers sont affectées par les changements de végétation.

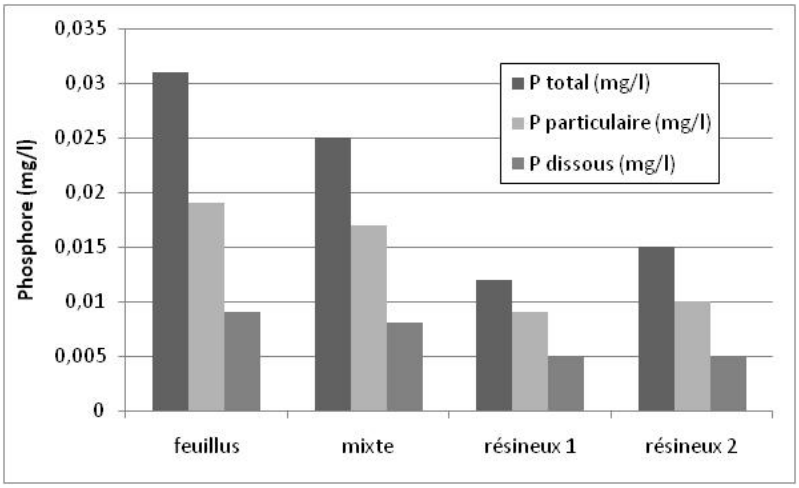

figure 18 : concentrations moyennes en phosphore total, phosphore particulaire et phosphore dissous ($P\text{-}PO_4$) dans les eaux de quatre petits bassins versants forestiers du Morvan calculées pour 2 cycles hydrologiques (1999-2001)

Les travaux sur les flux de COD, de phosphore ou d'azote à l'échelle de petits bassins versants en contexte peu ou pas anthropisés sont très peu nombreux (Zhang *et al.*, 2008) et les approches comparatives visant à mettre en évidence les changements de végétation encore moins. En outre, la complexité des processus impliqués, s'agissant notamment de la production de ces nutriments dans le sol, nécessite de multiplier les cas d'étude afin d'avoir une bonne représentativité des situations.

La stratégie pourrait être la suivante :

Objectif 1 : constituer un jeu de données formé de composition en nutriments acquises sur des ruisseaux drainant des couverts végétaux, des sols et des substrats uniques et connus. Cela peut être réalisé sur la base de données issues de la littérature, complétées des études spécifiques.

Objectif 2 : paramétrer les relations flux élémentaire – facteurs de contrôle, en les calibrant sur la base du jeu de données de l'objectif 1 (voir l'exemple des flux de nitrates sur le bassin versant du Cousin ; Linglois, 2003).

Objectif 3 : valider le modèle paramétrique à méso-échelle (400 km^2) puis à l'échelle des bassins fluviaux.

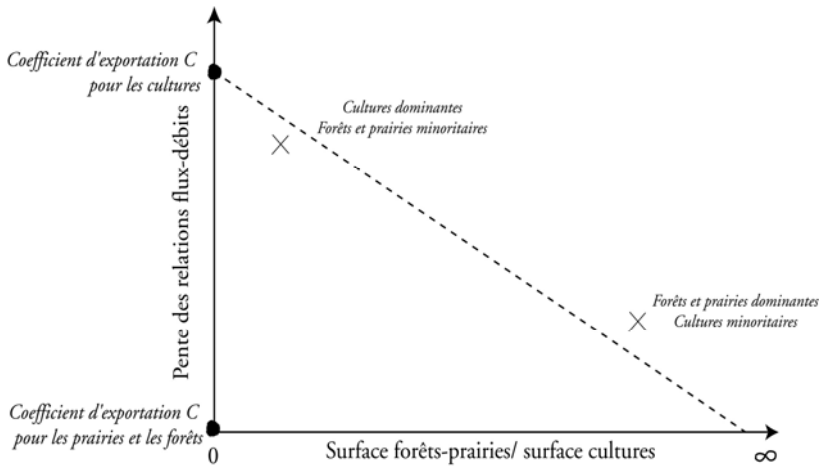

figure 19 : illustration de la paramétrisation de relations flux élémentaire – débit en fonction du couvert végétal ; exemple des flux d'azotes contrôlés par l'occupation du sol (Linglois, 2003)

La tâche est ambitieuse, mais elle pourrait se limiter dans un premier temps à l'opposition feuillus-résineux avec les hydro-systèmes du Morvan et ne pas dépasser le cadre des collaborations dijonnaises. Dans un second temps, un programme plus ambitieux à l'échelle du territoire national viserait à constituer une base de données sur les petits bassins versants versant peu anthropisés, sur le modèle des travaux de Meybeck (1986) sur les ruisseaux non pollués de France. Il impliquerait alors des collaborations extérieures et devrait être étendu à d'autres problématiques que les nutriments comme par exemple les éléments traces ou les Terre Rares.

5.3 La nécessité d'intégrer les processus biotiques : le sol bioréacteur

Il n'y pas de transfert de nutriments en solution si ceux-ci ne sont pas produits à moment donné sur le bassin versant. Les sols constituent sans nul doute un des lieux privilégiés de production de matières hydrosolubles. C'est l'endroit où les végétaux prélèvent des nutriments en même temps qu'ils les redonnent par production de litière. C'est aussi l'endroit où matières organiques et matières minérales se rencontrent et interagissent. C'est enfin là que les solutions de percolation acquièrent en partie leur composition en nutriments. Ces processus nombreux et complexes sont en grande partie soutenus par l'activité des populations microbiennes du sol qui dégradent, transforment, oxydent les matières organiques. L'ensemble de ces processus d'interface définissent ce que l'on pourrait appeler le « bio-fonctionnement » du sol, lequel est sous l'influence directe de la végétation (qui contrôle les apports de matières organiques) et du substratum géologique (qui contrôle le contexte physico-chimique).

La compréhension de ce bio-fonctionnement des sols ouvre un champ de recherche considérablement vaste où les enjeux sont forts :

- Aujourd'hui, comment le bio-fonctionnement du sol contrôle la qualité des eaux? Quelle est alors l'incidence des changements de végétation ? des fluctuations climatiques ?
- Au cours de l'histoire de la Terre, en quoi les changements globaux ont pu affecter le bio-fonctionnement du sol et modifier les transferts de nutriments continents-océans ?

Les relations climat – végétation – bio-fonctionnement du sol

Il s'agit alors d'établir les liens entre facteurs abiotiques (climat, substratum), facteurs biotiques (végétation, activité microbienne) et production/rétention de nutriments dans les sols. La multiplicité des facteurs et la complexité des processus implique de procéder par étapes en utilisant des dispositifs expérimentaux simplifiés. Par exemple, dans les travaux de thèse d'Anthony Gauthier, entrepris en collaboration avec Catherine Hénault (MSE, INRA-UB Dijon), Jean Lévèque (Biogéosciences, CNRS-UB Dijon) et Paul Nelson (James Cook University, Cairns), nous avons utilisé un dispositif expérimental dans lequel nous avons examiné la production de matières organiques hydro-solubles dans des sols similaires sous deux couverts végétaux différents en faisant varier la température. L'activité des populations microbiennes pendant les processus de production de matières organiques hydrosolubles à été caractérisée par la méthode des profils d'acide gras (PLFA). Les variables étaient donc abiotiques (température) et biotiques (végétation) et le bio-fonctionnement du sol était caractérisé par les PLFA, le $\delta^{13}C$ du carbone organique extractible et la quantité de carbone organique extractible.

Les tout premiers résultats sont encourageants et semblent montrer des relations assez nettes entre le type de communautés microbiennes dégradantes (bactéries vs champignons) et la quantité et la qualité des matières organiques hydrosolubles (Hénault *et al.*, 2008). Ceci nous aiderait alors à comprendre comment et pourquoi les matières organiques hydrosolubles sont produites.

Le bio-fonctionnement des sols à l'échelle du bassin versant

Il resterait alors à transférer ces relations à plus large échelle. Le $\delta^{13}C$ du COD pourrait être un traceur de l'activité microbiologique et du bio-fonctionnement du sol, à condition que cette signature isotopique observée à l'échelle du microcosme (et qui reste à confirmer) soit i) transmise à l'échelle du bassin versant et ii) ne soit pas gommée par la forte hétérogénéité des processus. Nous avons pu constater (Amiotte-suchet *et al.*, 2007) que cela n'était pas très évident. Il est par ailleurs possible que la composition isotopique du carbone ne soit pas suffisamment discriminante et sensible. La recherche d'autres traceurs, notamment moléculaires, doit être mise en place.

J'ai conscience du caractère imprécis, incomplet et quelque peu spéculatif de cette dernière piste de travail. Cependant, la prise en compte des facteurs biotiques, y compris à l'échelle du bassin versant, me semble incontournable. En outre, les collaborations locales peuvent suffirent, dans un premier temps, à entreprendre de tels travaux. L'UMR CNRS Biogéosciences est en mesure de conduire des investigations poussées sur la composition des matières organiques (J. Lévèque, O. Mathieu) ; l'UMR INRA Microbiologie des Sols maîtrise les techniques de pointe en matière d'identification et de caractérisation des populations microbiennes (C. Hénault, PA Maron, L. Ranjard). L'ensemble est complété par des dispositifs de terrain opérationnels (site expérimental de la Forêt de Breuil-Chenue, sites du programme Agro-écologie de la parcelle cultivée), sur lesquels les équipes ont l'habitude de travailler ensemble.

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SELECTION D'ARTICLES

Articles pouvant contribuer à une meilleure compréhension du mémoire et présentés dans l'ordre où ils apparaissent dans le mémoire

Amiotte Suchet, P., Probst, J.L., Ludwig, W., (2003) Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO2 uptake by continental weathering and alkalinity river transport to the oceans. Global Biogeochem. Cycles, 17((2)), 1038, doi : 10.1029/2002GB001891.

Ludwig, W., Amiotte Suchet, P., Probst, J.-L., (1999) Enhanced chemical weathering of rocks during the last glacial maximum: a sink of atmospheric CO2? Chem. Geol, 159, 147-151.

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Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans

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[1] The silicate rock weathering followed by the formation of carbonate rocks in the ocean, transfers CO_2 from the atmosphere to the lithosphere. This CO_2 uptake plays a major role in the regulation of atmospheric CO_2 concentrations at the geologic timescale and is mainly controlled by the chemical properties of rocks. This leads us to develop the first world lithological map with a grid resolution of $1° \times 1°$. This paper analyzes the spatial distribution of the six main rock types by latitude, continents, and ocean drainage basins and for 49 large river basins. Coupling our digital map with the GEM-CO2 model, we have also calculated the amount of atmospheric/soil CO_2 consumed by rock weathering and alkalinity river transport to the ocean. Among all silicate rocks, shales and basalts appear to have a significant influence on the amount of CO_2 uptake by chemical weathering. *INDEX TERMS:* 1030 Geochemistry: Geochemical cycles (0330); 1060 Geochemistry: Planetary geochemistry (5405, 5410, 5704, 5709, 6005, 6008); 1645 Global Change: Solid Earth; 1886 Hydrology: Weathering (1625); *KEYWORDS:* lithological map, global carbon cycle, spatial distribution, river basins, riverine inputs to oceans, modeling

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1. Introduction

[2] The significance of rock weathering in the global carbon cycle has already been discussed by many authors, such as *Berner et al.* [1983], *Meybeck* [1987], *Amiotte Suchet and Probst* [1993a, 1993b, 1995], *Ludwig et al.* [1998, 1999], *Gaillardet et al.* [1999]. Recently, it has been demonstrated that the riverine inputs of carbon to the ocean have to be taken into account in the regional distribution of sources and sinks of CO_2 in the ocean [*Aumont et al.*, 2001]. The chemical and physical erosion of land materials releases into rivers carbon which is subsequently discharged into the oceans (dissolved organic (DOC) and inorganic (DIC) carbon and particulate organic (POC) and inorganic (PIC) carbon). The present-day riverine flux of carbon is estimated to be about 1 Gt C yr^{-1} (0.8 to 1.2 according to literature estimates); DIC, PIC, DOC and POC fluxes represent, respectively, 38%, 17%, 25% and 20% of the overall carbon flux. Most of the carbon transported by the rivers originates from atmospheric CO_2, except PIC and half of the DIC which are supplied by the physical and chemical erosion of carbonates.

[3] The chemical erosion of inorganic materials consists in dissolving or hydrolyzing primary minerals of rocks and soils. The chemical reactions require CO_2 and release DIC, as can be seen, for example, in the equation for albite hydrolysis,

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2Na^+ + 4H_4SiO_4, \quad (1)$$

or in the equation for the calcite dissolution,

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-. \quad (2)$$

[4] In river water, bicarbonates can be assumed to be equal to the alkalinity. All bicarbonate flux released by silicate hydrolysis (equation (1)) originates from the atmospheric CO_2, while it is only half for carbonate dissolution

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Table 1. Proportions of Different Rock Types Exposed on the Continents as Calculated in This Work and Compared to Results From Other Studies

Rock Type	This Work	*Blatt and Jones* [1975]	*Meybeck* [1987]	*Gibbs and Kump* [1994]
Sandstones, sands	26.2	–	15.8	23.9
Shales	25.4	–	34.4	12.6
Carbonate rocks	13.4	–	15.9	9.3
Total sedimentary rocks	65.0	66.0	66.1	45.8
Intrusive igneous rocks	–	9.0	–	–
Metamorphic rocks	–	17.0	–	–
Total shield rocks (intrusive igneous + metamorphic)	27.5	26.0	26.0	20.0
Acid volcanic rocks	2.3	–	3.8	–
Basalts	5.2	–	4.1	–
Total volcanic rocks	7.5	8.0	7.9	6.8
Total crystalline rocks	35.0	34.0	33.9	26.8
Fold belts	–	–	–	27.5
Total	100.0	100.0	100.0	100.1

(equation (2)). The flux of CO_2 that is consumed by weathering processes is mainly produced by soil organic matter oxidation,

$$CH_2O + O_2 \rightarrow CO_2 + H_2O. \quad (3)$$

[5] On a geological timescale, the fluxes of CO_2 consumed by carbonate dissolution (equation (2)) on the continents are balanced by the CO_2 fluxes released to the atmosphere by carbonate precipitation in the oceans. Consequently, with regard to the CO_2 content in the atmosphere, it is only the fluxes of CO_2 consumed by silicate rock weathering which represent a net sink of CO_2. This is the reason why future research on weathering must take into account the relative outcrop abundance of silicate and carbonate rocks when investigating the CO_2 uptake by silicate rock weathering and the subsequent riverine alkalinity transport. Recently, *Dessert et al.* [2001] have shown the impact of the Deccan Traps, one of the largest continental flood basalts (65.5 Myr ago), on chemical weathering and atmospheric CO_2 consumption on Earth. They estimated that the weathering of Deccan Traps basalts could be responsible for a 20% reduction of CO_2 content in the atmosphere, accompanied by a global cooling of 0.55°C. This result underlines the major role that the basalt outcrop abundance on Earth could play on the global carbon cycle and on the climatic evolution of the Earth.

[6] In this paper, we will examine the influence of the abundance of the different rock types on the atmospheric/soil CO_2 uptake by rock weathering and on the riverine transport of inorganic carbon to ocean. Until now, the spatial distribution of outcrop abundance for the different rock types has not been well known in detail at a global scale.

[7] The main difficulty in constructing a global data set of rock type exposures on the continents is that the information given by geological maps is inadequate. Indeed, geological maps focus on the age of rocks (for sedimentary rocks), on their deformation and on their structural position (sedimentary basin, mountain range, etc.), but information concerning the chemical and physical nature of rocks is often insufficient. This lack of information is problematic, especially for the chemical composition of sedimentary rocks, which is highly variable. Shield rocks are quite homogeneous from a chemical point of view.

[8] Few studies attempted to estimate the abundance of various rock types on the continents, and these estimates evolved with the knowledge in geology and the available data during the last century. In a first summary, *Clarke* [1924] proposed that continental outcrops were composed of 75% of sedimentary rocks and of 25% of combined igneous and metamorphic rocks. The first modern estimates have been proposed by *Blatt and Jones* [1975]. They established that the land surfaces were composed of 8% of extrusive crystalline rocks, 9% of intrusive crystalline rocks, 17% of metamorphic and precambrian crystalline rocks and 66% of sedimentary rocks. To do so, they used a sampling technique generating 3000 points, distributed over the entire land area. *Blatt and Jones* [1975] themselves noticed that the information collected for sedimentary rocks did not allowed to characterize them precisely. *Meybeck* [1987] greatly refined these results with calculations based on volume estimates determined by *Ronov and Yaroshevskyi* [1972, 1976] and taking into account of the wide diversity of sedimentary rocks (see Table 1).

Table 2. Lithological Description of the Six Rock Types Composing the Present-Day Lithological Map

Category	Description
Sand and sandstones	eolian, fluvial and marine sandy sediments not carbonated: mainly sands, sandstones and conglomerates
Shales	clastic and argilaceous sediments of various origin, not or poorly carbonated: clays, clay-shales, evaporites, . . .
Carbonate rocks	all rocks with more than 50% of carbonate minerals: mainly limestones, marls, dolomites and metamorphic limestones
Shield rocks	commonly every rocks composing shield regions: intrusive and metamorphic acid rocks (schists, micaschists, gneisses, granites, granodiorites, diorites)
Acid volcanic rocks	effusive acid rocks: mainly rhyolites and similar volcanic rocks
Basalts	effusive basic rocks more or less differentiated (mainly basalts s.l., dolerites and andesites) + igneous basic rocks (gabbros)

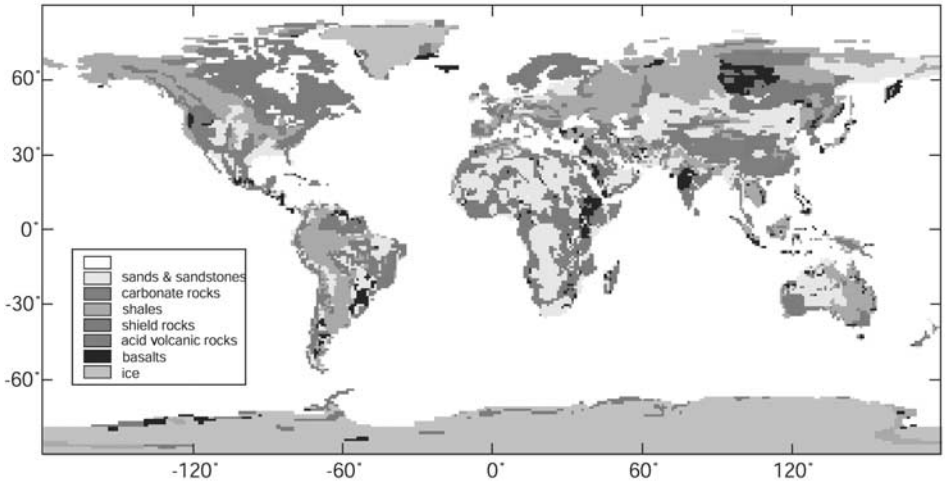

Figure 1. Present-day exposures of the six major rock types on land area (1° × 1° resolution). See color version of this figure at back of this issue.

[9] However, all these results do not take into account the spatial distribution of rock types, which is essential in the study of the weathering of these rocks at the global scale. *Bluth and Kump* [1991] made a very original work on the construction of paleogeologic maps and proposed a world map for what they called "the recent," with a resolution of 2° by 2°. This map corresponds to the Pliocene period and should be very close to a present-day map without Quaternary exposures. This map has been refined by *Gibbs and Kump* [1994] in order to correct for underrepresentation of shield rocks. Their calculations for global exposures are given in Table 1.

[10] The lithological associations that *Gibbs and Kump* [1994] distinguished are sandstones, shales, carbonate rocks, extrusive igneous rocks (i.e., volcanic rocks), shield rocks and fold belts. Two comments can be made concerning this map: The first one is that it has not been constructed from the observation of the present-day exposures, which could lead to some discrepancies. The second one is that about 27% of the total exposures are defined as "fold belts" and cannot be precisely characterized. Consequently, compared to the results of *Blatt and Jones* [1975] and *Meybeck* [1987], the work of *Gibbs and Kump* [1994] underestimates shield rock and sedimentary rock exposures (Table 1). This could be explained by the inclusion of sedimentary and shield rocks in the fold belts category.

[11] Consequently, the first objective of this paper is to propose a worldwide lithological map in a numeric format with a grid resolution of 1° × 1°. The basic data will be available on a web site and could be used in future researches on global biogeochemical cycles. The second objective is to estimate what is the impact of the abundance and distribution of the rock outcrops on the present-day rate of CO_2 consumed by rock weathering and on riverine alkalinity fluxes.

2. Data and Methods

[12] In this work, we have built a global map of the main rock types exposed on the continental areas today. This map has been constructed and digitized from synthetic lithological and soil maps published by the *Food and Agriculture Organization* (*FAO-UNESCO*) [1981] for each continent. These maps constitute the basis of our lithological map. Although the scale used by FAO-UNESCO to represent the maps is very coarse (about $1/50 \times 10^6$), we consider that it is sufficient to build up a global numeric map with a resolution of 1° by 1° (i.e., a square of about 111 by 111 km on the equator). The FAO-UNESCO synthetic lithological maps provide quite complete and precise information about the general lithology of continental areas for Central and South America, Africa, Asia and Australia, which allows us to distinguish carbonate rocks, shales and sands and sandstones among the sedimentary rocks. However, for North America and Europe, lithological information is often not accurate enough to identify separately carbonates, shales and sandstones. Finally, the FAO-UNESCO maps do not include Antarctica. Therefore, additional information has been collected from various sources. Notably, the UNESCO World Geological Atlas [*Choubert and Faure-Mauret*, 1981] has been used to complete the outlines of some geological formations and to build a comprehensive lithologic map for the ice free area of Antarctica. In addition, the paleogeographical maps of Ronov and coworkers [*Ronov and Khain*, 1961; *Khain et al.*, 1975; *Ronov et al.*, 1979], concerning the Mesozoic and Cenozoic periods, have been consulted to complete the lithology of the sedimentary units reported by FAO-UNESCO for Europe and North America.

[13] Obviously, the lithological description of sedimentary units varies from one source to another, which leads us to form large groups. We have distinguished very few different categories of rock types, which are sands and sandstones, shales, carbonate rocks, combined intrusive igneous rocks and metamorphic rocks (i.e., shield rocks), acid volcanic rocks, and basalts. A brief description of each category is given in Table 2.

[14] These rock categories have been first defined according to the available information and they also reflect the chemical composition and the behavior of rocks with regard

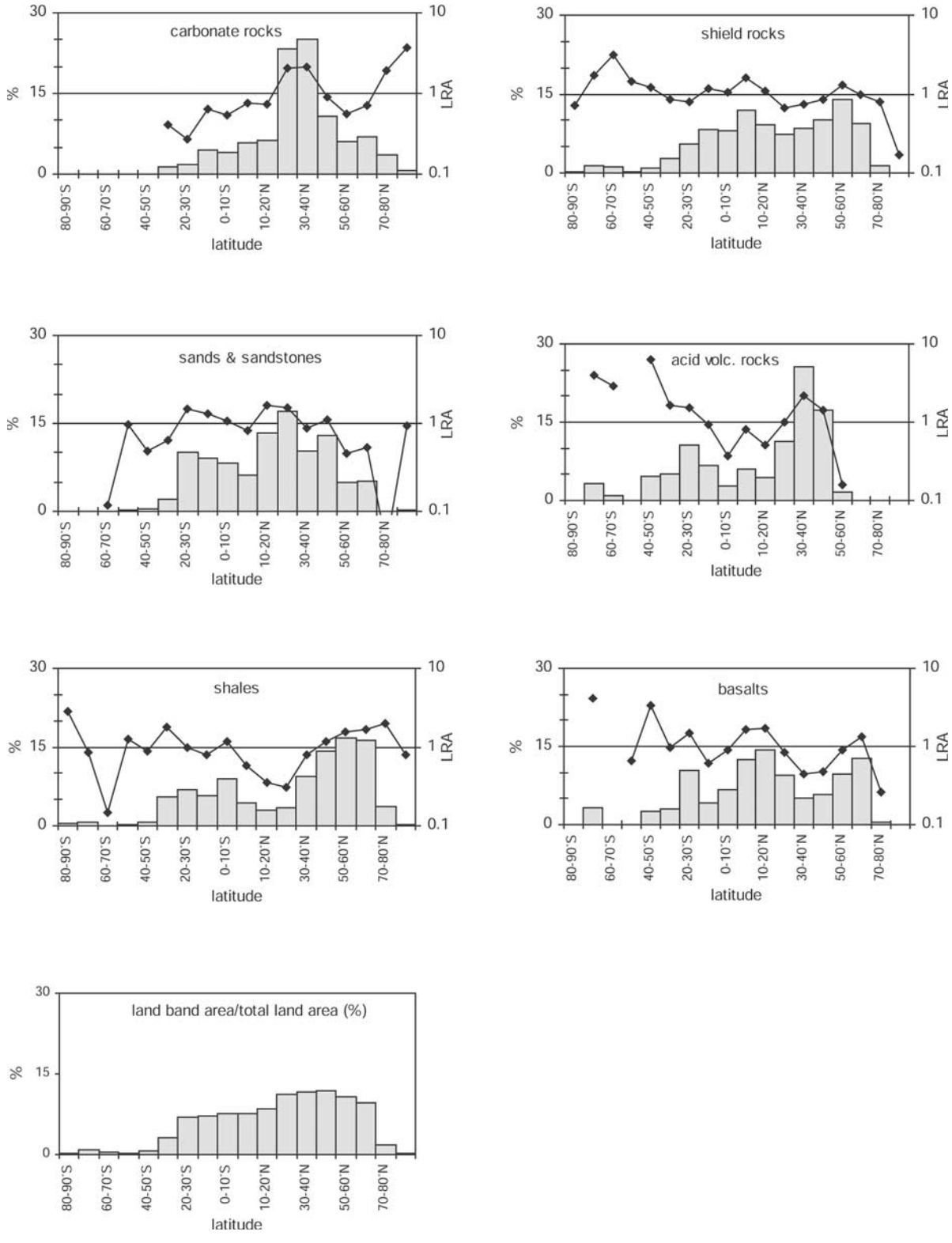

Figure 2. Latitudinal distribution of major rock types outcropping on land areas. Left Y axis and bar chart: ratio (in percent) of the rock type area at a given latitude to its worldwide area. Right Y axis and black curve: Latitudinal Relative Abundance: ratio (in percent) of the latitudinal proportion of rock type area (i.e., the percentage of the latitudinal land area occupied by a given rock type) to the latitudinal proportion of total land areas (i.e., the percentage of the world wide land area located at the given latitude). A LRA ratio below 1 means that the rock type is underrepresented; when it is above 1, the rock type is overrepresented.

Table 3. Relative Abundance of the Six Different Rock Types Exposed on Land by Continent (Endoreic and Exoreic Area) and by Ocean Drainage Basins[a]

	Sands and Sandstones		Shales		Carbonate Rocks		Shield Rocks		Acid Volcanic Rocks		Basalts		Total Land Areas	
	a	b	a	b	a	b	a	b	a	b	a	b	Percent of Land Area Without Ice	Percent of Land Area With Ice
Africa exoreic	19.8	38.5	0.3	0.6	12.2	12.1	20.9	42.6	0.0	0.0	16.4	6.2	13.5	12.2
Africa endoreic	23.0	55.9	1.2	2.8	14.5	17.9	7.7	19.7	0.0	0.0	7.7	3.7	10.8	9.8
Africa total	42.8	46.3	1.5	1.6	26.7	14.7	28.6	32.4	0.0	0.0	24.0	5.1	24.3	22.0
Antarctic	0.0	0.8	1.2	23.3	0.0	0.0	2.6	54.8	4.1	7.2	3.5	13.9	1.3	9.4
Asia exoreic	17.2	19.4	29.5	31.9	27.1	15.4	20.4	24.0	6.7	0.7	39.3	8.6	23.4	21.2
Asia endoreic	11.7	49.2	3.6	14.5	7.6	16.2	4.2	18.6	0.0	0.0	1.8	1.5	6.3	5.7
Asia total	28.9	25.7	33.0	28.2	34.6	15.6	24.6	22.9	6.7	0.5	41.1	7.1	29.7	26.9
Australia exoreic	1.7	14.3	6.2	50.1	0.3	1.1	2.8	24.2	4.4	3.1	4.4	7.2	3.2	2.9
Australia endoreic	5.5	51.0	2.7	24.1	1.4	6.7	1.5	14.5	4.3	3.4	0.2	0.3	2.8	2.6
Australia total	7.2	31.7	8.9	37.8	1.7	3.7	4.3	19.6	8.7	3.3	4.6	3.9	6.0	5.4
Europe exoreic	2.8	11.0	11.8	44.5	7.4	14.8	6.3	26.0	1.5	0.5	4.2	3.2	6.7	6.1
Europe endoreic	0.5	6.6	5.5	71.2	3.2	21.8	0.0	0.0	0.0	0.0	0.1	0.4	2.0	1.8
Europe total	3.3	10.0	17.3	50.5	10.7	16.4	6.3	20.1	1.5	0.4	4.3	2.6	8.7	7.9
North America exoreic	7.3	11.6	18.4	28.4	22.4	18.3	19.7	33.1	42.7	5.9	8.4	2.6	16.4	16.1
North America endoreic	0.1	7.9	0.0	0.0	0.0	0.0	0.0	0.0	10.7	92.1	0.0	0.0	0.3	0.2
North America total	7.3	11.6	18.4	28.0	22.4	18.0	19.7	32.6	53.4	7.3	8.4	2.6	16.7	16.3
South America exoreic	10.3	20.9	19.0	36.9	3.9	4.0	13.7	28.9	21.8	3.8	14.1	5.6	13.1	11.8
South America endoreic	0.0	2.7	0.5	46.3	0.0	0.0	0.2	22.2	3.7	28.7	0.0	0.0	0.3	0.3
South America total	10.4	20.5	19.6	37.1	3.9	3.9	13.9	28.8	25.5	4.3	14.1	5.4	13.3	12.1
Total exoreic	59.2	20.1	86.4	28.2	73.3	12.6	86.3	30.7	81.3	2.4	90.3	6.0	77.6	79.7
Total endoreic	40.8	47.9	13.6	15.3	26.7	15.9	13.7	16.8	18.7	1.9	9.7	2.2	22.4	20.3
Total	100.0	26.3	100.0	25.3	100.0	13.4	100.0	27.6	100.0	2.3	100.0	5.1	100.0	100.0
Arctic Ocean	11.2	14.3	25.5	45.9	14.4	11.6	10.9	21.4	0.0	0.0	17.9	6.9	15.7	14.0
North Atlantic	21.0	16.7	24.3	27.2	30.0	15.0	30.4	36.9	20.1	1.9	9.7	2.3	25.3	23.6
South Atlantic	28.2	34.5	8.6	14.9	8.8	6.8	19.8	37.1	7.4	1.1	15.3	5.6	16.4	14.4
Pacific	15.5	16.2	20.1	29.6	18.4	12.1	17.6	28.1	55.3	6.8	23.5	7.3	19.3	17.0
Indian Ocean	19.6	25.4	11.3	20.5	20.7	16.9	13.3	26.3	10.3	1.6	24.2	9.4	15.5	13.6
Mediterranean	4.5	14.5	8.9	39.7	7.6	15.3	5.0	24.5	1.9	0.7	5.5	5.3	6.3	5.5
Below 60° south	0.1	0.8	1.4	23.3	0.0	0.0	3.0	54.8	5.1	7.2	3.8	13.9	1.7	11.8
Total	100.0	20.1	100.0	28.2	100.0	12.6	100.0	30.7	100.0	2.4	100.0	6.0	100.0	100.0

[a]Column a is percent of the total area of each rock type, and column b is percent of the area of each continent or each ocean drainage basin.

to the chemical weathering. For example, as shown by *Amiotte Suchet and Probst* [1993a, 1993b], basic igneous rocks (basalts, gabbros) are, on average, more rapidly weathered than acid volcanic rocks, which are themselves less resistant than granites and gneisses. One of the most important points in the definition of rock categories is the presence of carbonate minerals. Several authors have demonstrated that weathering rates exponentially increased with the amount of carbonate minerals in rocks (among other, *Peters* [1984], *Meybeck* [1987], *Amiotte Suchet and Probst* [1993a, 1993b], and *Gibbs and Kump* [1994]). Therefore, rocks containing significant amounts of carbonate minerals are classified as carbonate rocks (Table 1). However, because of the coarse scale at which information has been collected (this information is necessarily simplified), carbonate minerals can sometimes be present in sedimentary rocks other than strictly carbonate rocks. As already emphasized by *Amiotte Suchet and Probst* [1993a, 1993b, 1995] and *Gibbs and Kump* [1994], the mineralogical composition of shales is highly variable, notably with respect to the presence and the proportion of carbonate minerals. In this work, it can be considered that shales include different argilaceous and clastic rocks, which can contain up to 50% of carbonate mineral. In practice, well-identified carbonate rocks (limestones, dolomites, marls, metamorphic limestones) have been classified as ''carbonate rocks'' and well-identified noncarbonated clastic sediments have been classified as ''sand and sandstones.'' The remaining ''suspect'' sedimentary rocks have been classified together with argilaceous sedimentary rocks as ''shales.''

[15] Compared to the 18 major rock types that have been distinguished by *Meybeck* [1987], our six categories may be considered as oversimplified. However, it will be demonstrated below that these are sufficient to be used in the quantification of global erosion. Nevertheless, some shortcomings can be noticed. Evaporitic rocks, which are not clearly described in the sources we used (probably because their occurrence is highly variable in space), have been included in shales. This is an obvious problem that must be addressed in the future because gypsum and rock salt deposits composing evaporites are easily dissolved and affect significantly river transport of dissolved solids. Finally, in the following, the results concerning acid volcanic rocks should be cautiously interpreted because outcrops are often very small and do not always appear at the scale we worked.

3. Spatial Distribution of Different Rock Types Over the Continents

3.1. Worldwide Abundance of Major Rock Types

[16] The $1° \times 1°$ lithological world map developed in this work is presented in Figure 1. The basic data are available at http://www.obs-mip.fr/omp/umr5563/4equ/hg/IGCP459/

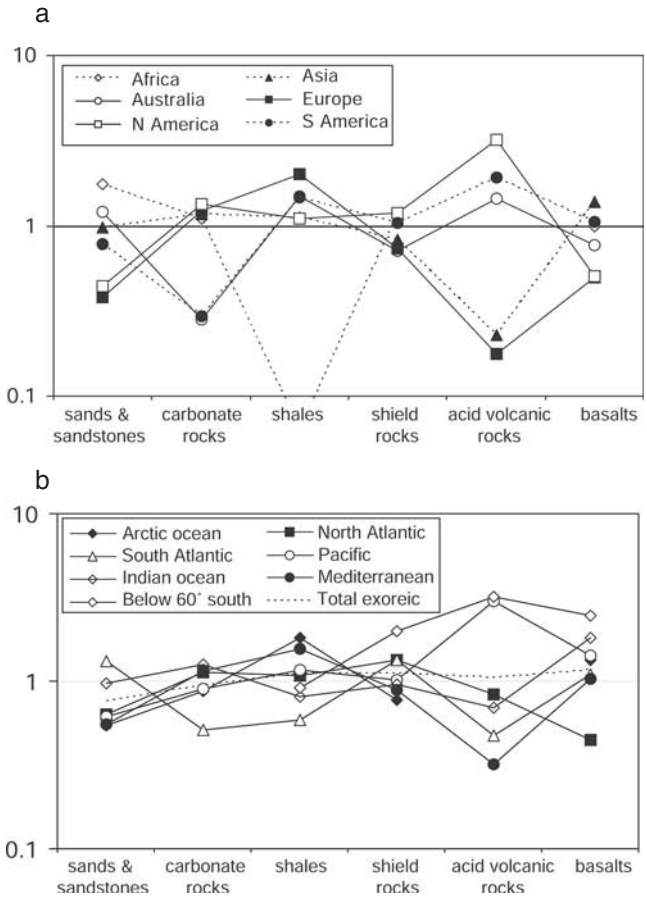

Figure 3. Relative abundance of rock types (a) on each continent and (b) on each ocean drainage basin normalized to the relative abundance of rock types on the total land areas (calculations have been executed considering total continental areas without ice).

litho.html. Using this digitized map, the outcrop areas of each rock type on land have been calculated and their relative abundance is presented in Table 1. Concerning the proportion of total sedimentary (one third) and crystalline rocks (two thirds), our results are very close to those of *Blatt and Jones* [1975] and of *Meybeck* [1987]. This confirms that the calculations made by *Gibbs and Kump* [1994] should be corrected by the redistribution of the fold belts toward shield rocks (about 7%) and toward sedimentary rocks (about 20%). Inside these two main categories, our estimates are in agreement with those of *Meybeck* [1987], except for clastic rocks. Indeed, the equivalent proportions of sands/sandstones and shales differ from those of *Meybeck* [1987], who proposed that shales are 2 times more abundant than sands and sandstones. This difference is probably due to the basis data used by *Meybeck* [1987] from *Ronov and Yaroshevskyi* [1972, 1976], who have considered sandstones sensus stricto and who probably grouped together sands and shales. This could indicate that the proportion of sands represents about 10%.

[17] The latitudinal distribution of each lithology (Figure 2), based on the map developed in this work, shows that all rock types are present at almost all latitudes but their relative abundance is highly variable from one latitude to an other. Figure 2 compares for each rock type the outcrop abundance by latitude with the distribution of land areas using a Latitudinal Relative Abundance (LRA) ratio (see Figure 2 caption for more explanation). A LRA ratio below 1 means that the rock type is underrepresented; when it is above 1, the rock type is overrepresented. It can be observed that shield rocks and sand/sandstones are equally distributed compared to the land areas (except for the high latitudes), whereas the other rocks exhibit higher or lower LRA according to the latitude. Most of the carbonate rocks (about 60%) are distributed between 20°N and 50°N. They appear to be overrepresented in comparison with the proportion of land areas, not only between 20°N and 40°N, but also at the higher northern latitudes (70°N–90°N). Shales are more abundant between 30°N and 70°N and between 0° and 40°S. The minimum LRA ratio observed between 0° and 30°N mainly corresponds to the African continent. Concerning the volcanic rocks (basalts and acid volcanic rocks), their latitudinal distribution is more heterogeneous than for the other rocks. More than half of the acid volcanic rocks outcrops between 20°N and 50°N, but their LRA is also rather important for the southern latitudes (20°S–50°S). The basalts are distributed over three main latitudinal zones: 36% between 0° and 30°N (Deccan Traps and Ethiopia), 23% between 50°N and 70°N (Iceland, Siberia and Kamchatka) and 10% between 20°S and 30°S (Parana Traps).

[18] The surface exposures of the different rock types can be also calculated for each continent, considering exoreic and endoreic areas, and for each oceanic basin (Table 3 and Figure 3). Most of sands and sandstones are located in Africa and in Asia, with a nonnegligible part that are not drained toward the ocean (endoreic areas). Shales follow more or less the proportion of the continental surfaces, except for Africa, where they are poorly represented, and for Europe, where they are largely represented (Figure 3a). Carbonate rocks show a homogeneous distribution, except for Australia and South America where outcrops are quite sparse. Shield rocks (plutonic and metamorphic rocks) follow quite closely the proportion of continental surfaces. The location of basalts is related to the occurrence of the trap structures (Deccan and Siberia in Asia, Parana in South America), and consequently they are poorly represented in Europe and North America. The acid volcanic rocks present a more heterogeneous distribution over the different continents: highly represented in North and South America and Australia, very poorly represented in the other continents.

[19] Finally, when looking at ocean drainage basins (Figure 3b), the distribution is more homogeneous than for the continents, except for volcanic rocks. Nevertheless, each ocean drainage basin presents a substantial enrichment or depletion for at least one rock type, which is very important to take into account with regard to the weathering products released to the rivers and transported into the ocean. Indeed, the waters flowing into the South Atlantic Ocean are draining continental areas depleted in shales, carbonates and acid volcanic rocks. The Pacific Ocean drainage basin is enriched in acid volcanic rocks

Table 4. Lithological Composition of 40 Major River Basins of the World (in Percent of the Basin Area)

	Basin Number	Area, 10^6 km^2	Runoff,[a] km^3 yr^{-1}	Sands and Sandstones	Shales	Carbonate Rocks	Shield Rocks	Acid Volcanic Rocks	Basalts
Amazon	1	5.83	6223	16.7	50.7	3.9	26.8	1.9	0.0
Amour	2	1.87	407	11.9	28.0	0.0	53.6	0.0	6.5
Colorado	3	0.67	28	55.6	0.0	0.0	10.4	34.0	0.0
Columbia	4	0.62	269	1.4	12.9	0.0	43.9	33.4	8.4
Danube	5	0.74	140	3.3	66.7	14.5	15.5	0.0	0.0
Don	6	0.39	31	0.0	94.1	5.9	0.0	0.0	0.0
Fraser	7	0.24	104	0.0	68.8	0.0	21.7	9.5	0.0
Ganges-Brahmaputra	8	1.64	1313	15.4	31.5	33.8	18.0	0.0	1.4
Godavari	9	0.30	147	3.9	0.0	0.0	61.6	0.0	34.5
Huangho	10	0.79	41	27.6	5.9	7.6	58.9	0.0	0.0
Yenisei	11	2.44	665	6.4	12.3	6.9	38.4	0.0	36.0
Indigirka	12	0.34	54	39.9	60.1	0.0	0.0	0.0	0.0
Indus	13	0.88	251	16.8	24.0	26.0	33.1	0.0	0.0
Irrawaddi	14	0.40	459	30.6	14.1	44.0	11.3	0.0	0.0
Kolyma	15	0.59	122	72.3	27.7	0.0	0.0	0.0	0.0
Lena	16	2.32	393	10.8	38.7	11.2	34.2	0.0	5.1
Limpopo	17	0.31	27	25.0	0.0	14.2	39.2	0.0	21.6
Mackenzie	18	1.47	260	0.0	53.9	20.6	25.5	0.0	0.0
Magdalena	19	0.26	313	23.8	28.5	4.8	23.8	19.1	0.0
Mekong	20	0.82	623	8.4	43.2	21.4	18.2	2.9	5.8
Mississippi	21	3.13	570	25.3	47.6	18.1	8.7	0.3	0.0
Murray	22	1.11	40	0.9	72.3	0.0	21.2	2.7	2.9
Niger	23	1.50	166	57.8	0.0	6.3	35.1	0.0	0.8
Nile	24	1.84	125	31.9	0.0	2.5	45.1	0.0	20.4
Ob	25	3.01	477	19.8	71.9	2.7	2.7	0.0	3.0
Orange	26	0.66	26	68.8	0.0	9.8	16.5	0.0	4.8
Orinoco	27	0.96	759	17.7	46.8	1.3	30.4	0.0	3.8
Parana	28	2.84	666	27.3	43.9	1.2	14.5	0.8	12.3
Sao Francisco	29	0.59	119	14.0	8.0	39.8	38.1	0.0	0.0
Senegal	30	0.36	15	64.5	3.2	0.0	29.1	0.0	3.3
Severnaia Dvina	31	0.30	97	10.9	78.4	10.8	0.0	0.0	0.0
Si Kiang	32	0.44	419	0.0	0.0	82.4	17.6	0.0	0.0
St. Lawrence	33	0.87	360	0.0	6.1	24.9	69.0	0.0	0.0
Tigris-Euphrates	34	0.93	156	17.2	25.8	42.5	2.2	11.3	1.0
Yana	35	0.21	25	50.6	49.4	0.0	0.0	0.0	0.0
Yangtze-Kiang	36	1.74	908	13.9	7.9	44.0	34.2	0.0	0.0
Yukon	37	0.78	169	0.0	85.4	0.0	14.6	0.0	0.0
Zaire	38	3.60	1298	46.6	0.0	10.1	41.9	0.0	1.4
Zambesi	39	1.31	109	45.9	0.0	13.6	38.7	0.0	1.8
Total 39 selected basin		49.11	18 379	22.3	32.2	11.8	27.1	1.6	5.0

[a]According to our digitized runoff map (discussed by *Ludwig et al.* [1998, 1999]) from the Atlas of World Water Balance [*Korzoun et al.*, 1977].

and depleted in sands and sandstones. The Mediterranean is depleted in acid volcanic rocks and in sands and sandstones. The North Atlantic drainage basin is depleted in sands/sandstones and in basalts. Finally, the Indian Ocean drainage basin is only enriched in basalts due to the Deccan Traps and to the Ethiopia, and the continental areas draining below 60°S are enriched in shields and volcanic rocks.

3.2. Average Lithology of Large River Basins

[20] The lithological composition of 39 large river basins has been determined on the basis of drainage basin limits defined by *Pinet and Souriau* [1988] and *Ludwig et al.* [1996]. We limited the calculations to river basins comprising at least 20 grid cells of 1° by 1° in order to avoid errors caused by the resolution of the lithological map compared to the river basin size. Results (Table 4) show that the average lithological composition calculated for the set of selected river basins is close to that of the whole continental area (Table 1) showing that the set of drainage basins is representative of the worldwide distribution of the different rocks types. Nevertheless, inside the sedimentary rocks, sands and sandstones as well as carbonate rocks are somewhat underrepresented on the set of river basins with regard to the world average.

[21] As seen in Table 4 and Figure 4, the percentage of each rock type is greatly variable from one river basin to another. If one groups together the different rock types according to their chemical alterability and their CO_2 consumption rate (high rate for carbonates, moderate rate for basalts plus shales and low rate for shields plus sands/sandstones), three sets of river basins can be distinguished (Figure 4). The first group represents the highest percentage of carbonates (20 to 80%) and comprises most of the Himalayan rivers (Si-Kiang, Yangtze, Irrawady, Indus, Mekong) plus the St. Lawrence, the Tigris-Euphrate and the Sao Francisco. The other two groups have less than 20% of carbonates, one dominated by shields and sands/sandstones (at least 60%) which comprises most of the African rivers, and the other one by shales and basalts (at least 40%)

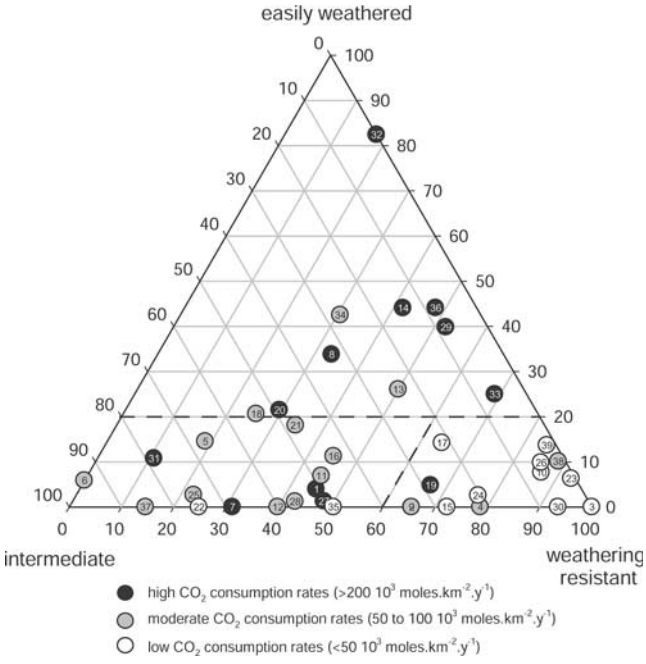

Figure 4. Typology of the major river drainage basins according to their lithological characteristics and to their weathering CO_2 consumption rates (numbers in circles refers to basin numbers in Table 4). Easily weathered rocks: carbonate rocks; intermediate: basalts, shales; weathering resistant: shield rocks, acid volcanic rocks, sands and sandstones.

which includes most of the Siberian and North and South American rivers.

4. Implication for Global Atmospheric/Soil CO_2 Consumed by Weathering

4.1. Lithology and Atmospheric/Soil CO_2 Consumed by Weathering: The GEM CO_2 Model

[22] The flux of atmospheric/soil CO_2 consumed by rock weathering (F_{CO2}) is mainly a function of runoff (Q) and of the rock type that is drained by surface water, as already demonstrated by *Amiotte Suchet and Probst* [1993a, 1993b, 1995]. Empirical relationships were established using data published by *Meybeck* [1986] concerning runoff and alkalinity concentrations of 232 monolithologic watersheds in France. These watersheds were grouped into the main six categories of rocks outcropping on the continents as described in Table 2. For each watershed, F_{CO2} fluxes were determined considering that for streams draining silicate rocks, F_{CO2} was equal to the whole alkalinity flux, and for streams draining carbonate rocks, F_{CO2} was equal to half of the alkalinity flux. Then, linear models between F_{CO2} and Q were determined for each of the six rock categories (Figure 5). These relationships form the Global Erosion Model for atmospheric/soil CO_2 consumed by chemical weathering (GEM-CO2 [*Amiotte Suchet and Probst*, 1995]). As seen in Figure 5, F_{CO2} increases as runoff increases but with a different rate according to the rock type. Similar relationships have been proposed by *Gibbs and Kump* [1994] using the data on North American streams. Thus, F_{CO2} is 17 times higher on carbonate rocks than on shield rocks. F_{CO2} consumed by weathering of the other rock types ranges between these two extremes. It must be noticed that F_{CO2} is twice as high for the weathering of basalts as for the weathering of acid volcanic rocks, although these rocks are structurally very similar.

[23] The GEM-CO2 model calculates F_{CO2} at a continental scale using our lithological map and the global distribution of runoff digitized from the UNESCO Atlas of World Water Balance [*Korzoun et al.*, 1977] and is discussed in detail by *Ludwig et al.* [1998, 1999]. In the GEM-CO2 model, it is assumed that sands and sandstones, shield rocks, basalts, acid volcanic rocks and shales are strictly silicate rocks and do not contain any carbonate minerals. That means that all bicarbonates ions are considered to come from the atmospheric/soil CO_2. This assumption is not correct, of course, especially for shales which can contain a nonnegligible but highly variable proportion of

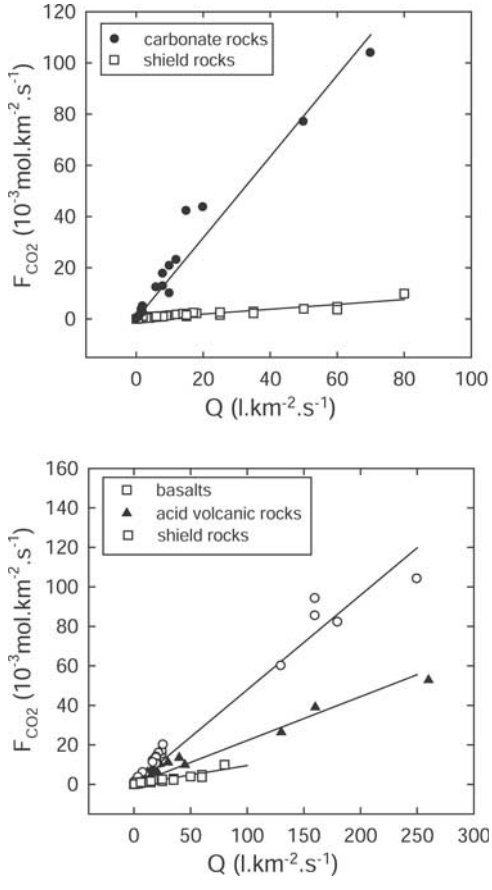

Figure 5. Linear models between the flux of CO_2 consumed by weathering (FCO_2) and the drainage intensity (Q) determined for the main rock categories (after *Amiotte Suchet and Probst* [1993b]). Slope values of the linear models are 0.095 for shield rocks, 1.586 for carbonate rocks, 0.222 for acid volcanic rocks, 0.479 for basalts, 0.152 for sands and sandstones (not represented in the figure) and 0.627 for shales (not represented in the figure).

Table 5. Global Budget of Atmospheric/Soil CO_2 Consumed by Weathering and Corresponding Alkalinity for Each Lithological Class[a]

	Sands and Sandstones	Shales	Carbonate Rocks	Shield Rocks	Acid Volcanic Rocks	Basalts	Total
Atmospheric/soil CO_2 consumed, F_T	1.10	8.57	8.63	1.50	0.21	1.49	21.49
Atmospheric/soil CO_2 consumed, F_S	30.92	250.84	478.26	40.36	67.31	215.04	159.46
River alkalinity (HCO_3^-), F_T	1.10	8.57	17.26	1.50	0.21	1.49	30.11
River alkalinity (HCO_3^-), F_S	30.92	250.84	956.53	40.36	67.31	215.04	223.48
Area, 10^6 km^2	35.42	34.16	18.03	37.13	3.05	6.94	134.74
Drainage intensity, $mm.yr^{-1}$	195.73	400.06	301.55	424.85	303.18	448.94	340.32
Percent of total CO_2 consumed worldwide	5.10	39.88	40.14	6.98	0.96	6.95	100.00
Percent of the world area	26.3	25.3	13.4	27.6	2.3	5.1	100.00

[a]Calculations include exoreic and endoreic area; F_T, total annual flux in 10^{12} moles yr^{-1}; FS, specific annual flux in 10^3 moles km^{-2} yr^{-1}.

carbonate minerals so that at the continental scale, this proportion is very difficult to estimate. On average, *Garrels and Mackenzie* [1971] estimated the proportion of carbonate minerals to be about 6%. Even so, the validation of GEM-CO2 on large river basins shows that calculated alkalinity fluxes are very close to observed fluxes [*Amiotte Suchet and Probst*, 1995; *Ludwig et al.*, 1998]. This is probably because the weathering CO_2 consumption rate of shales is intermediate between carbonates and shield rocks; consequently, the overestimations could compensate locally for the underestimations.

4.2. Global Budget of Atmospheric/Soil CO_2 Consumed by Different Rock Types

[24] Using GEM-CO2, a global budget of atmospheric/soil CO_2 consumption has been established for each rock type (Table 5). First, it can be observed that CO_2 consumption by carbonate rocks accounts for 40% of the worldwide atmospheric/soil CO_2 uptake and supplies 57% of the total alkalinity river input to the ocean, even if carbonates cover only 13% of the total continental area. Keeping in mind that the carbonate dissolution on the continent is balanced by the carbonate precipitation in the ocean, the carbonate weathering on land should have no effect on the CO_2 budget in the atmosphere.

[25] The remaining 60% of CO_2 uptake is attributed to silicate rock weathering which can also precipitate as carbonate in the ocean, but only pro parte according to the availability of calcium plus magnesium released by silicate weathering. Thus, it is important to distinguish among the silicates the contribution of the different rock types to the global atmospheric/soil CO_2 uptake. Shales (29% of the silicate rock outcrops) account for 40% of the total CO_2 consumed worldwide and almost 67% of the total CO_2 consumed by weathering of silicate rocks. Weathering of sands/sandstones or shield rocks, which are as abundant as shales, consumes a much lower proportion of atmospheric/soil CO_2 (about 5% and 7%, respectively), while weathering of basalts (only 5% of the continental area) represents almost 7% of the global weathering CO_2, and 12% of CO_2 consumed by silicate weathering only.

[26] A CO_2 and alkalinity transport budget by lithology can also be established for the 39 major world river basins (Table 6). The results show a wide variety of situations in which F_{CO2} and alkalinity fluxes reflect the drainage intensity and the lithological composition of the drainage basin as well.

[27] Figure 6 compares observed and calculated alkalinity (HCO_3^-) fluxes for most of the 39 selected basins. As already mentioned by *Ludwig et al.* [1998], this comparison gives best results for rivers in tropical wet climate, whereas for other rivers, GEM-CO2 underestimates alkalinity fluxes. This is especially surprising for temperate wet rivers because the empirical relationships of the model were based upon data of watersheds located in the temperate wet climate. This may be explained by the fact that, at the scale of large river basin, these watersheds represent more the headwater regions with a small residence time of the water. So, the model fits best in tropical wet climate where the very humid climate leads to a low residence time of the water in the basin. As the residence time of water becomes higher, the chemical concentration of water increases and fluxes are higher. *Ludwig et al.* [1998] have shown that, after correction using a climatic factor, fluxes were fitted well.

[28] Figure 4 allows us to analyze the relations between the lithology of the large river basins and their weathering CO_2 consumption rates. It appears that most of the drainage basins dominated by weathering resistant rocks (shield rocks, acid volcanic rocks, sands and sandstones outcrops >60%) exhibit the lowest weathering CO_2 fluxes (less than 50 10^3 moles km^{-2} yr^{-1}) and alkalinity river transports (less than 60 $\times$ 10^3 moles km^{-2} yr^{-1}). Concerning the other drainage basins, those dominated by carbonate rocks (easily weathered rock outcrop >20%) show generally higher weathering CO_2 uptake and alkalinity river fluxes (200 to 1150 $\times$ 10^3 moles km^{-2} $yr^{-1}$and 360 to 2292 $\times$ 10^3 moles km^{-2} yr^{-1}, respectively) than those dominated by intermediate rocks (basalts and shales outcrops > 50%; 50 to 200 $\times$ 10^3 moles km^{-2} yr^{-1} and 60 to 226 $\times$ 10^3 moles km^{-2} yr^{-1}, respectively). However, this trend is modulated by the influence of the runoff: For example, the Amazon and Orinoco river basins (basins number 1 and 27, respectively) show high weathering CO_2 fluxes whereas few carbonate rocks outcrop in their drainage basin. Inversely, the Tigris-Euphrate river (basin number 34), characterized by large carbonate rock outcrops, shows moderate weathering CO_2 fluxes because of its low runoff. The average CO_2 consumption by weathering in the 39 selected basins distributed by rock type shows the same pattern as that determined in Table 5 for the whole land areas, excepted for basalts, which contribute to only 3.6% of the CO_2 consumed by rock weathering in the selected basins compared to about 7% of the CO_2 consumed worldwide.

Table 6. Budget of Atmospheric/Soil CO_2 Consumed by Weathering of Main Rock Types for 39 Major River Basins of the World as Calculated by GEM-CO2

			CO_2 Consumed by Weathering of (Percent of Total Consumed)							Flux of Consumed CO_2, 10^3 moles km^{-2} yr^{-1}			Flux of Alkalinity,[a] 10^3 moles km^{-2} yr^{-1}	
	Basin No.	Area (10^6 km^2)	Sands and Sandstone	Shales	Carb. Rocks	Shield Rocks	Acid Volcanic Rocks	Basalts	All Silicate Rocks	Total River Basin	Silicate Rock	Carb. Rocks	Total Calculated (1)	Total Observed (2)
Amazon	1	5.83	4.0	76.1	14.4	4.8	0.6	0.0	85.6	509.49	435.96	73.53	583.03	462.0
Amour	2	1.87	4.3	59.3	0.0	23.7	0.0	12.7	100.0	54.85	54.85	0.00	54.85	124.0
Colorado	3	0.67	79.6	0.0	0.0	11.4	9.0	0.0	100.0	6.31	6.31	0.00	6.31	67.0
Columbia	4	0.62	0.4	52.8	0.0	16.8	14.1	15.9	100.0	119.88	119.88	0.00	119.88	374.0
Danube	5	0.74	1.8	38.5	56.9	2.8	0.0	0.0	43.1	136.44	58.82	77.62	214.05	
Don	6	0.39	0.0	81.2	18.8	0.0	0.0	0.0	81.2	55.88	45.39	10.50	66.38	
Fraser	7	0.24	0.0	89.3	0.0	7.6	3.1	0.0	100.0	187.16	187.16	0.00	187.16	390.0
Ganges-Brahmaputra	8	1.64	7.4	31.3	55.9	5.1	0.0	0.4	44.1	430.48	190.03	240.46	670.94	1116.0
Godavari	9	0.30	3.2	0.0	0.0	42.3	0.0	54.5	100.0	85.08	85.08	0.00	85.08	474.0
Huangho	10	0.79	8.2	1.5	65.2	25.1	0.0	0.0	34.8	14.60	5.08	9.52	24.13	235.0
Yenisei	11	2.44	2.2	16.1	44.4	6.5	0.0	30.9	55.6	136.27	75.80	60.47	196.74	279.0
Indigirka	12	0.34	23.6	76.4	0.0	0.0	0.0	0.0	100.0	58.55	58.55	0.00	58.55	
Indus	13	0.88	4.8	6.7	71.5	17.0	0.0	0.0	28.5	107.91	30.74	77.16	185.07	654.0
Irrawaddi	14	0.40	5.1	14.6	78.3	2.0	0.0	0.0	21.7	906.50	196.84	709.66	1616.16	
Kolyma	15	0.59	54.4	45.6	0.0	0.0	0.0	0.0	100.0	49.35	49.35	0.00	49.35	
Lena	16	2.32	6.1	31.8	42.3	14.1	0.0	5.7	57.7	61.26	35.35	25.91	87.17	237.0
Limpopo	17	0.31	8.2	0.0	50.4	19.5	0.0	21.9	49.6	25.96	12.87	13.09	39.05	37.0
Mackenzie	18	1.47	0.0	61.9	35.0	3.1	0.0	0.0	65.0	115.28	74.91	40.38	155.66	291.0
Magdalena	19	0.26	10.4	41.1	25.7	6.6	16.3	0.0	74.3	422.53	314.07	108.47	531.00	703.0
Mekong	20	0.82	1.9	36.6	50.4	3.7	1.3	6.1	49.6	476.77	236.59	240.18	716.94	526.0
Mississippi	21	3.13	4.7	38.9	54.9	1.4	0.2	0.0	45.1	128.71	58.06	70.64	199.35	309.0
Murray	22	1.11	2.8	71.1	0.0	11.6	7.3	7.3	100.0	12.03	12.03	0.00	12.03	
Niger	23	1.50	42.3	0.0	21.2	35.4	0.0	1.1	78.8	16.86	13.28	3.58	20.44	72.0
Nile	24	1.84	4.1	0.0	25.5	6.6	0.0	63.7	74.5	27.73	20.66	7.07	34.80	122.0
Ob	25	3.01	7.0	80.6	5.0	0.2	0.0	7.2	95.0	82.34	78.22	4.13	86.47	236.0
Orange	26	0.66	35.7	0.0	11.9	0.8	0.0	51.6	88.1	11.21	9.88	1.33	12.54	27.0
Orinoco	27	0.96	7.2	69.9	1.6	15.3	0.0	5.9	98.4	238.06	234.25	3.81	241.87	219.0
Parana	28	2.84	17.6	33.9	3.5	7.9	0.1	37.1	96.5	71.57	69.10	2.47	74.04	119.0
Sao Francisco	29	0.59	3.1	7.0	86.9	3.0	0.0	0.0	13.1	171.20	22.40	148.80	320.00	
Senegal	30	0.36	62.8	2.3	0.0	15.2	0.0	19.7	100.0	6.97	6.97	0.00	6.97	
Severnaia Dvina	31	0.30	2.7	70.8	26.5	0.0	0.0	0.0	73.5	218.21	160.30	57.90	276.11	798.0
Si Kiang	32	0.44	0.0	0.0	98.1	1.9	0.0	0.0	1.9	1156.77	21.52	1135.25	2292.02	1411.0
St. Lawrence	33	0.87	0.0	5.7	80.4	13.8	0.0	0.0	19.6	200.64	39.23	161.41	362.05	600.0
Tigris-Euphrates	34	0.93	2.7	16.2	72.5	0.2	7.9	0.5	27.5	131.28	36.04	95.23	226.51	
Yana	35	0.21	25.2	74.8	0.0	0.0	0.0	0.0	100.0	43.44	43.44	0.00	43.44	71.0
Yangtze-Kiang	36	1.74	2.1	5.6	89.0	3.3	0.0	0.0	11.0	463.05	50.86	412.18	875.23	921.0
Yukon	37	0.78	0.0	98.1	0.0	1.9	0.0	0.0	100.0	123.44	123.44	0.00	123.44	467.0
Zaire	38	3.60	35.4	0.0	51.3	11.9	0.0	1.4	48.7	93.68	45.60	48.08	141.76	82.3
Zambesi	39	1.31	13.9	0.0	73.8	9.7	0.0	2.7	26.2	34.52	9.06	25.46	59.98	29.0
39 selected basins		49.11	5.7	43.4	41.1	5.6	0.7	3.6	58.9	186.80	110.12	76.68	263.48	
Arctic Ocean		16.34	3.9	49.4	34.3	4.0	0.0	8.2	65.7	99.56	65.38	34.19	133.75	
North Atlantic		26.33	4.3	50.1	32.7	8.5	0.7	3.7	67.3	227.14	152.84	74.30	301.44	
South Atlantic		17.08	20.8	17.0	31.0	16.2	1.1	13.9	69.0	89.92	62.04	27.88	117.80	
Pacific Ocean		20.07	2.7	43.4	38.0	5.5	1.2	9.2	62.0	334.57	207.36	127.21	461.78	
Indian Ocean		16.14	6.3	19.4	62.2	5.2	0.9	6.0	37.8	213.52	80.61	132.91	346.43	
Mediterranean		6.56	1.6	33.2	59.3	1.7	0.5	3.6	40.7	150.00	61.12	88.88	238.88	
Below 60° south		1.73	0.5	33.4	0.0	21.2	15.0	29.9	100.0	74.02	74.02	0.00	74.02	

[a](1) calculated by GEM-CO2, this study, (2) taken from a compilation of literature data by *Ludwig et al.* [1998].

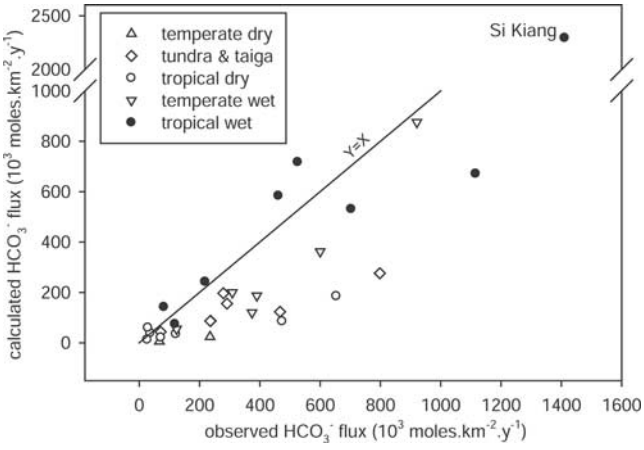

Figure 6. Comparison of the observed HCO_3^- fluxes with the fluxes calculated with GEM-CO2 (see data in Table 6).

[29] For the ocean basins (Table 6), the distribution is much more homogeneous: About two thirds of the weathering CO_2 fluxes and half of the river alkalinity input originate from silicate rocks for the Arctic, North and South Atlantic and Pacific Oceans, whereas, for the Mediterranean Sea and the Indian Ocean, the contribution of silicate rock weathering represents only about 40% and 25%, respectively, for the overall CO_2 flux and alkalinity river input.

[30] If we look at the latitudinal distributions of weathering CO_2 consumption by the different rock types (Figure 7), it appears clear that weathering of shales represents a major sink for atmospheric/soil CO_2 ($0.4-1.8 \times 10^{12}$ moles yr^{-1} per 5° latitude) in the Northern Hemisphere between 35° and 70° and in the Southern Hemisphere between 5° and 40°, even if the shales outcrop are less abundant than the shield ones. Concerning the other rock type, the latitudinal weathering CO_2 fluxes follow more or less the outcrop areas, except for sands and sandstones between 25°S and 15°N and between 35°N and 55°N, for carbonate rocks between 15°S and 10°N and for acid volcanic rocks between 0° and 10°N and between 30°S and 45°S. Most of these exceptions can be attributed to high or low drainage intensities at the corresponding latitudes.

5. Conclusion

[31] A compilation of lithological, soil and geological maps available for regional and continental areas allowed us in this study to construct for the first time a world lithological map with a grid resolution of $1° \times 1°$. The basis data of this lithological map are now available on a website (http://www.obs-mip.fr/omp/umr5563/4equ/hg/IGCP459/litho.html) and can be used for future studies on global biogeochemical cycles, particularly for chemical weathering and fluvial transports of dissolved elements into the oceans. This work gives, for the first time on a global scale, access to the spatial distribution of the main rock types with regard to their chemical weathering rate: plutonic and metamorphic rocks (shield rocks), acid volcanic rocks, basalts, sands and sandstones, shales and carbonates. Unfortunately, evaporitic rocks could not be taken into account because their outcropping areas are always very limited.

[32] The worldwide outcrops of each rock type that could be calculated from these data are comparable to previous estimates [*Blatt and Jones*, 1975; *Meybeck*, 1987]: Two thirds of the continental rocks are sedimentary rocks (sands and sandstones, shales and carbonates), of which carbonates represent only 20%, and one third are crystalline rocks (intrusive igneous and metamorphic, acid volcanic and basalts). Basalts represent only 15% of the total crystalline rocks area. A careful analysis of the spatial distribution of each rock type shows that shield rocks and sands/sandstones are equally distributed over the latitudes, contrary to the other rocks. Indeed, carbonates are more abundant in the Northern Hemisphere between 20°N and 40°N and between 70°N and 90°N, shales are more abundant between 30°N and 70°N and between 0° and 40°S, half of the acid volcanic rocks outcrops between 20°N and 50°N, and 70% of basalt areas stretch out between 0° and 30°N and between 50°N and 70°N and between 20°S and 30°S, corresponding to large areas of basaltic traps. If we look at the spatial distribution by continents, there also appear to be some discrepancies: Most of the sands and sandstones are located in Africa and in Asia covering pro parte endoreic areas. Shales are poorly represented in Africa, carbonates are quite sparse in Australia and South America, basalts are poorly represented in Europe and in North America, and finally, acid volcanic rocks are highly represented in North and South America and in Australia. Looking at the different ocean drainage basins, the distribution appears to be more homogeneous, except for volcanic rocks. Thus, the rivers flowing into the Pacific Ocean and below 60°S are draining land areas where acid volcanic rocks are more abundant, and the Indian Ocean drainage basin is enriched in basalts.

[33] An average lithological composition could be also calculated for 39 large river basins showing that the total land area drained by these rivers is representative of the world distribution. Nevertheless the abundance of each rock type is greatly variable from one drainage basin to another. Consequently, some river basins (carbonate outcrop abundance greater than 20%) appear to be very sensitive to the chemical weathering and present high weathering CO_2 consumption rates while some others (outcrop abundance of shields, sands and sandstones greater than 60%, with less than 20% of carbonates) appear to be very resistant to chemical alteration and present low CO_2 consumption rates. Drainage basins where the outcrop abundance of shales and basalts represent more than 40% and carbonates less than 20% are intermediate between the previous two groups.

[34] As we have already shown in previous works [*Amiotte Suchet and Probst*, 1993a, 1993b, 1995], the flux of CO_2 consumed by rock weathering is greatly variable according to the rock types: Shield rocks present the lowest values, and the CO_2 flux consumed by sands/sandstones, acid volcanic rocks, basalts, shales and carbonates are respectively 1.5, 2.3, 5.0, 6.6 and 16.7 times greater than the CO_2 flux consumed by shield rocks. Consequently, the relative outcrop abundance of the different rock types as well as their spatial distribution in relation to the latitudinal

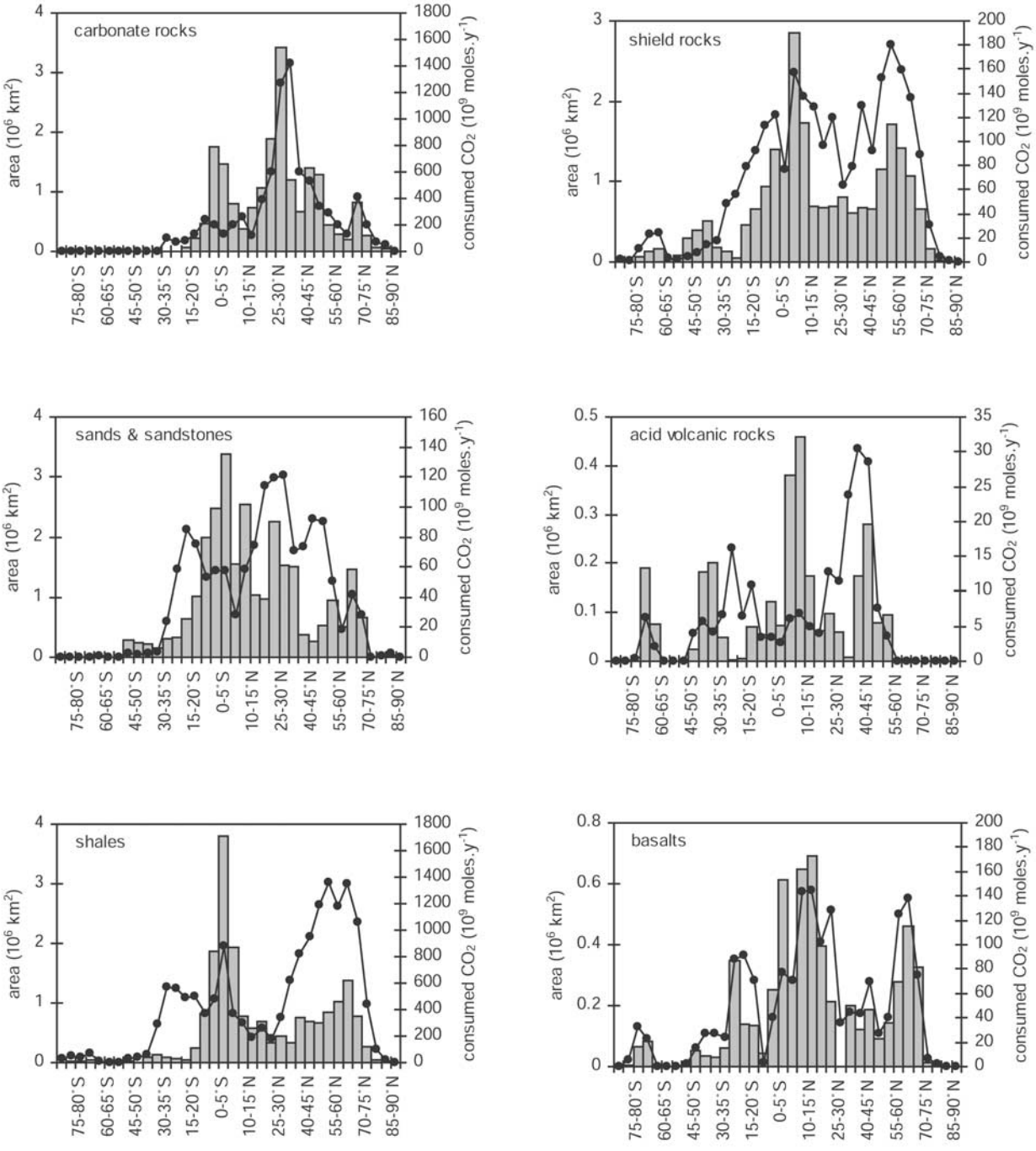

Figure 7. Latitudinal distribution of the weathering CO_2 consumption by rock type. The curve represents the outcrop areas.

and altitudinal variations of the main hydroclimatic factors (precipitation, runoff and temperature) have a great influence on the global CO_2 consumed by rock weathering and on the riverine transports of dissolved elements into the oceans. Coupling the GEM-CO_2 modeling [*Amiotte Suchet and Probst*, 1995] with the spatial distribution of the different rock types, it was possible in this study to estimate for each large river basin and for the global scale, the CO_2 uptake by each rock type. The dissolution of carbonates and the chemical alteration of shales consume both 80% (40% each) of the total CO_2 uptake by continental weathering, even if their respective outcrop area represent only 13% and 25% of the total land area. On the contrary, sands, sandstones and shield rocks consume a total of only 12% (5%

and 7%, respectively) of the total CO_2 uptake while their outcrop areas occupy 54% of the continents (26% and 28%, respectively). Finally, the contribution of volcanic rock (acid and basalts) weathering to the total CO_2 flux (8%) is proportional to their outcrop abundance (7%). Nevertheless, the chemical alteration of basalts which cover only 5% of the total land areas represents 7% of the total CO_2 uptake.

[35] Consequently, by combining large areas of shales (even if they may contain a small amount of carbonate mineral) or basalts with high temperature and high runoff intensity must lead to high weathering CO_2 consumption, which could play a significant role in the CO_2 content in the atmosphere and consequently in the global climate on Earth, as recently shown by *Dessert et al.* [2001] for the Deccan Traps 65.5 Myr ago. In the same way, during glacial periods, huge ice sheets and large areas of emerging continental shelves must change the proportion and the spatial distribution of the main lithologies and consequently could have a great influence on the weathering CO_2 flux and on the riverine transports of dissolved elements, as proposed by *Gibbs and Kump* [1994] and *Ludwig et al.* [1998] for the Last Glacial Maximum (18,000 years BP).

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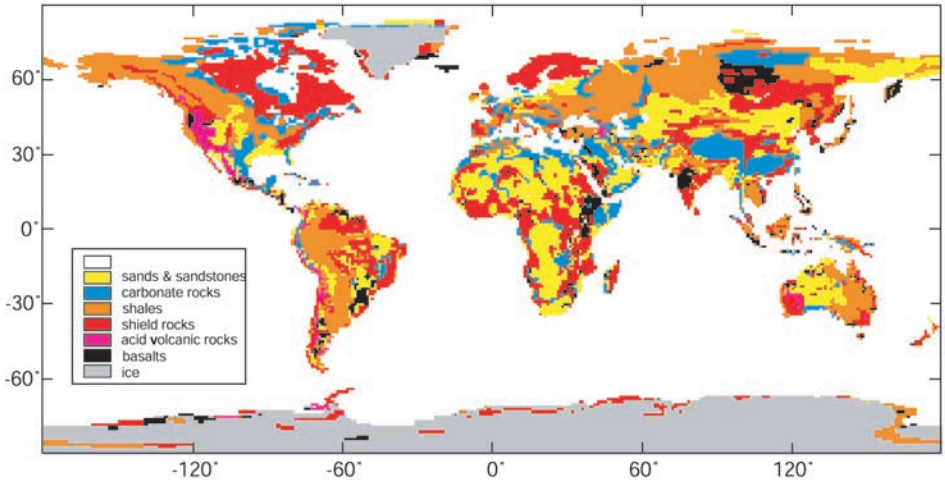

Figure 1. Present-day exposures of the six major rock types on land area (1° × 1° resolution).

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Enhanced chemical weathering of rocks during the last glacial maximum: a sink for atmospheric CO_2?

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Abstract

It has been proposed that increased rates of chemical weathering and the related drawdown of atmospheric CO_2 on the continents may have at least partly contributed to the low CO_2 concentrations during the last glacial maximum (LGM). Variations in continental erosion could thus be one of the driving forces for the glacial/interglacial climate cycles during Quaternary times. To test such an hypothesis, a global carbon erosion model has been applied to a LGM scenario in order to determine the amount of CO_2 consumed by chemical rock weathering during that time. In this model, both the part of atmospheric CO_2 coming from silicate weathering and the part coming from carbonate weathering are distinguished. The climatic conditions during LGM were reconstructed on the basis of the output files from a computer simulation with a general circulation model. Only the predicted changes in precipitation and temperature have been used, whereas the changes in continental runoff were determined with an empirical method. It is found that during the LGM, the overall atmospheric CO_2 consumption may have been greater than today (by about 20%), mainly because of greater carbonate outcrop area related to the lower sea level on the shelves. This does not, however, affect the atmospheric CO_2 consumption by silicate weathering, which alone has the potential to alter atmospheric CO_2 on the long-term. Silicate weathering and the concomitant atmospheric CO_2 consumption decreased together with a global decrease of continental runoff compared to present-day (both by about 10%). Nevertheless, some uncertainty remains because the individual lithologies of the continental shelves as well as their behavior with respect to chemical weathering are probably not well enough known. The values we present refer to the ice-free continental area only, but we tested also whether chemical weathering under the huge ice sheets could have been important for the global budget. Although glacial runoff was considerably increased during LGM, weathering under the ice sheets seems to be of minor importance.

Keywords: Atmospheric CO_2; Last glacial maximum; Chemical weathering

1. Introduction

Continental erosion represents a permanent transfer of carbon from the atmosphere to the oceans. Atmospheric/soil CO_2 is consumed both by organic matter formation and by chemical rock weathering, and subsequently discharged as dissolved organic

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carbon, particulate organic carbon, and dissolved inorganic carbon to the oceans by rivers. The latter occurs mainly in the form of bicarbonate ions (HCO_3^-). In the long-term, the consumption of atmospheric CO_2 resulting from carbonate weathering on the continents is balanced in relatively short time scales by carbonate sedimentation in the oceans, where all CO_2 is released back to the ocean/atmosphere system. This is not the case for all CO_2 consumed by silicate weathering or by organic matter erosion. Here, a part of this carbon is lost to the lithosphere by carbonate precipitation and organic matter sedimentation, and only returns to the ocean/atmosphere system via metamorphism/volcanism and by the slow oxidation of old organic carbon in sedimentary rocks. Because the latter processes strongly depend on the tectonic activity on Earth, this lithospheric release of CO_2 can be quite variable over geological time scales.

Evidence from polar ice cores reveals a close coupling of the level of CO_2 in the atmosphere and global climate over at least the last 250,000 years (e.g., Neftel et al., 1988; Barnola et al., 1989; Alley et al., 1993), although it remains uncertain how sensitive climate is to variations in atmospheric CO_2, and to what extent these variations cause rather than result from climate change. Nevertheless, it has been widely accepted that changing the atmospheric CO_2 consumption by continental erosion can have an influence on climate on Earth, but some controversy about the involved mechanisms exists. On the one hand, it was proposed that continental erosion should act as a negative feedback to global temperature change (e.g., Walker et al., 1981; Berner et al., 1983), which is mainly controlled by the rate of sea floor spreading and hence an increase of volcanic outgassing of CO_2. Assuming that a higher global temperature causes more weathering, this process should bring atmospheric CO_2 again down to lower levels, and vice versa. Berner (1991, 1994) showed that such a mechanism could explain the general climatic variations observed during Phanerozoic times. On the other hand, Raymo et al. (1988) and Raymo (1994) suggested that the long-term removal rate of CO_2 from the atmosphere by chemical weathering is rather a function of relief than other factors, and that atmospheric temperature exerts only a weak control on global chemical erosion rates. They postulated that the global cooling during the late Cenozoic may be related to the built-up of the Tibetan plateau as a result of the collision of India and Asia, leading to a considerable increase of atmospheric CO_2 consumption by continental erosion.

The above mentioned processes operate on a multimillion-year time scale, but weathering may also have an influence on climate in much shorter time scales. In particular, continental erosion has been discussed as a potential candidate for being involved in the glacial/interglacial climate cycles during Quaternary times. Using an 11-box model for the oceanic carbon cycle, Munhoven and François (1996) showed that an increase of chemical silicate weathering by a factor of 2 to 3.5 during the last glacial maximum (LGM) could result in variations of atmospheric CO_2 that are close to those documented by ice cores. They justify such an assumption by the findings of Froelich et al. (1992), indicating considerably greater river fluxes of dissolved silica for the LGM than for the present-day. Gibbs and Kump (1994) confirmed the trend of generally increased weathering rates during the LGM, although they found this increase to be less important than that postulated by Munhoven and François (1996), and mainly to be related to an increase of carbonate erosion on the emerged shelves.

The purpose of this paper is to test the hypothesis of increased chemical weathering rates and river bicarbonate fluxes during the LGM. A global carbon erosion model that has been developed to simulate the present-day river fluxes (Amiotte-Suchet and Probst, 1995) was applied to a LGM scenario in order to determine the amount of atmospheric CO_2 consumed by the chemical weathering of rocks during that time. Contrary to the modelling study of Gibbs and Kump (1994), in our model both the CO_2 consumption by silicate weathering and by carbonate weathering is distinguished. It is therefore possible to test whether silicate weathering especially may have been sensitive to the changes in the environmental conditions during the LGM.

2. Data and methods

2.1. Model description

The fluxes of atmospheric CO_2 consumed by rock weathering (in the following F_{CO_2} for absolute val-

ues, and $F^s_{CO_2}$ for specific values, i.e., fluxes divided by the corresponding area) are mainly a function of runoff and of the rock type that is drained by the surface waters. This could been shown by Amiotte-Suchet and Probst (1993a,b, 1995), and by Amiotte-Suchet (1995) using data published by Meybeck (1986) about runoff and HCO_3^- concentrations in 232 monolithologic watersheds in France. The watersheds were grouped into six lithological classes representative for the major rock types outcropping on the continents, and the empirical relationships between $F^s_{CO_2}$ and runoff intensity (Q) were determined for each of the six classes. A linear relationship between $F^s_{CO_2}$ and Q for each rock type was found. Then, these relationships were validated on the level of large river basins. According to the stoichiometry of the weathering reactions, F_{CO_2} is considered to be equal to the HCO_3^- fluxes in waters draining silicate rocks, and to be equal to half of the HCO_3^- fluxes in waters draining carbonate rocks. These relationships can be seen, for example, in the following equations for the hydrolysis of albite (Eq. (1)) and for the dissolution of calcite (Eq. (2)):

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2Na^+ + 4H_4SiO_4 \quad (1)$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (2)$$

For a given runoff intensity, $F^s_{CO_2}$ varies considerably for different rock types. $F^s_{CO_2}$ is 17 times greater for carbonate rocks, the rock type with the greatest specific CO_2 consumption, than for plutonic and metamorphic rocks, the rock type with the lowest specific CO_2 consumption. In the order of decreasing specific CO_2 consumption, the six rock types can be classified as follows: carbonate rocks, shales, basalts and gabbros, acid volcanic rocks, sands and sandstones, and plutonic and metamorphic rocks. Together, these relationships form the Global Erosion Model for atmospheric CO_2 consumption by rock weathering—GEM-CO_2 (Amiotte-Suchet and Probst, 1995). Bluth and Kump (1994) investigated CO_2 consumption by rock weathering based on data from different rivers and found similar relationships. Note that the present-day distribution of F_{CO_2} on the continents calculated by Amiotte-Suchet and Probst (1995) is available via ftp in a spatial resolution of $1° \times 1°$ longitude/latitude at the Carbon Dioxide Information Analysis Centre CDIAC (ftp cdiac.esd.ornl.gov/pub/db1012).

2.2. Reconstruction of the LGM climate

For the simulation of the Earth's climate prevailing during the LGM, we used in this study the monthly temperature and precipitation climatologies calculated by the ECHAM2 general circulation model (GCM). They exist both for a LGM simulation run (*lgm*) and for the corresponding present-day control run (*contr*), and they are available via ftp from the Deutsches Klima Rechenzentrum (Hamburg, Germany). More details on the ECHAM2 model are given by Lautenschlager and Herterich (1990), and by Lautenschlager (1991). Esser and Lautenschlager (1994) used the same model in order to estimate the change of carbon in the terrestrial biosphere from LGM to present with a global carbon cycle model. Since these ECHAM2 climatologies only exist in the $5.625° \times 5.625°$ longitude/latitude resolution of the model (so-called T21 resolution), the following algorithm was applied to derive $0.5° \times 0.5°$ grid point climatologies from the model files:

$$ValM_i = ValO_i \times ValM_j / (ValO_i)_j \quad (3)$$

ValM is either the monthly temperature (K) or precipitation (mm) value of the model; ValO is the corresponding value of the present-day temperature and precipitation data sets; and i and j are indices for the grid points in the $0.5° \times 0.5°$ (i) and in the T21 (j) resolution, respectively. As present-day data sets, we used the data of Legates and Willmott (1992) for temperature and for the monthly precipitation values (in percent of the annual values), whereas for mean annual precipitation a digitized and gridded version of the Atlas of World Water Balance of Korzoun et al. (1977) was used. $(ValO_i)j$ is the area-weighted average of all i that fall into j. Because this is a common practice also in other studies (e.g., Esser and Lautenschlager, 1994; Gibbs and

Kump, 1994), the final LGM climatologies were then obtained by subtracting the ECHAM2-derived anomalies from the present-day distributions according to:

$$\mathrm{ValO}_{(\mathrm{lgm})i} = \mathrm{ValO}_{(\mathrm{present-day})i} - \left(\mathrm{ValM}_{(\mathrm{contr})i} - \mathrm{ValM}_{(\mathrm{lgm})i}\right) \quad (4)$$

For precipitation, it could happen that Eq. (2) yields negative values. In these cases, the grid point values were set to 0. Esser and Lautenschlager (1994) derived the LGM precipitation data set in their study by applying the relative changes between the LGM and control run of the ECHAM2 model to the actual precipitation distribution, and not the absolute changes. This method avoids negative values, but it risks altering the global precipitation change predicted by the model with respect to the absolute values. None of the methods is without shortcomings. Note that the method we applied respects the absolute amount of precipitation change predicted by ECHAM2, except for the grid elements which are set to 0. Cutting off negative values overestimates to some extent the global LGM precipitation. In the LGM data set we created, this overestimation is about 1.5% of total precipitation, which is globally of small importance, confirming the applicability of our method.

When applied to the total continental area (about 152×10^6 km^2 for present-day and 173×10^6 km^2 for the LGM), the so-created LGM climatologies show a global cooling of 6.7°C compared to present-day (from 9.6 to 2.9°C), and a reduction of global precipitation of 77 mm (from 817 to 740 mm). Both the changes in continental area during the LGM related to the sea level fall as well as the appropriate LGM ice-coverage of the continents were taken from the reconstructions of Peltier (1994). These reconstructions exist as $1° \times 1°$ longitude/latitude global data files in 1000 year intervals since the LGM and are available via ftp from the World Centre for Paleoclimatology/National Geophysical Data Centre (Boulder, USA). We interpolated all data files to a $0.5° \times 0.5°$ longitude/latitude grid point resolution since we did all our calculations in this finer resolution. For the present-day situation, we followed the vegetation map of Olson et al. (1983) in order to define which of the Earth's $0.5° \times 0.5°$ grid points belong to the continents, and which belong to the oceans. Also the present-day extension of the polar ice sheets was taken from this data set. Finally, all fluxes we calculated refer to the exoreic parts of the continents only. Here we assumed that the endoreic regions during the LGM have been the same as today.

2.3. Determination of continental runoff

Among all potential controlling factors, mean annual runoff is globally the most important for the CO_2 consumption by rock weathering on the continents (Probst, 1992; Amiotte-Suchet and Probst, 1993a,b, 1995; Probst et al., 1994a; Amiotte-Suchet, 1995). The reliability of all simulations dealing with weathering rates and river carbon fluxes therefore strongly depends on the accuracy of the method applied to determine this parameter. From the ECHAM2 output files, runoff intensity can be derived by taking the difference between the precipitation and evaporation fields, but this value turns out to be negative many times, which makes this method less suitable for the determination of runoff during the LGM. For this reason, we derived this parameter by an empirical method based upon multiple regression analyses with the digitized and gridded runoff maps of Korzoun et al. (1977) and a great number of global environmental data sets (Ludwig and Probst, 1998).

In this modelling (Ludwig, in press), precipitation and temperature (which is uniquely used to derive potential evapotranspiration according to Holdridge, 1959), are the main parameters determining runoff. In agreement with the empirical relationship proposed by Pike (1964), it can be shown that the mean annual runoff ratio (RR, runoff divided by precipitation) generally increases the more precipitation exceeds potential evapotranspiration:

$$\mathrm{RR} = 1 - 1/\left(1 + (\mathrm{APPT}/\mathrm{APE})^2\right)^{0.5} \quad (5)$$

APPT is the mean annual precipitation total (mm), and APE the mean annual potential evapotranspiration (mm). In addition, large seasonal variability in precipitation can also increase the runoff ratio compared to a more uniform precipitation distribution. We characterized this parameter by using a slightly

modified form of the precipitation index originally proposed by Fournier (1960). Therefore, we named it Four (see Ludwig et al., 1996a). Finally, it is important to point out that morphology also represents a non-negligible controlling factor for runoff. Given the same temperature and precipitation values, greater slope increases runoff ratio, while greater elevation decreases it. The effect of basin slope is especially important in this respect, leading to considerably greater correlation coefficients than using the climatic variables alone. The fact that elevation has been retained in our empirical modelling may directly relate to the shortcoming of the method to estimate potential evapotranspiration from temperature data only (Ludwig, in press).

For all continental grid points, the following equation describes the relationship best:

$$RR = 0.73\,RR_{PIKE} + 1.06\,Slope + 0.78 \times 10^{-3}\,Four - 0.82 \times 10^{-4}\,Elev - 0.10 \quad (6)$$

RR_{PIKE} is the theoretical runoff ratio calculated according to Eq. (5), Slope is the mean grid point slope in radians (Moore and Mark, 1986), Four is in millimeters, and Elev is the modal grid point elevation in meters (Fleet Numerical Oceanography Center, 1992). We further grouped the grid points according to the major climate types to which they belong and repeated the regressions within these subgroups. In all cases, the above given parameters were found to be the dominant controlling factors in the same order as in Eq. (5), although the regression coefficients naturally varied to some extent. Only in the tundra and taiga climate was Four not found to be significant, which can be explained with the important contribution of snow melt to runoff in this climate type (seasonal variability of precipitation should be only of minor importance when a considerable amount of precipitation is temporarily stored as snow).

The advantage of this empirical modelling is that it allows a relative easy prediction of continental runoff with high precision. A validation with a set of 60 major world river basins (Ludwig and Probst, 1998) reveals for the present-day situation a correlation coefficient between the empirically determined

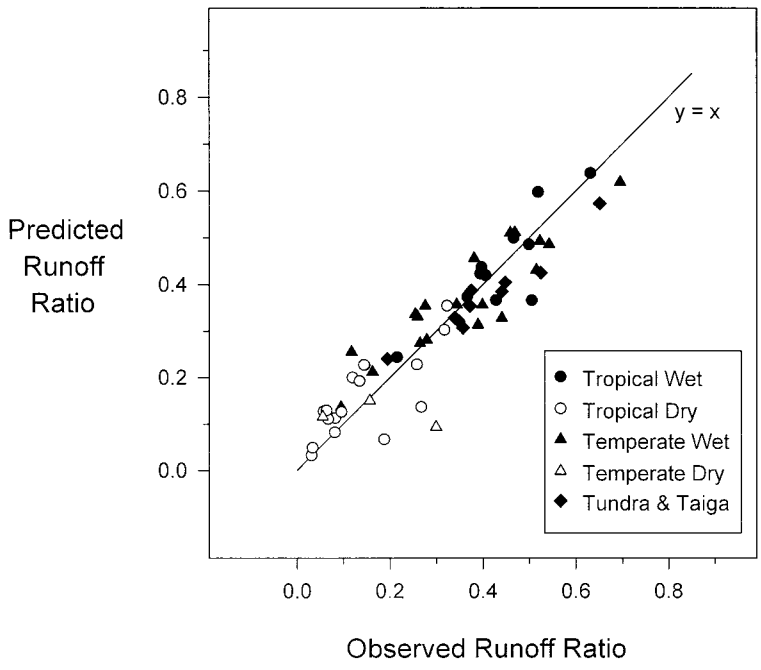

Fig. 1. Comparison of the mean runoff ratio empirically determined with the mean runoff ratio according to Korzoun et al. (1977) for 60 major river basins.

RR and the RR resulting from the runoff and precipitation maps of Korzoun et al. (1977) of $r^2 = 0.85$ (Fig. 1). The correlation coefficient for the resulting runoff intensities (according to $Q = \mathrm{RR} \times$ mean annual precipitation) is $r^2 = 0.97$.

3. Results and discussion

3.1. Atmospheric CO_2 consumption at the present-day

When GEM-CO_2 is applied to the total ice-free and exoreic continental area on the basis of a global lithological map created by Amiotte-Suchet (1995) and a global data set for drainage intensity (Korzoun et al., 1977), the model result yields a total amount of 0.23 gigatons of atmospheric carbon per year (Gt C year^{-1}) that is discharged to the present-day oceans. The corresponding water flux is 41750 km^3 year^{-1}. About 61% of F_{CO_2} is due to silicate weathering, and about 39% due to carbonate weathering, which means that an additional amount of 0.09 Gt C year^{-1} enters the oceans from the dissolution of carbonate minerals. These values compare well with other literature estimates, confirming the applicability of GEM-CO_2. More details on the spatial distribution of $F^s_{CO_2}$ can be found in Probst et al., 1994b; Probst et al., in press; Amiotte-Suchet and Probst, 1995; Ludwig et al., 1996b, 1998.

3.2. Atmospheric CO_2 consumption during the LGM

In order to calculate the corresponding fluxes for the LGM, we assumed that the lithological and morphological characteristics of the continents during the LGM were the same as for today. We therefore only changed in our simulation the data set for runoff intensity derived from the reconstructed LGM climatologies (see above). The major problem is that the morphological and lithological characteristics for the grid elements which became land area during the LGM as a result of the lower sea level (in the following: 'new' continental grid points—see Table 1) are not known. Consequently, neither our empirical modelling of runoff nor GEM-CO_2 can be applied to these grid elements, and it is thus not possible to calculate one definitive value for global F_{CO_2} during the LGM. Thus, as an approximation, we used the following method to estimate the global CO_2 consumption by chemical rock weathering. For each climate type, for each continent, and for each of the continental areas which drain to the different ocean basins, the average F_{CO_2} and runoff values were calculated only on the basis of the grid points that belong to the exoreic and ice-free continental area both for the present-day and for the LGM (in the following: 'old' continental grid points—see Table 1). At the same time, runoff on the new grid points was estimated by a triangular interpolation of the runoff ratios between the old continental grid points over the oceans and the applying of them to the LGM precipitation values (also other methods such as the application of Eq. (5) have been tested, but this results only in minor differences). The total F_{CO_2} fluxes within each category can then be established according to:

$$F_{CO_2} = \left(F^s_{CO_2-\mathrm{old}} \times \mathrm{Area}_{\mathrm{old}}\right) + \left(F^s_{CO_2-\mathrm{old}} \times \mathrm{Area}_{\mathrm{new}} \times Q_{\mathrm{new}}/Q_{\mathrm{old}}\right) \quad (7)$$

The units are Tg C year^{-1} for F_{CO_2}, t km^{-2} year^{-1} for $F^s_{CO_2}$, $10^6 \times$ km^2 for Area, and mm for Q. Finally, the arithmetic mean of the global F_{CO_2} values in the three categories was selected as the best estimate for the global atmospheric CO_2 consumption by chemical rock weathering during LGM (Table 2).

The above described method assumes that $F^s_{CO_2}$ on the new grid points linearly increased or decreased according to the variations in runoff intensity compared to the old continental grid points. This procedure can be justified by the dominant role of continental runoff as a controlling factor for F_{CO_2} (see above), but it is only true if the average lithology of the new continental grid points is about the same as on the old grid points. The latter is naturally questionable. For this reason, we also made several sensitivity runs by assuming different types of lithology on the new continental grid points in order to get an idea about the resulting differences in the amount of atmospheric CO_2 consumption by chemical rock weathering during the LGM (Table 3). Differences between the sensitivity runs and the above described

Table 1
Comparison of the distribution of present-day continental area and major climate types with the situation during the last glacial maximum

	Present-day area[a]		Last glacial maximum area[a]			
	Total (10^6 km^2)	Exoreic, no ice (10^6 km^2)	Total (10^6 km^2)	Exoreic, no ice		
				Total (10^6 km^2)	'Old' (10^6 km^2)[b]	'New' (10^6 km^2)[c]
Polar (ice covered)	15.26	–	42.55	–	–	–
Polar (no ice)	3.89	3.89	6.33	6.10	3.71	2.39
Tundra and Taiga	24.09	23.21	20.74	17.99	17.12	0.87
Temperate Dry	16.18	9.63	15.88	10.04	9.28	0.76
Temperate Wet	18.56	16.92	12.32	11.15	9.69	1.46
Tropical Dry	25.53	21.79	23.61	20.77	17.85	2.92
Tropical Wet	25.07	24.93	26.08	25.99	22.99	3.00
Desert	23.88	5.96	25.35	7.51	6.61	0.90
Total	152.47	106.33	172.86	99.55	87.24	12.31
Africa	33.00	18.29	33.88	19.17	18.30	0.87
Europe	12.70	9.56	16.19	7.16	6.16	1.00
North America	25.40	23.02	29.61	12.07	10.27	1.80
South America	18.16	17.73	19.62	18.65	17.29	1.36
Asia	41.03	32.52	48.34	36.73	30.77	5.96
Australia	8.33	4.48	9.66	5.77	4.45	1.32
Antarctics	13.85	0.73	15.56	–	–	–
Total	152.47	106.33	172.86	99.55	87.24	12.31
Arctic Ocean	17.55	16.98	22.42	11.90	10.75	1.15
North Atlantic	38.86	27.30	43.31	19.37	17.18	2.19
South Atlantic	18.55	16.96	19.58	17.86	16.85	1.01
Pacific	29.98	21.02	35.24	24.00	19.12	4.88
Indian Ocean	23.90	16.59	26.63	19.33	16.62	2.71
Mediterranean	9.77	6.74	10.13	7.09	6.73	0.36
Below 60° South	13.85	0.73	15.56	–	–	–
Total	152.47	106.33	172.86	99.55	87.24	12.31

[a] For the ocean basins, this is the continental area that is drained to the different basins.
[b] This is the area that is continental both for present-day and for LGM.
[c] This is the area that is continental only for LGM due to the lower sea level.

method, therefore, can help to estimate the importance of shelf lithology on global F_{CO_2}.

The most plausible way to increase river carbon fluxes at the global scale would be to increase continental area concomitantly with an increase of runoff. Assuming that weathering is negligible under ice sheets (this point is also discussed below), the effective erodible area of the continents was not much different during the LGM than today because the loss of area caused by the extension of the ice sheets was more or less compensated for by a greater exposure of shelf area due to the sea level fall (Fairbanks, 1989). In our LGM scenario this area decreases slightly by about 6% (Table 1). A crucial question for the atmospheric CO_2 consumption by chemical rock weathering during LGM is hence whether the amount of runoff on the continents has been significantly different.

Due to a steeper temperature gradient towards the poles, the humid climate zones of the mid and high latitudes were considerably smaller during the LGM compared to today (Fig. 2). Note from Table 1 that the temperate wet and the tundra and taiga climates were reduced by about 34% and 22%, respectively. This is not without consequences for the total amount of water running off the continents, since both climate types are important contributors to global runoff (Table 2). Consequently, runoff on the old continen-

Table 2
Continental runoff and atmospheric CO_2 consumption by rock weathering during the last glacial maximum

	Runoff (km^3)			F_{CO_2} (Tg C $year^{-1}$)			F_{CO_2} from silicate weathering	
	Old area[a]	New area[b]	Total	Old area[a]	New area[b]	Total	(Tg C $year^{-1}$)	% of today
Polar (no ice)	1108	1105	2213	9.11	9.09	18.19	9.80	489.9
Tundra and Taiga	3782	701	4483	21.68	4.02	25.70	16.52	67.8
Temperate Dry	927	69	996	7.38	0.55	7.93	2.36	102.6
Temperate Wet	5118	874	5992	31.25	5.34	36.58	17.47	75.7
Tropical Dry	2363	773	3135	15.11	4.94	20.05	7.96	83.7
Tropical Wet	17624	3551	21174	89.85	18.10	107.95	82.60	105.1
Desert	203	25	228	1.32	0.17	1.48	0.64	318.9
Total	31124	7097	38221	175.69	42.19	217.89	137.35	98.1
Africa	3784	226	4010	14.01	0.84	14.85	6.64	100.6
Europe	1641	570	2211	13.75	4.77	18.52	8.76	78.3
North America	3528	1140	4668	22.24	7.19	29.42	18.18	78.1
South America	9541	687	10228	47.70	3.44	51.14	43.50	97.1
Asia	12046	4138	16184	76.29	26.21	102.50	57.08	110.7
Australia	584	336	920	1.71	0.98	2.69	2.67	127.1
Antarctics	–	–	–	–	–	–	–	–
Total	31124	7097	38221	175.69	43.42	219.11	136.84	98.0
Arctic Ocean	1362	106	1469	7.19	0.56	7.76	5.86	41.1
North Atlantic	9794	1534	11328	56.89	8.91	65.80	48.26	97.9
South Atlantic	4400	295	4695	16.06	1.08	17.14	11.11	103.8
Pacific	9141	4155	13296	56.56	25.71	82.27	52.80	110.7
Indian Ocean	5491	966	6457	30.57	5.37	35.94	15.68	118.0
Mediterranean	935	42	977	8.42	0.37	8.79	4.24	88.4
Below 60° South	–	–	–	–	–	–	–	–
Total	31124	7097	38221	175.69	42.01	217.70	137.96	98.4
Best estimate				175.69	42.54	218.23	137.38	98.2

The values are based on the assumption that average lithology on the new grid points is the same as that on the old grid points.
[a]Area that is continental both for present-day and for LGM.
[b]Area that is continental only for LGM due to the lower sea level (emerging shelves).

tal grid points was globally reduced by about 9%. This general picture of on average more arid conditions during the LGM is also in agreement with observations. Reconstruction of vegetation distribution based on palynological, pedological, and sedimentological evidence globally indicates a greater

Table 3
Atmospheric CO_2 consumption by rock weathering during the last glacial maximum on the new grid points for different lithologies

Lithological character of the new continental grid points (emerging shelves)	Total F_{CO_2}				F_{CO_2} from silicate weathering	
	Old area (Tg C $year^{-1}$)[a]	New area (Tg C $year^{-1}$)	Total (Tg C $year^{-1}$)	% of today	(Tg C $year^{-1}$)	% of today
All sandstones	175.69	15.40	191.09	83.1	125.10	89.4
All carbonates	175.69	128.90	304.59	132.4	112.60	80.5
All shales	175.69	56.30	231.99	100.9	166.10	118.7
30°S–30°N carbonates, rest shales	175.69	105.80	281.49	122.4	132.20	94.5
30°S–30°N carbonates, rest sandstones	175.69	89.30	264.99	115.2	115.70	82.7

[a]See Table 2.

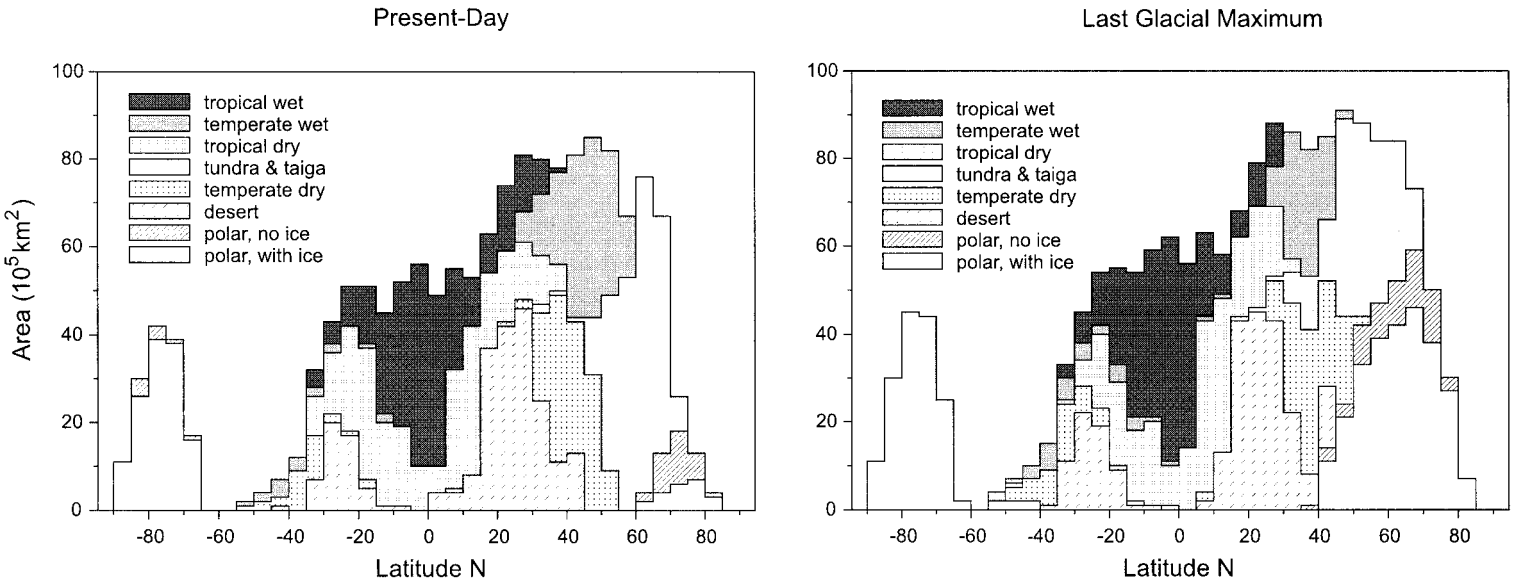

Fig. 2. Holospheric distribution of the major climate types on Earth at present, and as reconstructed for the last glacial maximum. Definition of the climate types is based only on temperature and precipitation data (Ludwig et al., 1996a).

aridity during the LGM than today (Adams et al., 1990; Adams and Faure, 1996). Also from palaeohydrological evidences, Starkel (1988) concluded that water discharge by rivers was generally lower during the LGM than today.

On the emerging shelves, however, runoff intensity was clearly greater than on the rest of the continents (by about 62%). This is mainly due to the fact that large parts of this area emerged in the tropics of the low latitudes, where by far most of the water runs off the continents (Table 2). Also in the high latitudes, runoff was locally increased, especially close to the margins of the ice sheets (such as the North Sea), where the GCM simulation results in a significant increase of precipitation compared to present-day. The high runoff intensity on the new continental grid points thus partly compensated for the greater aridity on the old grid points, but this effect on the whole is not strong enough to increase runoff. Thus, the total amount of water running off the continents was about 9% lower during the LGM than at present-day, and the more humid shelves hence only compensated for the reduction in the erodible continental area.

Consequently, application of GEM-CO_2 to the simulated LGM conditions results also in a reduction of the amount of atmospheric CO_2 consumed by rock weathering, at least as far as the old grid points are concerned. $F^{s}_{CO_2}$ was especially reduced in the tropical parts of South and Middle America, Africa, and SE Asia, as well as in many parts of North Asia (Fig. 3). However, the values were increased both in North America and northern Europe close to the ice-sheets, and in large parts of the southern hemisphere. Under the assumption that the average lithology on the new grid points was about the same as that on the old grid points, we calculate the global reduction of F_{CO_2} to be about 5% lower than the present-day value (Table 2). Although there is no fundamental difference in the share of F_{CO_2} coming from silicate weathering between today and the LGM, a slight increase of the relative importance of silicate weathering during the LGM can be noted (from 60.8% to 63.3%), and the global value for F_{CO_2} from silicate weathering remains about the same as that for today (-1%).

Assuming different rock types to be on the emerging shelves than on the rest of the continental area (Table 3) allows the total F_{CO_2} to vary substantially, that is between about -20% and $+30\%$ compared to the present-day value. Lowest values are found by allowing only sandstones to outcrop on the shelves, the rock type with the weakest specific CO_2 consumption. Greatest values result from an overall coverage of the exposed shelf by carbonates, the rock type with by far the greatest specific CO_2 consumption. In the latter case, however, F_{CO_2} from silicate weathering would only be about 80% of today's value.

It is interesting to compare our results with the results of Gibbs and Kump (1994) who investigated the changes of bicarbonate fluxes on glacial/interglacial time scales in a similar study as ours. Both studies are in a way complementary, since Gibbs and Kump proposed a global lithological map that is also valid for the emerging shelf grid points. However, they do not distinguish between the share of bicarbonates resulting from silicate weathering and that resulting from carbonate weathering. They found that river HCO_3^- fluxes during the LGM may have been with about 20% greater than today because of a greater exposure of carbonate rocks on the shelves, and that the global runoff value from the ice-free regions of the continents remained nearly unchanged.

Using the lithological map published by Gibbs and Kump (1994), we estimate the proportion of carbonates, shales, and sandstones on the emerging shelves to be about 45%, 40%, and 15% respectively. By far most of the carbonates are situated in the lower latitudes of 30°S to 30°N. When combining these estimates with our results (Table 3), GEM-CO_2 also predicts an increase of total F_{CO_2} of about 20% during the LGM, which is in good agreement with the study of Gibbs and Kump. At the same time, however, F_{CO_2} from silicate weathering alone is about 10% lower than that for the present-day. The latter percent is about equivalent to the reduction in continental runoff. This implies that F_{CO_2} from silicate weathering is probably more closely coupled to climate change (runoff) than F_{CO_2} from carbonate weathering, and is in disagreement with the idea of F_{CO_2} as one of the principal driving forces for lower atmospheric CO_2 during glacial times.

The above values given for an increase in total F_{CO_2} by about 20% together with a 10% decrease in F_{CO_2} from silicate weathering during the LGM may

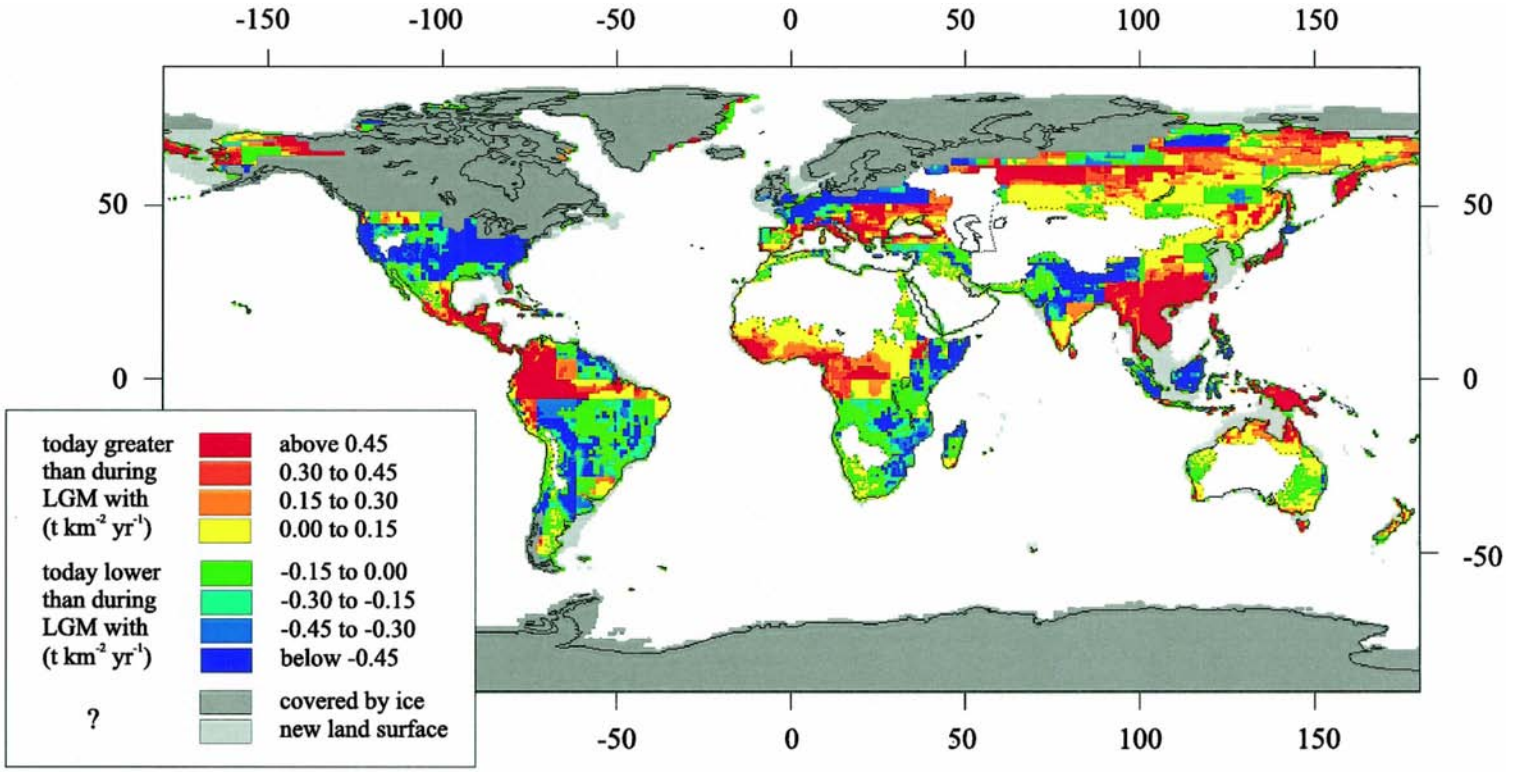

Fig. 3. Atmospheric CO_2 consumption by rock weathering: differences between present-day and the last glacial maximum. The white parts of the continents are endoreic.

be considered as best estimates on the basis of the data available for this study. Nevertheless, our results also show that the different types of lithology outcropping on the shelves can have a non-negligible effect on the global figures, and a refinement of our estimates requires more information on precise shelf lithology. Another major unknown is the exact nature of the weathering status of the sediments that are currently on the seafloor and which were exposed during the LGM. Having already been through the weathering cycle, it is not obvious that shelf sediments would undergo significant weathering if exposed (Gibbs and Kump, 1994).

3.3. Chemical weathering under the ice sheets

Another open question in our reconstruction of atmospheric CO_2 consumption during the LGM is whether the above assumption that no chemical weathering takes place underneath ice sheets is correct or not. Chemical weathering could have occurred at least at the ice sheet margins, where melt waters were in contact both with atmospheric CO_2 and large amounts of fine-grained glacial debris (Gibbs and Kump, 1994). When analysing melt waters from a Swiss glacier, Sharp et al. (1995) found chemical weathering rates substantially higher than the global average. They concluded that deglacial meltwater discharge pulses could remove considerable amounts of CO_2 from the atmosphere, and that glacially driven chemical weathering may have an important role in carbon cycling over glacial-interglacial time scales. If high consumption rates hold also for extended parts of the LGM ice sheets, the continental area subjected to chemical weathering was considerably greater for the LGM than for today, which is probably not a negligible term in our budgets.

In order to test such an hypothesis, we determined the amount of annual precipitation falling on the ice sheets during LGM on the basis of our precipitation data set. Compared to present-day, the specific value exactly doubled from 206 to 412 mm. Given the assumption that the extension and thickness of the ice sheets did not change from one year to another, this can be taken as a maximum value for the amount of glacial runoff within one year, except that it has to be reduced for the water lost by evaporation. From the present-day data of Korzoun et al. (1977), we estimate that the runoff ratio in glacial regions may be close to 0.9, although even this value is naturally somewhat speculative because of the scarcity of measurements in these regions. The runoff ratio during the LGM should have been lower because much of the northern ice was at lower latitudes, and evaporation should have been more important. Nonetheless, given the huge continental area that has been covered by the ice sheets (Table 1) and taking a runoff ratio of 0.9 means that glacial runoff could have been as great as 15750 km^3 $year^{-1}$ during the LGM. This value is about 3/4 of the runoff from the tropical wet climate (Table 2), and about six times the present-day value (2620 km^3 $year^{-1}$).

We then multiplied this value for glacial runoff times the average concentration of carbon coming from atmospheric CO_2 that was found in the study of Sharp et al. (1995). This value is an average of the two years of observation, about 1.12 mg C l^{-1}. The authors reported a nearly linear relationship between F_{CO_2} and Q in their data, so that this concentration should have been relatively constant in the waters they analyzed. Thus, the total amount of F_{CO_2} related to glacial weathering during the LGM is calculated as 17.6 Tg C $year^{-1}$, a value that is about 8% of F_{CO_2} on the rest of the continents in Table 2 (average lithology scenario). This value is an absolute maximum because it assumes that all of the glacial runoff water has been in contact with the underlying rocks. In reality, this is only the case for a small part of the water. At many places the ice sheets bordered directly on the sea (Fig. 3), and a considerable amount of glacial runoff may have occurred in the form of ice-calving. Moreover, extrapolating chemical weathering rates from valley glaciers to ice sheets is also highly questionable because the amount of meltwater production, the exposure of that water to atmospheric CO_2, and the amount of fresh reactive mineral surfaces created by abrasion under ice sheets would tend to differ substantially from that under small temperate glaciers (Hallet et al., 1996). Because of the much lower temperatures, the base of the ice sheets during the LGM were probably entirely frozen to its bed over large areas.

For these reasons, we conclude that the total amount of F_{CO_2} related to glacial weathering during the LGM probably was only a small part of the value

calculated above, and hence nearly negligible in our budgets. Of course, studies of solute yields from glaciated basins are relatively limited in numbers (Hallet et al., 1996), and more data are needed to improve our knowledge on glacial weathering rates. In this context it is also clear that comparing specific yields from glaciated basins with other regions or with global averages as done by Sharp et al. (1995) is not necessarily very meaningful because it does not take into account the large variability of runoff intensity and lithology that can exist. Note that the catchment investigated by Sharp et al. (1995) has a runoff intensity of about 2000 mm $year^{-1}$, which is nearly twice the value of the Amazon Basin, and five times the world average (Ludwig and Probst, 1998). It is questionable that such a value can be extrapolated to the large ice sheets during glacial stages. Consequently, when investigating chemical weathering in glacial environments, Anderson et al. (1997) reported that although catchments occupied by alpine glaciers yield cation denudation rates greater than the world mean rate, they do not exceed rates in catchments with similar water discharge. Silicate mineral denudation rates were found to be distinctly lower in glacier-covered catchments than in their non-glacial counterparts, leading the authors to conclude that the concomitant consumption of atmospheric CO_2 does not appear to be unusually rapid in glacier covered basins.

4. Conclusions

In this study, a global erosion model (GEM-CO_2) has been applied to LGM climate conditions reconstructed by a GCM simulation in order to predict the amount of atmospheric CO_2 consumed by rock weathering. It is found that total F_{CO_2} during the LGM was probably even greater than today, assuming that lithology on the emerging shelves was dominated by widely outcropping carbonates, together with shales, and, to a minor extent, sandstones. However, carbonate outcrops do not affect F_{CO_2} coming from silicate weathering, which alone has the potential to alter atmospheric CO_2 in the long-term. Silicate weathering and the concomitant atmospheric CO_2 consumption would decrease under this scenario. Assuming that the average lithology on the emerging shelves was the same as that on the rest of the continents would result in an overall atmospheric CO_2 consumption by silicate weathering that is about the same as that for the present-day. The values we calculated refer to the ice-free and exoreic continental area only, but we tested also the hypothesis of increased weathering fluxes under the huge ice sheets during the LGM. The latter seems to have a very small impact on the global CO_2 budget. Therefore, our results do not confirm the assumption of weathering to be one of the reasons for global cooling during glacial times, as this has been previously discussed in the literature, and are rather in agreement with the general idea of a negative coupling of weathering rates and global temperature on Earth (see Section 1).

The reliability of our findings is naturally strongly dependent on the reliability of the GCM outputs. Such computer simulations are still in an early stage of development, and there has been some discussion in the literature whether the prescribed sea surface temperatures normally used to constrain the simulations are too warm (Crowley, 1994; Broecker, 1995). This has to be kept in mind when looking at our results. Nevertheless, the prediction that the LGM world was more arid than today is confirmed by palynological, pedological, and sedimentological evidences. Finally, one has to point out that atmospheric CO_2 consumption by continental erosion does not only consist of the chemical weathering of rocks. The erosion of organic matter also represents a drawdown of CO_2 from the atmosphere. Quantitatively, this is even more important than the CO_2 consumption by rock weathering in the present-day carbon cycle (Ludwig et al., 1996b, 1998). Also variations in this flux have the potential to alter atmospheric CO_2 over longer time scales, especially when changes in the ratio of organic matter input to organic matter burial in sediments in the oceans are considered. Further studies on the role of continental erosion in the glacial/interglacial carbon cycle should therefore also include the behavior and fate of the river fluxes of organic matter.

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Storage and release of fossil organic carbon related to weathering of sedimentary rocks

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Abstract

The biogeochemical carbon cycle, which plays an undeniable role in global climate change, is defined both by the size of carbon reservoirs (such as the atmosphere, biomass, soil and bedrock) and the exchange between them of various mineral and organic carbon forms. Among these carbon forms, fossil organic carbon (FOC) (i.e., the ancient organic matter stored in sedimentary rocks) is widely observed in modern environments but is not included in the supergene carbon budget. Using a digitized map of the world and an existing model of CO_2 consumption associated with rock weathering, we establish the global distribution of FOC stored in the first meter of sedimentary rocks and a first estimation of annual FOC delivery to the modern environment resulting from chemical weathering of these rocks. Results are given for the world's 40 major river basins and extended to the entire continental surface. With a mean value of 1100 10^9 t, mainly controlled by shale distribution, the global FOC stock is significant and comparable to that of soil organic carbon (1500 10^9 t). The annual chemical delivery of FOC, estimated at 43 10^6 t yr^{-1} and controlled by the areal distribution of shales and runoff, is of the same order of magnitude as the FOC output flux to oceans. Chemical weathering of bedrock within the Amazon basin produces one-quarter of the total global flux of FOC derived from chemical weathering, and thus is expected to govern FOC release on a global scale. These results raise important questions concerning the role of FOC in the modern carbon cycle as well as the origin and the budget of carbon in soils and rivers.

Keywords: global carbon cycle; spatial distribution; major river basins; weathering; fossil organic carbon flux; fossil organic carbon storage

1. Introduction

Fossil organic carbon (FOC) is derived from ancient organic matter (OM) (kerogen, in the language of petroleum geologists) buried with mineral matter in sedimentary basins. During burial, time, temperature, and pressure affect the chemical and physical properties of OM until a

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graphitic form is attained [1]. In the right geological setting, and especially where uplift has occurred, sedimentary rock bearing this ancient OM and its corresponding FOC can outcrop at the continental surface. FOC then can be delivered to modern environments through the mechanical erosion and chemical weathering of these sedimentary rocks (Fig. 1). Previously, the role of FOC in modern environments was considered only in the context of a carbon balance (i.e., to balance the burial of organic carbon through the total mineralization of FOC at outcrop), with an annual flux of 100 10^6 t, and hence to maintain a constant atmospheric level of O_2 and CO_2 [2]. However, because a part of this FOC escapes from diagenetic processes during the geological cycle, it is believed also to be partially recalcitrant to mineralization at outcrop.

FOC has been identified as being ubiquitous in rivers [3–6] and, more recently, in soils [7], and even in recent marine sediment [8,9]. In light of these observations, it is extraordinary that FOC has never been quantified in the supergene organic carbon budget (Fig. 1, [10–12]). Only two studies propose an annual estimate of FOC delivery to the world's oceans, one describing delivery by world river basins (80 10^6 t yr^{-1}, [13]) and the other by small mountainous rivers (40 10^6 t yr^{-1}, [14], Fig. 1). Other authors have suggested that on the order of 40–70 10^6 t yr^{-1} of FOC may be reburied [15]. There currently is no quantitative information available regarding the transport of FOC by rivers before its delivery to the oceans. Providing meaningful global-scale data concerning the contribution of FOC from the continental surface is not straightforward. This shortcoming is aggravated by the lack of distinction between FOC and black carbon (the combustion residue of fossil fuel and present vegetation [16]), which, to a certain extent, invalidates estimates of these types of inert carbon [8]. In determining the contribution of FOC to modern environments, the initial step in the delivery of FOC – i.e., its release through mechanical erosion and chemical weathering of sedimentary rocks from its storage in the upper part of these (sub)-outcropping rocks – must be considered (Fig. 1). One study claims that the chemical weathering of carbonates and shales produces 100 10^6 t yr^{-1} FOC [17], partitioned between soils, rivers, and, through mineralization, the atmosphere, and no data exist for the amount of FOC produced by mechanical erosion except for that produced by small mountainous watersheds [40 10^6 t yr^{-1}, 14].

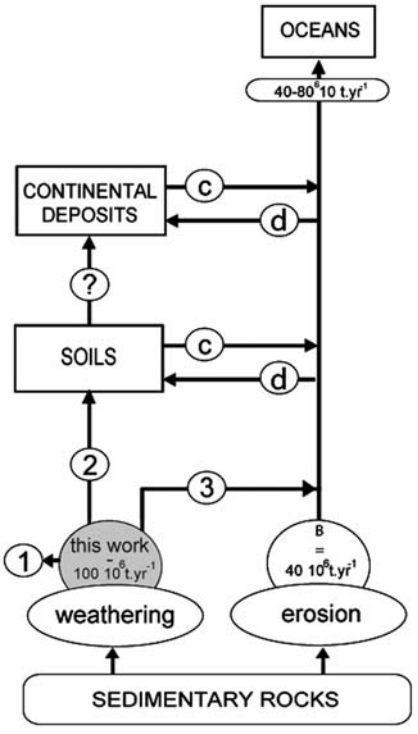

Fig. 1. Relations and exchanges of FOC within continental surfaces. The letters refer to terms in Eq. (6): FOC fluxes from weathering of rocks, from [17] and this study (*A*); FOC fluxes from erosion for mountainous coastal catchments [14] and other world rivers (not quantified) (*B*); FOC supplied from the remobilisation processes (*C*); deposition of FOC in continental reservoirs (*D*); mineralization occurring during transport of FOC (black arrows) and within reservoirs (*E*). FOC main fate processes after release by chemical weathering indicated by (1) mineralization; (2) input to soils; (3) direct input to rivers.

Here we present an estimate of the FOC flux contributed by the chemical weathering of sedimentary rocks. We use a GIS survey to estimate the original FOC stock contained in the upper layers of sedimentary rocks for the world's 40 major river basins, and extend it to the entire continental surface. We then estimate the FOC flux attributable to the chemical weathering of carbonates and shales, and its distribution for the watersheds studied and on a global scale. These initial results might provide a useful starting point for further investigations concerning the contribution of FOC to continental surfaces and hence to the supergene carbon cycle.

2. Methods

The general approach used here was to calculate the amount of FOC in storage and the FOC yield originating from the chemical weathering of shales and carbonates for the whole continental surface, and then to calculate average budgets for the world's 40 major river basins. Numerical maps of FOC storage and FOC chemical yield were established at the global scale using GIS software at a $1° \times 1°$ grid resolution and world maps of river basin limits, continental rock lithology [18], and continental runoff [19]. The global distribution of the lithology used

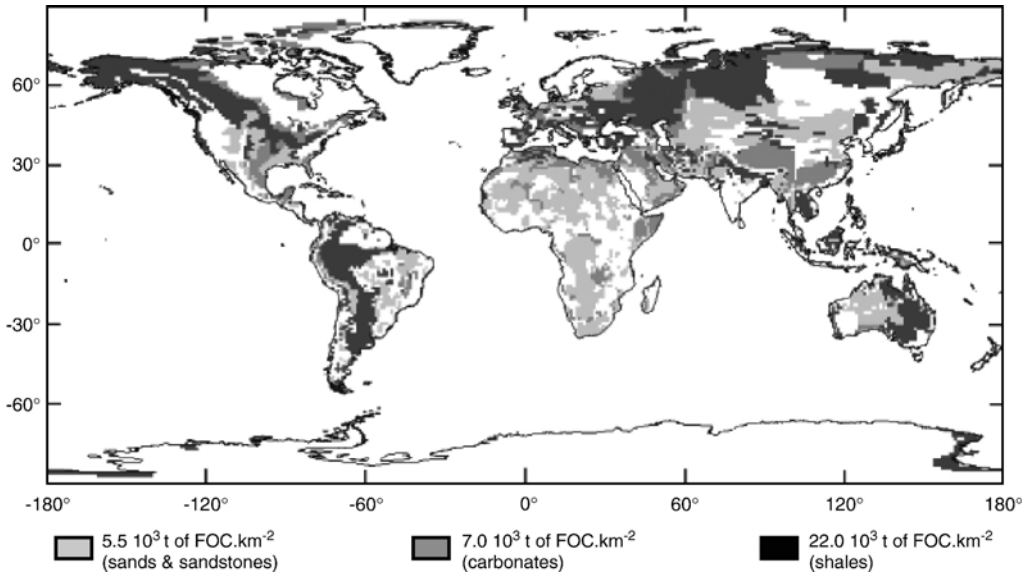

Fig. 2. Estimated storage ($\times 10^3$ t km^{-2}) of FOC in the first meter of sedimentary rock for the entire continental surface. Values shown are for sand/sandstone, carbonates, and shales, and were calculated using the average total organic carbon for these rock type (see Table 1).

divides sedimentary rock into three simplistic categories: carbonates (defined as all rocks with more than 50% of carbonate minerals), shales (defined as poorly carbonated clastic and argillaceous sediments), and sands/sandstones (i.e., sandy sediments with various origins).

The spatial distribution of FOC in the first meter of sediment (Fig. 2) was calculated for each $1° \times 1°$ grid cell on the basis of the average carbon content for sedimentary rocks [20] and the density [21] of carbonates, shales, and sandstones/sands (Table 1). Because the model is run at the global scale, it is assumed that local changes in total organic carbon values and rheologic behavior of a rock type will be smoothed. The FOC amount stored within the world's 40 largest drainage basins was calculated in units of 10^9 t (Table 2) or in t km^{-2} (as Fig. 2), combining the numerical FOC map (Fig. 2) with river basin limits.

Evaluation of the chemical FOC yield requires the average FOC contents and densities of the carbonate and shales (Table 1). Input of FOC to modern environments from rock weathering was estimated using GEM-CO_2, an approach that models CO_2 consumption by chemical weathering of rocks to calculate weathering rates [22]. For carbonate and silicate minerals, chemical weathering mainly is controlled by acid hydrolysis reactions with soil CO_2, which then is released in solution as HCO_3^- [18]. Therefore, for a given rock type, the chemical erosion flux (F_W in mol km^{-2} s^{-1}) is proportional to the CO_2 consumption and can be calculated as follows:

$$F_W = \sum (F_W^X) \quad (1)$$

$$F_W^X = R^X . I_{CO2} . Q \quad (2)$$

where R^X is the molar quantity of chemical compound X released by rock weathering for one mole of soil CO_2 consumed, and is determined using the average chemical composition of stream-draining single rock types [23]. I_{CO_2}, referred to as the weathering index, is the rate of CO_2 consumed by chemical weathering of a given rock (in mol l^{-1}) under the same weathering conditions derived from the GEM-CO_2 model. It is based on the relation between CO_2 consumption by rock weathering and runoff for single rock types [24]. Q is the drainage intensity [19] (in l km^{-2} s^{-1}).

Table 1
Description and the main rock parameters used in this study (proportion of rocks and lithological description [18], OC content [20] and density [21])

	Proportions on continental surface	OC content	Density	Lithological description
	(%)	(wt.%)		
Shales	25.4	1.00	2.2	Clastic and argilaceous sediments (poorly carbonated)
Carbonates	13.4	0.28	2.5	All rocks with more >50% of carbonates minerals
Sand and sandstones	26.2	0.24	2.1	All sandy sediments

Table 2
Budget of FOC stock and flux from the chemical weathering of shales and carbonates of the 40 major river drainage basins ranged following decreasing area

Basins	Number	Area	Runoff	Areal extent (in 10^6 km^2, from the lithologic abundance in % of the basin area)			FOC stock	FOC input by carbonates	FOC input by shales	Global FOC input
		(10^6 km^2)	(km^3 yr^{-1})	Carbonates	Shales	Sands and sandstones	(10^9 t)	(10^6 t yr^{-1})	(10^6 t yr^{-1})	(10^6 t yr^{-1})
Amazon	1	5.846	6223	228.0	2,963.9	976.3	73	0.159	10.583	10.741
Congo	2	3.665	1298	370.1	0.0	1,707.7	12	0.064	–	0.064
Mississipi	3	3.156	570	571.2	1502.1	798.4	41	0.082	0.732	0.814
Ob	4	3.010	477	81.3	2164.0	595.9	51	0.005	0.933	0.938
Parana	5	2.835	666	34.0	1244.6	774.0	32	0.003	0.322	0.324
Yenisey	6	2.488	665	171.7	306.0	159.2	8	0.055	0.251	0.305
Lena	7	2.337	393	261.7	904.4	252.4	22	0.022	0.211	0.233
Nile	8	1.910	125	47.8	0.0	609.3	4	0.005	–	0.005
Amur	9	1.895	407	0.0	530.5	225.5	13	–	0.284	0.284
Yangtze	10	1.746	908	768.2	137.9	242.7	10	0.264	0.210	0.474
Ganges–Brahmaputra	11	1.637	1,313	553.1	515.5	252.0	17	0.145	1.030	1.175
MacKenzie	12	1.564	260	322.2	843.0	0.0	19	0.022	0.491	0.513
Niger	13	1.504	166	94.8	0.0	869.6	5	0.002	–	0.002
Zambeze	14	1.370	109	186.3	0.0	628.6	5	0.012	–	0.012
Saint-Laurent	15	1.131	360	281.7	69.0	0.0	3	0.052	0.047	0.099
Murray–Darling	16	1.109	40	0.0	801.7	10.0	18	–	0.044	0.044
Orinoco	17	0.972	759	12.6	455.1	172.1	11	0.001	0.747	0.749
Tigris–Euphrates	18	0.934	156	396.9	241.0	160.6	9	0.033	0.093	0.126
Indus	19	0.877	251	228.1	210.6	147.4	7	0.025	0.030	0.055
Mekong	20	0.855	623	182.9	369.3	71.8	9	0.073	0.669	0.742
Yukon	21	0.816	169	0.0	696.8	0.0	14	–	0.440	0.440
Huang He	22	0.795	41	60.4	46.9	219.4	3	0.003	0.001	0.004
Danube	23	0.741	140	107.5	494.4	24.5	12	0.021	0.182	0.203
Colorado	24	0.674	28	0.0	0.0	374.8	2	–	–	0.000
Orange	25	0.663	26	64.9	0.0	455.9	3	*0.000*	–	0.000
Kolyma	26	0.637	122	0.0	176.3	460.3	6	–	0.062	0.062
Columbia	27	0.623	269	0.0	80.3	8.7	2	–	0.184	0.184
Sao Francisco	28	0.594	119	236.4	47.5	83.2	3	0.033	0.033	0.066
Xun Jiang (Pearl River)	29	0.444	419	366.1	0.0	0.0	3	0.186	–	0.186
Irrawaddy	30	0.402	459	176.9	56.7	123.0	3	0.105	0.249	0.355
Don	31	0.387	31	22.8	363.8	0.0	8	0.002	0.082	0.084
Senegal	32	0.365	15	0.0	11.7	235.2	2	–	0.000	0.000
Indigirka	33	0.362	54	0.0	217.4	144.3	5	–	0.072	0.072
Limpopo	34	0.315	27	44.7	0.0	78.7	1	0.002	–	0.002
North Dvina	35	0.303	97	32.8	237.8	33.1	6	0.006	0.219	0.226
Godaravi	36	0.299	147	0.0	0.0	11.6	0	–	–	0.000
Magdalena	37	0.267	313	12.8	76.1	63.6	2	0.010	0.207	0.217
Fraser	38	0.236	104	0.0	162.6	0.0	4	–	0.185	0.185
Yana	39	0.225	25	0.0	111.1	113.8	3	–	0.032	0.032
Mehandi	40	0.170	94	0.0	74.1	9.5	0	–	0.023	0.023
Total 40 selected basins		**50.177**	–	5917.9	16112.1	11093.1	**448**	**1.392**	**18.648**	**20.040**
Total continental surface without ice		**133.600**	–	–	–	–	**1061**	**3.160**	**39.744**	**42.904**

Excepted area, all parameters are from the compilation of Amiotte-Suchet et al. [18]; values of Mehandi river basin: lithological abundance [68], areal extent and runoff [19].

The mass of rock weathered (and thus the amount of FOC input to the modern environment) is estimated taking into account the average insoluble residue (R) as follows:

$$M_w = a.F_W^X \quad (3)$$

with:

$$a = 100/(100 - R) \quad (4)$$

Finally, the amount of FOC input to the modern environment (F_{FOC}) is calculated as follows:

$$F_{FOC} = b.M_w \quad (5)$$

where b is the FOC content of sedimentary rocks. The weathering of shales, which have an insoluble residue of 94% [25], was assumed to release Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and SO_4^{2-}, whereas the weathering of carbonate rocks, which have an insoluble residue of 24.2% [20], was assumed to release only Ca^{2+} and CO_3^{2-}. For these calculations, sands/sandstones were not considered, as they were assumed to be largely insoluble and consume very little CO_2 during chemical weathering [24].

3. Results

3.1. FOC at the continental surface: Global storage and distribution

We estimated the FOC stored in the first meter of sedimentary rocks for the world's 40 major watersheds (50.2 10^6 km^2). The choice of a thickness of 1 m was dictated by the need for comparison with the storage of organic carbon in soils, which usually is assessed for this same thickness [10]. As the numerical map (1° × 1°; Fig. 2) indicates, the global distribution of FOC stocks is heterogeneous, and values for each grid cell differed accordingly: 22 (shales), 7 (carbonates), and 5 (sands/sandstones) 10^3 t km^{-2}. These values are related to the average FOC content of these rock types (Table 2). The absence of FOC in a large part of North America, northern Europe, western Siberia, the main part of India, and South America is understandable as their bedrock is composed of shield rocks, acid volcanic rocks, and basalts, which are devoid of FOC. For the river basins, the overall stock of FOC is about 448 10^9 t, and at the global scale, this stock reaches a value of 1100 10^9 t (Table 2). Using existing data on lithologic abundance and surface watersheds [18], our modelling indicates that the Amazon, the world's largest drainage basin (5.846 10^6 km^2), stores the largest amount of fossil carbon (>73 10^9 t), followed by the basins of the Ob (51 10^9 t), the Mississippi (41 10^9 t), the Parana (32 10^9 t), and the Lena (22 10^9 t) (Table 2). These five watersheds contain 40% of the FOC stored in the 40 watersheds but make up only about 30% of the total surface area considered. Conversely, the Zaire basin, although considered to be the second major watershed in terms of area (3.7 10^6 km^2), stores only 12 10^9 t, and the Yenisei, which is larger than the Lena basin, stores only 8 10^9 t. This is explained by a relatively low abundance of shale in these watersheds (0 and 16.1% for the Zaire

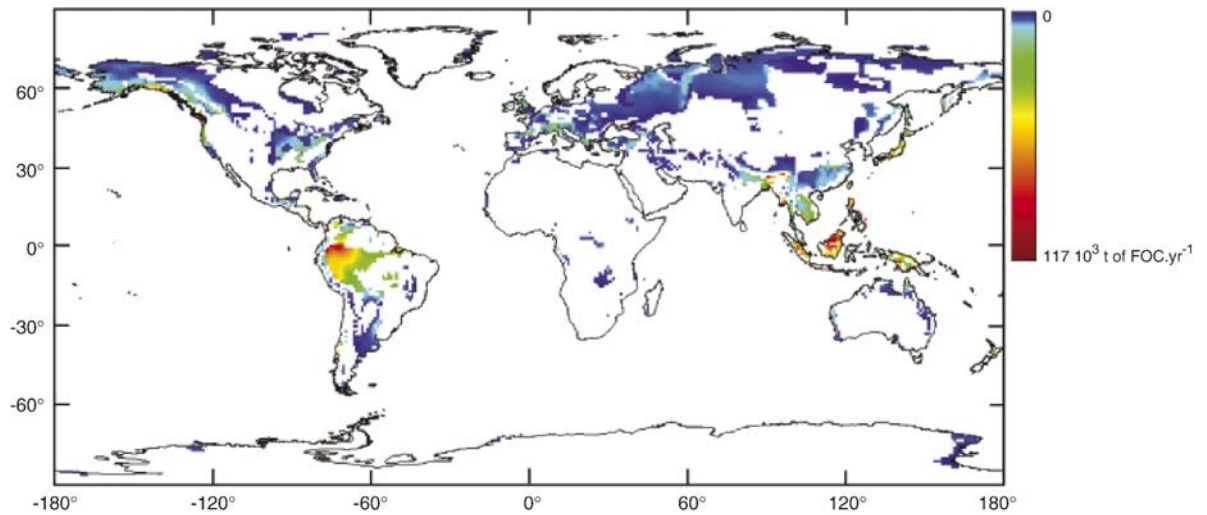

Fig. 3. Annual FOC fluxes for each grid cell (1° × 1° resolution, in 10^3 t yr^{-1}) delivered by chemical weathering of carbonate and shale for the entire continental surface. Values were calculated on the basis of the CO_2 consumption by rock weathering. Tropical climatic zones near the equator provide most of the FOC yielded by rock weathering.

and Yenisei basins, respectively). Thus, at both basin and global scales, shales, because of their high FOC content (1%), exert a strong control on the amount and distribution of the stock of FOC (Fig. 2, Table 2).

3.2. FOC chemical input and global distribution

On its own, the large amount of FOC stored in the first meter of sedimentary rock is insufficient evidence for a significant FOC contribution to the supergene carbon cycle. Rather, its importance in this cycle is controlled strongly by the dual chemical weathering/mechanical erosion affecting these rocks, which deliver their FOC content to modern environments (soils, rivers, and the atmosphere). Using GEM-CO_2 modelling [22], we present a world map of FOC yield resulting from the chemical weathering of shales and carbonates (Fig. 3). The map, with grid cells values ranging from 0 to 117 10^3 t yr^{-1}, shows a heterogeneous distribution different from that of the FOC stock. Although the map presents strong evidence for shale distribution as a major factor controlling FOC yield, because of the large proportion of insoluble residue associated with shales compared to that associated with carbonates (Table 1), two other parameters must be considered: the chemical weathering index of sedimentary rocks, and runoff [24]. If the

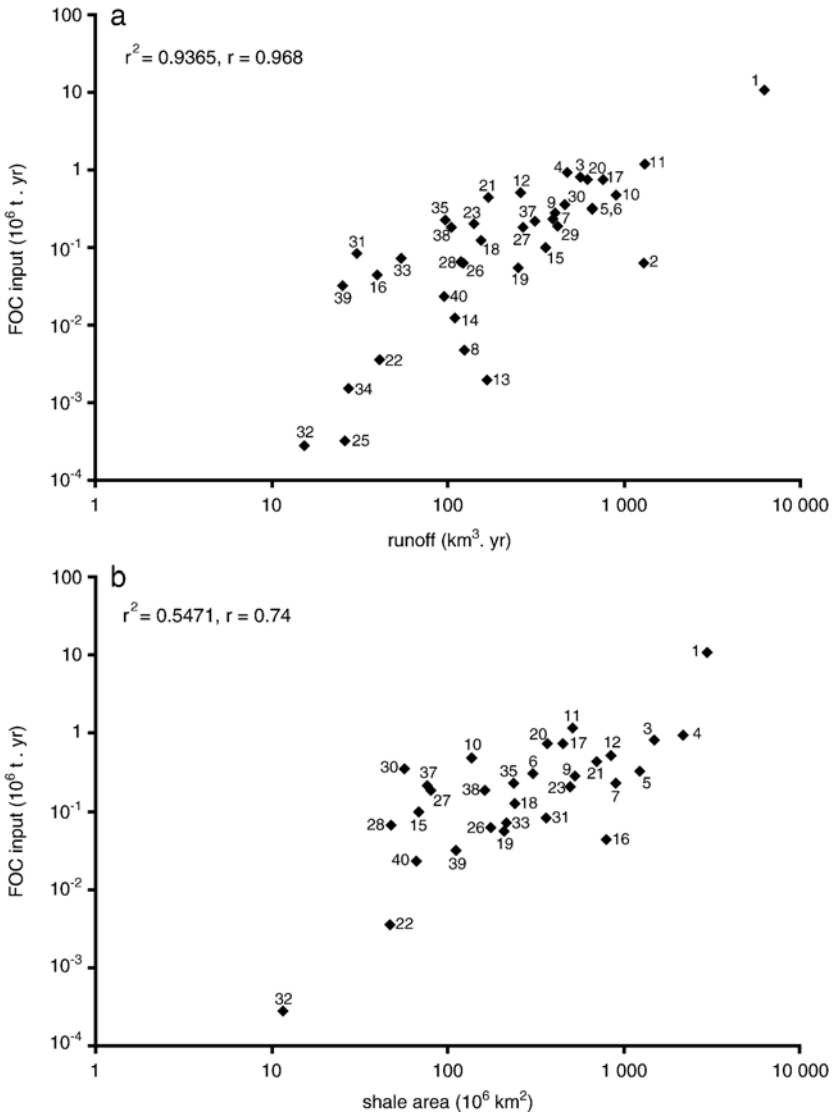

Fig. 4. Correlation between a) runoff and FOC input (values from Table 2) on a log–log scale; b) areal extent of shale and FOC input (values from Table 2) on a log–log scale. Statistical parameters indicate that FOC yield is more sensitive to runoff than to the areal extent of shale.

chemical weathering index is fixed and is greater for carbonates than for shales, runoff acts as a positive feedback in rock weathering [22,24], and consequently in the delivery of FOC.

The roles of runoff and the areal extent of shales are illustrated in Fig. 4a and b, respectively. From a general point of view, the importance of runoff is attested to by the coefficient of determination r^2 (0.94, Fig. 4a) and the Pearson test (α threshold = 0.050, r = 0.97). However the greater importance of runoff compared to the areal extent of shales is due to the Amazon drainage basin; if the Amazon is not included, the coefficients of determination are quite similar 0.66 for runoff and FOC, and 0.647 for shale surface area and FOC.

The importance of runoff on FOC release is apparent. This is illustrated by the comparison of the Don and Orinoco river basins, which have a similar areal extent of shale: 363.8 and 454.1 10^3 km^2, respectively, and a small areal extent of outcropping carbonate (22.8 and 12.6 10^3 km^2, Table 2). The total FOC yielded by the Orinoco. however, is nearly nine times greater than that yielded by the Don drainage basin (0.749 and 0.084 10^6 t yr^{-1}, respectively). This large discrepancy is unambiguously correlated to their runoff values, i.e., 759 km^3 yr^{-1} for the Orinoco and only 31 km^3 y^{-1} for the Don [18], whose drainage basin is in a dry temperate climate [11]. Two drainage basins with a dry tropical climate (the Nile and the Niger, [11]) do not show the same trend as the other basins; the different values for these two African drainage basins result from the low areal extent of shale and carbonate outcrops (Table 2).

The FOC input to the continental surface also is a function of the areal extent of shales (Fig. 4b), which is not surprising given their high FOC content. As an extreme example, the Niger and Yukon drainage basins, which have similar runoff values (166 and 169 km^3 yr^{-1}, respectively) and a small areal extent of carbonate outcrops, have very different FOC fluxes (Table 2). The FOC produced by the Yukon basin is 220 times greater than that of the Niger (0.440 vs. 0.002 10^6 t yr^{-1}, respectively), resulting from the fact that the Yukon basin has a large proportion of shales (85.4% of its total area, i.e., 696.8 10^3 km^2), whereas the Niger basin is devoid of shales (Table 2). However, the relation between the areal extent of shales and FOC yield is less strong than that between runoff and FOC yield, as indicated by the Pearson test (r = 0.74) and the coefficient of determination between shale surface area and FOC input (r^2 = 0.55, Fig. 4b).

The strong relation between runoff and FOC yield explains why the global distribution of FOC stock and its release do not coincide spatially (Figs. 2 and 3). The total annual FOC yield for the 40 drainage basins combined is 20.04 10^6 t, which corresponds to about half of the total global annual yield (42.90 10^6 t). With an annual FOC yield of 10.74 10^6 t, the Amazon watershed delivers the single greatest amount of FOC to continental surfaces. The FOC yield from the Amazon drainage basin is substantially higher than those of other major basins such as the Ganges–Brahamaputra, the Ob, the Mississippi, or the Parana, which, at 1.175–0.324 10^6 t FOC yr^{-1} each, deliver about one-tenth the FOC yield of the Amazon basin. The Congo basin is excluded as there is no shale outcropping in its watershed. The high delivery by the larger drainage basins corresponds to one-half of the total FOC delivery yielded by the 40 drainage basins examined.

At the global scale, on the basis of our results, it is expected that a quarter of the FOC released to the Earth's surface is produced by the Amazon drainage basin. In turn, this exceptional contribution implies that chemical weathering occurring in the Amazon area governs the FOC flux originating from the chemical weathering of shales and carbonates within the world's continental surfaces.

4. Discussion

The data provided by the model can be compared to other values of OC in general and to FOC fluxes in continental surfaces in particular. Such a comparison is essential for evaluating whether the model results are meaningful and for determining the major implications. A useful approach is to evaluate the model results in the context of the global FOC transport budget. The transport of FOC from continental surfaces toward the world's oceans can be expressed as:

$$A + B + C - D - E = 80\ 10^6\ \text{t yr}^{-1} \quad \text{FOC export to the world's oceans [13]} \tag{6}$$

where

- A supply from chemical weathering of rocks (43–100 10^6 t yr^{-1})
- B supply from mechanical erosion of rocks (40 10^6 t yr^{-1}, [14])
- C supply from remobilisation of floodplain sediments
- D deposition in continental surface reservoirs
- E depletion by mineralization

The model presented here provides the flux of FOC yielded by the chemical weathering of rocks, that is, term A in the FOC budget.

4.1. FOC inputs from weathering and erosion of continental rocks

The first two terms in Eq. (6) express the supply of FOC from chemical weathering and mechanical erosion of rocks. The first meter of continental rocks contains a stock of FOC close to 1100 10^9 t, and hence is comparable to that of total soil organic carbon (1500 10^9 t, [10]). Soils develop at the expense of the underlying rock, and FOC has been observed in soils, fluvial sediment, and lacustrine sediment using optical [26–30] and geochemical [28,31] markers. The amount of FOC in soil organic carbon likely is significant but has not yet been quantified.

The model presented here provides an estimate of FOC contributed to the global FOC budget from the chemical weathering of rocks (term A in Eq. (6)). This estimate can replace the previous value [17] of term A in Eq. (6). The FOC flux determined from our model (43 10^6 t yr^{-1}) is about half that estimated previously [100 10^6 t yr^{-1}, 17]. The value previously calculated was an initial and simplistic attempt that relied largely on approximations based on the extrapolation of results from watersheds to climatic zones and from watersheds to the global scale without taking into consideration the existing rock types. For that reason, we believe the results provided by our model, which takes into account rock type, chemical alteration, and runoff, are more reliable.

The mechanical erosion of rocks contributes to the FOC flux leaving the continents (term B in Eq. (6)). Evidence of FOC resulting from the erosion of sedimentary rocks has been found in fluvial and marine sediment using radiocarbon measurements. For example, the occurrence of FOC in fluvial sediment has been widely documented for rivers draining small mountainous coastal catchments in active margin contexts, where topographic relief favors slope processes such as landslides and mass movements, e.g., in California [9,14,32], New Zealand [33] and Taiwan [4]. The occurrence of FOC also been documented for passive margin rivers, for example rivers in the northeastern U.S. [5,6], and the Rhine River [34].

The FOC flux contributed by the mechanical erosion of rocks has been estimated at about 40 10^6 t by Blair et al. [14]. This flux was obtained by extrapolating the flux from a small river in California (the Eel River) to small rivers at the global scale. This estimate assumes that the material eroded does not undergo deposition or mineralization (terms D and E in Eq. (6)), but rather is delivered directly to the oceans. This flux is very similar to that estimated by our model for the chemical weathering of rocks, indicating that the FOC flux provided to the supergene carbon cycle by chemical weathering and mechanical erosion are roughly equal in important.

The FOC flux from mechanical erosion estimated by Blair et al. [14] must be considered a minimum, as they considered only erosion from small river basins, and did not include erosion from the world's large river basins. Although large drainage basins are believed to contribute FOC to the world's oceans, this amount has yet to be quantified, largely because the methods used (e.g., radiocarbon and isotopic analyses) were poorly suited for the quantification of FOC. For example, sources of sediment in the Gulf of Mexico include either erosion of sedimentary rocks in the Mississippi basin [35] and/or erosion of younger soils [36]; the mix of sources, by which modern and terrestrial OM dilutes FOC, prevents FOC quantification or even characterization. Such uncertainties, however, can be resolved through use of other methods. For example, particulate OM microscopy, was successfully applied to the analysis of sediment from the Gulf of Lion (mainly Rhône sediments) [37].

The relative contributions of chemical weathering and mechanical erosion vary greatly depending on the characteristics of the river basin. For example, for the watershed of the Huang He River, the flux of FOC contributed by erosion (term B) greatly exceeds that contributed by chemical weathering (term A). Total FOC export from the Huang He watershed to the ocean is estimated at 4 10^6 t yr^{-1} [Meybeck, pers. com.], which greatly exceeds the contribution from chemical weathering along estimated from our model for this river (0.004 10^6 t yr^{-1}). The difference arises from the substantial occurrence of loess in the watershed [38], which Meybeck estimated to contain 0.5% FOC by weight, and which erodes easily even in the absence of substantial topographical relief. Thus even in cases where the contribution of FOC by chemical weathering (term A) is negligible, the release of FOC from sedimentary rocks (the sum of terms A and B) can be substantial if there is a high amount of erosion. Export of FOC to the marine environment by erosion also is enhanced when part of a watershed is subject to gully erosion of sedimentary rocks. Although this phenomenon can be highly localized, it can dominate the load of eroded material. This type of erosion was demonstrated for the Waipaoa River [33], and hypothesized for the Rhone River [39]. One of the main Rhone tributaries, the Durance River, includes a large area of badlands facies, which favor gully erosion [40]. This hypothesis is reinforced by the comparison of optical and geochemical signatures of OM in suspended loads with those of bedrock in small basins within the Durance watershed [27,31].

The total contribution from the chemical and mechanical weathering of rocks to the world's oceans (A+B in Eq. (6), equal to 83 10^6 t yr^{-1} FOC) is very similar to that estimated by Meybeck for the total export to the world's oceans (the right side of Eq. (6), 80 10^6 t yr^{-1}, [13]). Meybeck's estimate is the single estimate available of global FOC flux exported to the world's oceans. This estimate, however, accounts for all the processes included in Eq. (6), and thus cannot be reasonably compared simply to the sum of terms A and B. Instead, the contribution of FOC from the remobilization of floodplain sediment and the removal of FOC by mineralization and redeposition must be evaluated. Specifically, to quantify the remaining contributions to the global FOC transport budget (terms C, D, and E in Eq. (6)), several questions remain to be addressed: Does chemical weathering substantially contribute to particulate FOC found in rivers? What is the proportion of FOC in dissolved OC? How can we estimate the FOC flux associated with remobilization and mineralization? Consequently, great uncertainty surrounds the fate of FOC in modern environments after its release.

4.2. Fate of FOC: Remobilization, storage, and mineralization

Little research exists that quantifies or even provides examples of remobilization of FOC-containing sediment (term C of the Eq. (6)), although common sense suggests that it must occur. However, deposition and storage of FOC and FOC mineralization (terms D and E in Eq. (6)) are better understood, and to an extent explain the difference between the results provided by our model for a given watershed and the FOC output to the marine environment.

Among the numerous fates that FOC in continental rocks can undergo leading to mineralization, three can be considered as major on the basis of the quantity of FOC delivered to the atmosphere, to soils, and to rivers (Fig. 1). First, FOC can be entirely mineralised from the rock, releasing CO_2 to the atmosphere. Complete oxidation of FOC, however, is unrealistic, as the occurrence of FOC is widely recognised in all modern environments (see Introduction and Discussion sections for numerous references). Second, because soils develop at the expense of underlying rock, FOC from rocks can become mixed with SOC [7,31,33]. It is essential that the FOC in soils be accounted for in the global FOC budget. Finally, FOC can be released in rivers as shown for two experimental watersheds [31], where it was demonstrated that the rock-to-stream flux qualitatively and quantitatively preserves FOM. Once in the fluvial system, FOC can be mineralized. The amount of fluvial particulate organic carbon (POC) derived from autochthonous production and diverse allochthonous sources, including aged soils, resuspension of floodplain sediment, and rock-derived FOC, remains to be quantified. Mineralization of FOC in fluvial systems, however, likely would be attenuated, because of its association with mineral surfaces, such as fine clayey particles in suspension [14,41–43]. The preservation of FOC once in fluvial systems supports the hypothesis that FOC must contribute substantially to the amount of continental organic carbon delivered annually to the world's oceans [14,23], provided that some part of FOC does not undergo storage in soils or in recent continental sediments in floodplains.

Mineralization of organic carbon results mainly from oxidation by air, hydrolysis, and bacterial consumption, referred to together as (bio)geochemical weathering. (Bio)geochemical weathering of recalcitrant organic carbon, as FOC, occurs in soils, by-pass compartments (e.g., continental sediments), rivers, and recent ocean sediment. The last is illustrated by the weathering of black carbon – a form of OC even more recalcitrant and supposedly inert than FOC [16] – observed in turbidites [44]. Although evidence of FOC mineralization has been demonstrated [45], the amount of FOC mineralised remains difficult to establish [e.g., [31]], except for FOC in outcropping coal seams [46–48], where mineralization of FOC ranges from 20% to 45% [46,48] or black shales, where mineralization of FOC is total [45].

The physico-chemical properties of organic matter containing FOC control the proportion of labile and recalcitrant organic compounds undergoing a given mineralization process. These properties depend on the origin of the organic matter [49] and on its maturity [1]. As an example, the contrasting behaviour of geochemical markers during mineralization suggests that for soils, the greater the richness in hydrogenated components, the more rapid the mineralization [31,50].

Mineralization of FOC depends on the aggressiveness of the extrinsic factors promoting the mineralization, including water, oxygen concentration, and efficiency of the bacterial consortium for the degradation of organic compounds. The aggressiveness of these parameters is controlled by climate, geomorphology, and, since the Anthropocene, anthropogenic activities. Land-use changes resulting from human activities (e.g., deforestation, reforestation, and dams [e.g., [51,52]]) can act either to amplify or moderate the effects of climate and geomorphology on mineralization. For example, the reforestation of the Huang He River watershed decreased the sediment load from 1 to 2 10^9 t yr^{-1} [53] to 0.8 10^9 t [Meybeck, pers. comm.].

In addition to removal via mineralization, FOC can be removed from the global FOC transport budget through deposition and storage in continental reservoirs (term D in Eq. (6)). FOC storage and flux are controlled by many factors, including geology, relief, and climate. Geology influences FOC storage and flux by controlling relief, rock types, and diagenesis of FOM. Steep topographic relief increases the sediment load in rivers [54–56], increasing delivery of FOC to the oceans [15].

Climate has a large influence on resuspension and sediment storage (terms C and D) as well as on mineralization (term E). Climate controls runoff [57]; more runoff results in an increased suspended sediment load [57] and thereby an increase in FOC flux to the world's oceans. By affecting runoff, land cover, soil type, and micro-organism populations, climate controls the aggressiveness of mineralization processes. Climate also affects the yield of FOC from the chemical weathering of rocks (term A) by controlling rainfall.

The fate processes of FOC deposition and mineralization are closely linked. FOC deposition creates a positive feedback for mineralization, in that the longer the residence time in a continental reservoir the greater the intensity of mineralization. Sequestration of FOC tends to occur in the floodplains of large drainage basins rather than in small mountainous drainage basins [15], for which sequestration occurs in shelf/slope sediments offshore of the river mouth.

4.3. FOC production and removal in a river basin: The example of the Amazon River

The processes controlling the FOC transport budget can be examined by evaluating the production and fate of FOC in the Amazon River basin. On the basis of the model presented here, of the world's 40 largest river basins, the Amazon has the highest FOC input flux resulting from weathering (term A in Eq. (6))—close to 25% of the modelled global flux—but the POC associated with the suspended load at the mouth of the Amazon is dominated essentially by recent soil OM rather than refractory OM [58,59].

There are several potential explanations for the discrepancy between the FOC input flux from rocks in the Amazon basin and the delivery from this basin to the marine environment. A large river basin such as the Amazon has an enormous storage capacity [15], increasing the FOC residence time in the continental surface and thus its potential for mineralization.

One explanation is that shale outcrops, which cover about 50% of the watershed surface area, are located mainly in the lowlands of the drainage basin, where transport of the material resulting from the chemical weathering of these FOC-rich rocks is limited [60,61]. As demonstrated by the model presented here, the weathering of shales produces a large amount of FOC relative to other rock types. In contrast, rocks weathering in the Andean (mountainous) part of the basin are in an area where sediment transport capacity exceeds production. The majority of the Amazon sediment load thus comes from the Andean rivers [61], diluting FOC-rich lowland sediment. Further, deep weathering profiles in the lowlands may result in decreased chemical weathering of rocks in this area, limiting the FOC input to the surface.

Storage of FOC in the Amazon piedmont plain (term D in Eq. (6)) may also limit the output of FOC at the river's mouth. The maximum FOC fluxes occur in the area of the Andean cordillera (Fig. 3), where intense erosion feeds the Amazon basin lowlands. However, the presence of some weakly eroded thick and aged soils in the piedmont of the cordillera [62] suggests that an unknown but substantial amount of material originating from the Andes may be stored here, trapping and weathering FOC.

Intense mineralization of FOC in Amazon tributaries, soils [58], or floodplains (term D in Eq. (6), [59]) might also play a role in explaining the difference between FOC input and output fluxes from the Amazon basin. Extreme mineralization of FOC leads to the production of humic compounds [46,63,64]; these humic compounds may become mixed with those in recent OM, such that the resulting DOC, which accounts for 62% of the total OC export [65], might contain a substantial proportion of FOC. This FOC would not be taken into account when quantifying the total FOC output from the river basin. For fine POC, which represents 34% of the global export of OM [65], the FOC contained is likely diluted by soil derived OM and other refractory OM [58], including kerogen, to the point that it is not identifiable.

Finally, it is possible that the FOC output flux from the Amazon basin is underestimated because of confusion of FOC with charred particles (black carbon inherited from the combustion of modern vegetation). Such confusion has been demonstrated for recent oceanic sediment from the northwest Atlantic Ocean [8]. This confusion may also occur in soils, as it was demonstrated that black carbon stays preferentially on the ground and is incorporated into soils [66] where it can mix with FOC. A reassessment of black carbon in recent sediments and soils might be required.

The example of the Amazon basin illustrates the uncertainty surrounding the removal of FOC from the global FOC transport budget (terms D and E in Eq. (6)). The estimate of FOC storage in and flux through carbon reservoirs in continental surfaces might require revision.

Clearly, further investigation is required to better understand the relations between climate, geologic setting, and the nature of FOC.

5. Conclusions

By providing a first estimate of the spatial distribution of FOC and its flux derived from chemical weathering on a global scale, this study lays the foundation for investigating FOC delivery and occurrence in continental surfaces. The work presented here, coupled with the results of other investigations [13], provides estimates of the delivery of FOC to continental surfaces.

In the continental surface at the global scale, the modelled storage of FOC is 1100 10^9 t, and the annual flux resulting from the weathering of sedimentary rock is 43 10^6 t. The Amazon drainage basin, with a modelled flux of FOC of about 10.70 10^6 t resulting from the weathering of rocks, controls FOC input at a global scale. In relation to other OC fluxes in continental surface, the global modelled flux is significant and raises some fundamental questions whose answers might be found in the foreseeable future. First, the amount of organic carbon stored in soils requires re-evaluation if even a part of this fossil component can be mineralized. Consequently a re-evaluation of black carbon in soils also is required, as black carbon and FOC frequently occur together and exhibit the same physical and chemical properties. Second, the amount of organic carbon transported by fluvial systems requires reassessment taking into consideration the fossil component, which often is ignored in the literature. Hence, in the course of its supergene passage on the earth's surface, FOC can be mixed with present day organic carbon and black carbon in recent marine sediments and start a new carbon geological cycle. Recycled vitrinites, an organic gel-like material that frequently are observed in sedimentary rocks by organic petrographers [67], is evidence of such a loop in the carbon cycle.

These results indicate that the role of FOC in the global carbon cycle must be evaluated by the study of its fate in continental surfaces. Further, a focus on mineralization processes is required, including the parameters involved, and on quantification of the different fluxes between reservoirs, which are controlled by climate, geology, and anthropogenic activities, as well as mechanical erosion. Those more investigation is required to better understand the interactions between these forcing factors and the nature of FOC, and hence to quantify the terms in Eq. (6). These forcing factors have fluctuated over the course of geologic history and humans might have drastically modified and will continue to modify the input and the fate of FOC in continental surfaces.

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Dissolved silica in the Garonne River waters: changes in the weathering dynamics

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Abstract The major ion chemistry of the Garonne River is indicative of seasonal variations in the weathering dynamics of the drainage basin. Using the geochemical model MEGA for calculation of the contribution of atmospheric CO_2 to the total bicarbonate fluxes exported by the Garonne River allows estimations of the concentrations of the major dissolved elements that originate from silicate- and carbonate-rock weathering. The molecular ratio SiO_2/Al_2O_3 was calculated for the 1989–1992 period to identify the main type of weathering in the Garonne River, and montmorillonite was shown to be the major mineral occurring in the weathering products. The seasonal variations of the SiO_2/Al_2O_3 ratio also showed that removal of silica was accelerated during humid periods.

Introduction

Rivers carry ~90% of the continental matter transported to the oceans. This material originates from chemical weathering and mechanical erosion of continental rocks. The chemistry of most surface- and groundwaters allows us to unravel the interactions between rocks and rain or snowmelt waters. Many studies have reported on the weathering of primary minerals and the stability of the newly formed secondary minerals (review in Tardy 1982).

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The dominant secondary minerals of soils are clays, of which kaolinite and smectite are the most abundant. The distribution of these minerals in soils characterizes the weathering dynamics, as well as the geochemical balance of waters because of the removal of ions in weathering solutions and their involvement in secondary neoformations. Such studies have been conducted by Tardy (1969, 1971) and Gac (1980) using waters that drained silicate formations in small catchments. The aim of the present study was to evaluate the flux of dissolved Si in the Garonne River, to characterize the weathering stages on a basin-wide scale, and to qualify the degree of weathering by estimating the most abundant secondary minerals in the soils of the drainage basin. This study also sought to determine the large-scale weathering dynamics by examining the geochemistry of river waters that drain from both silicate and carbonate bedrocks; this is different from the complementary studies of Tardy (1969, 1971) which examined waters that had only drained from a small catchment on silicic rocks.

Setting of the Garonne basin

The city of La Réole is located ~100 km to the south of Bordeaux in south-western France, and represents the outlet of the basin drained by the Garonne River. The drained area of 52,000 km^2 includes most of the Aquitaine basin, which is bounded by the highlands of the Massif Central to the north-east, the Pyrénées Mountains to the south and the Atlantic Ocean to the west (Fig. 1). The Massif Central consists mainly of carbonate-rich marine sediments mostly of Jurassic age, as well as of Tertiary and Quaternary volcanics. The pre-Jurassic schists, gneisses and granites of the Pyrénées Mountains were thrust upwards by Mesozoic marine limestones ~40 Ma ago during the Alpine orogeny. The crystalline core of the Pyrénées Mountains also includes Precambrian granites. The floor of the Aquitaine basin was flooded by the westerly ocean several times during the Oligo-Miocene. Each retreat of the marine waters was followed by lacustrine-fluviatile deposits of limestones and of molasses above carbonates in transitional continental environments (Bourgeat and others 1984).
During the study period (1989–1992), the yearly discharge of the Garonne River ranged between 52 and 4790 $m^3 s^{-1}$,

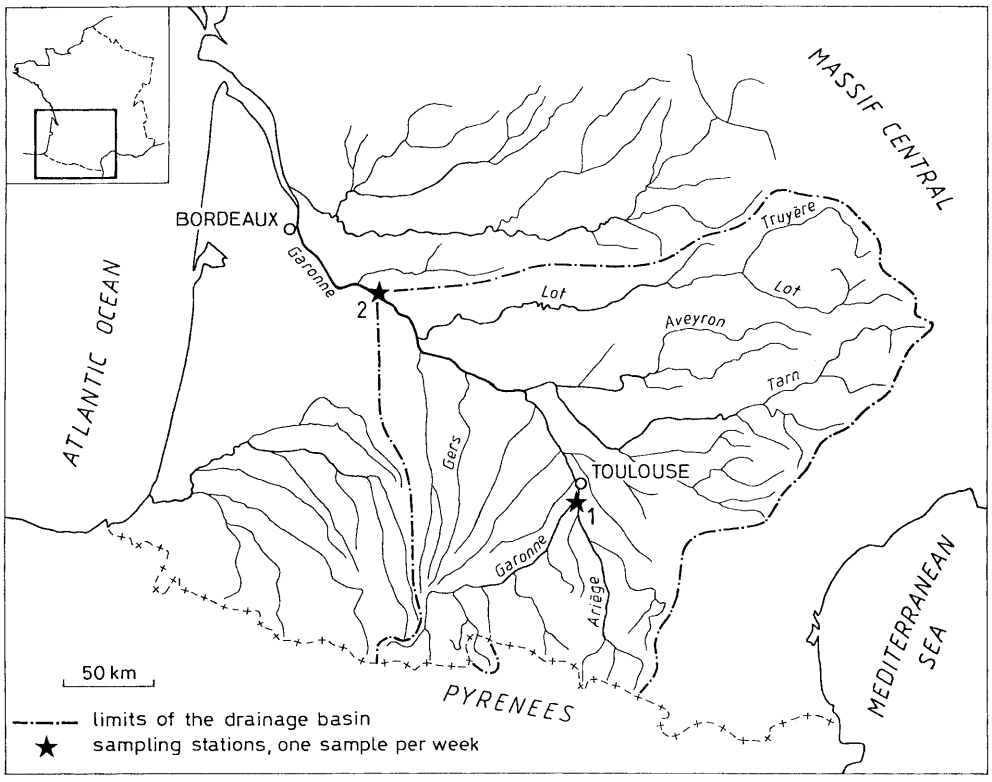

Fig. 1
Geographical sketch of the Garonne drainage basin with location of the two sampling stations

averaging 403 $m^3 s^{-1}$ at La Réole (station 2 in Fig. 1). The upstream Garonne River and the Ariège tributary contribute ~32% of the total Garonne discharge at the outlet, whereas the tributaries draining the Massif Central contribute ~62%. A comparison with the annual discharges recorded since 1910 reveals that the study period corresponds to a drought period, with a 25% water deficit in the upstream region and a 34% deficit in the downstream region. The greatest hydrological deficit was recorded in 1989 (50%).

Description of the samples and the analytical methods

The Garonne River was sampled weekly during the 1989–1992 period at two stations: one was located upstream (at Portet, station 1 in Fig. 1) and was dominated by the drainage of the Pyrénées Mountains, the other was located downstream (at La Réole, station 2 in Fig. 1) and recorded the influence of the whole basin (Fig. 1). The measured discharges were made available by the 'Service Hydrologique Centralisateur' (Toulouse) by speed exploration and gauging. The speed exploration method consists in measurements of runoff volumes at a given section in the basin along a vertical, and the integration of samples along the section between the bottom and surface of the stream. This procedure allows the determination of an average discharge in m^3 per second. The gauging method is based on the construction of gauging curves. The sampling was done in order to follow interannual variations of the major dissolved elements (Semhi 1996), and to quantify the amounts of atmospheric/soil CO_2 consumed by rock weathering. The water samples stored in polyethylene bottles, were pressure filtered through a Millipore HAWP 047-00 filter of 0.45-μm pore size, which consisted of an ester of cellulose (nitrate + acetate) filter. The major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analyzed by atomic absorption on a Z 8200 Hitachi spectrometer with an air–C_2H_2 gaseous mixture. La was added (0.5%) to the samples for Ca^{2+} and Mg^{2+} analyses. The measurements were made with an accuracy of 1 μmol l^{-1}. The major anions (NO_3^-, Cl^- and SO_4^-) were determined by liquid–ion chromatography on a Dionex chromatograph 4000I equipped with AG11 and AS11 columns using NaOH as an eluant. The detection limit was 1 μmol l^{-1}. Silica was analyzed by colorimetry with the same detection limit. The HCO_3^- concentrations were measured by alkalimetric titration with H_2SO_4 (0.02 N). The total analytical precision varies between 1 and 2%. The fluxes were calculated on the basis of following equation:

$$F_a = \sum_{i=1}^{n} C_{im} \cdot Q_{im}$$

where F_a is the annual flux (in kmol), n the number of measurement periods (in weeks), Q_{im} the weekly discharge (in $m^3 s^{-1}$), and C_{im} the weekly discharge-weighted mean of the concentration (in mmol l^{-1}) calculated as follows:

$$C_{im} = \frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2}$$

where C_1 and C_2 are the instantaneous concentrations of the first and last sample respectively, during each measurement period, and Q_1 and Q_2 are the corresponding discharges.

The contribution of the atmospheric input to the amounts of the major dissolved elements was estimated on the basis of the ratio between the concentrations of the dissolved elements $C_i(p)$ and the chlorides $Cl(p)$ in precipitation (Meybeck 1986; Table 1). The mean chloride concentration in the atmospheric precipitation over the Garonne basin was estimated by using the decrease in chloride concentrations (Cl) measured in precipitation at several stations in France (Ulrich and others 1994), relative to the distance of the sampling location (d) to the ocean (Fig. 2). The corrected concentrations from atmospheric input $C_{i(f)\mathrm{cor}}$ can be estimated as follows:

$$QC_{i(f)cor} = QC_{i(f)} - PC_{i(p)}$$

$$C_{i(f)cor} = C_{i(f)} - \frac{P}{Q} C_{i(f)p}$$

where $C_{i(f)}$ is the observed concentration of the dissolved elements, $C_{i(p)}$ the concentration of the same elements dissolved in precipitation P calculated on the basis of the above-mentioned $\frac{C_{i(p)}}{Cl_{(p)}}$ ratio, Q (in l km^{-2} s^{-1}) the annual mean discharge, and P (in l km^{-2} s^{-1}) the annual mean precipitation. The precipitation P was estimated by using the regression between the mean annual discharge Qs (in l km^{-2} s^{-1}) and the annual precipitation P (in cm), in the Garonne basin, on the basis of following regression:

$$Qs = 0.034\ P - 19.5$$

The geochemical model MEGA, which was developed to calculate the contribution of atmospheric CO_2 to the total bicarbonate fluxes exported by rivers, was used for this study (Amiotte Suchet 1995; Amiotte Suchet and Probst 1996). The modeling procedure decomposes the major element fluxes and it uses the stoichiometric dissolution or hydrolysis of the different minerals that are likely to react. It allows, after correction of the atmospheric input of cations and anions, the determination of the mineralogical origin of the major elements dissolved in the river waters. In the code, Na is supposed to be released by dissolution of halite (Eq. 1) and Na-silicates (for example, Eqs. 7, 8), Cl by dissolution of halite and sylvite (Eqs. 1, 2), K by dissolution of sylvite and orthose (Eqs. 2, 6), SO_4 by dissolution of gypsum (Eq. 3), Ca by dissolution of gypsum (Eq. 3), calcite (Eq. 4) and Ca-silicates (Eq. 9), and Mg by dissolution of dolomite (Eq. 5) and Mg-silicates (for example Eq. 10). The different reactions involved are:

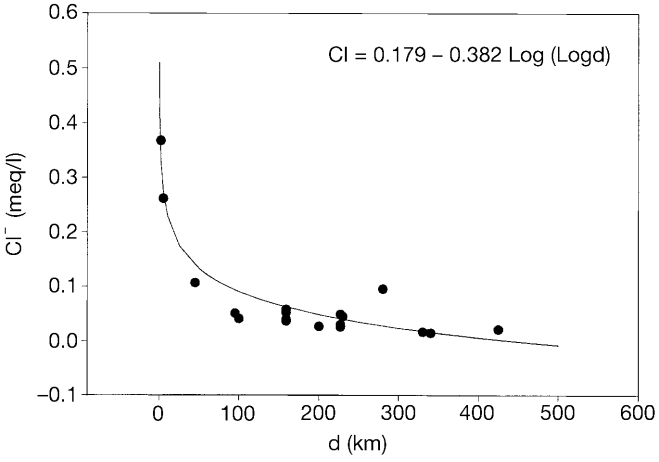

Fig. 2
Relationship between chloride concentrations (in meq l^{-1}) from precipitation and distance (in km) to the Atlantic coast (after Ulrich and others 1994)

Table 1
Mean chemical compositions of the Garonne waters during the 1989–1992 period (in mmol l^{-1}). *P* and *B* data from Probst and Bazerbachi (1986) during the 1980–1981 period; *E* and *P* data from Etchanchu and Probst (1988) during the 1971–1983 period

Elements	Upstream (Portet)		Downstream (La Réole)	
	This study	P and B	This study	E and P
Na^+	0.192	0.174	0.348	0.304
K^+	0.032	0.026	0.051	0.051
Mg^{2+}	0.134	0.206	0.247	0.247
Ca^{2+}	0.982	0.848	1.047	1.197
NO_3^{2-}	0.082	0.048	0.161	0.097
SO_4^{2-}	0.164	0.125	0.187	0.198
SiO_2	0.071	0.083	0.075	0.116
HCO_3^-	1.826	1.738	2.131	2.344
Cl^-	0.179	0.141	0.366	0.310

halite dissolution: $NaCl \rightarrow Na^+ + Cl^-$ (1)

sylvite dissolution: $KCl \rightarrow K^+ + Cl^-$ (2)

gypsum dissolution: $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$ (3)

calcite dissolution:
$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3$ (4)

dolomite dissolution:
$MgCaCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + Ca^{2+} + 2HCO_3$ (5)

hydrolysis of orthoclase to montmorillonite:
$2KAlSi_3O_8 + 2CO_2 + 4H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 2HCO_3^- + 2SiO_2$ (6)

hydrolysis of albite to kaolinite:
$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4SiO_2$ (7)

hydrolysis of albite to montmorillonite:
$2NaAlSi_3O_8 + 2CO_2 + 4H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 2SiO_2$ (8)

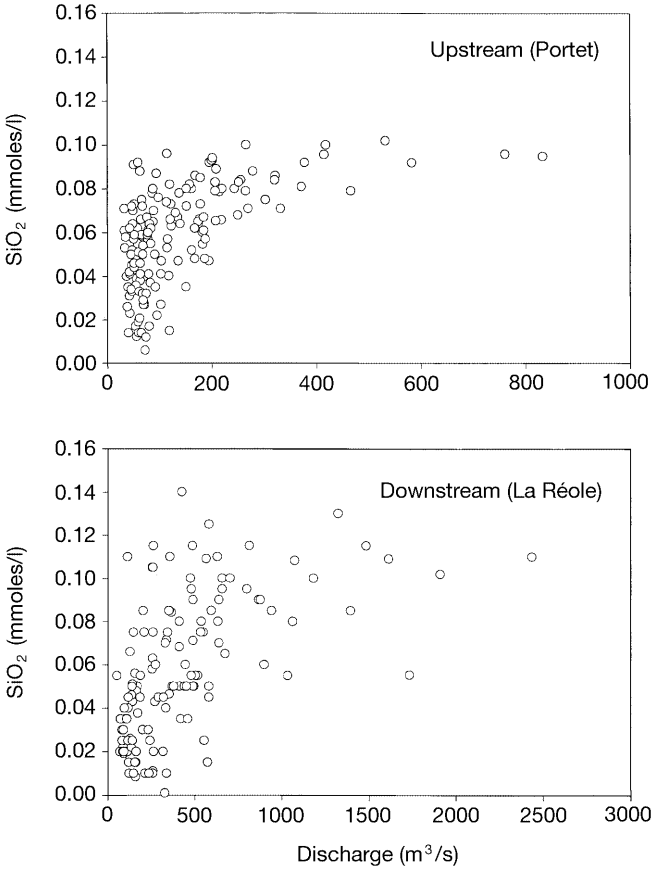

Fig. 3
Relationship between SiO_2 concentrations (in mmol l^{-1}) in waters and discharge ($m^3\ s^{-1}$) measured during the 1989–1992 period

hydrolysis of anorthite to kaolinite:

$$CaAl_2Si_2O_8 + 2CO_2 + 2H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca_{2+} + 2HCO_3^- \quad (9)$$

hydrolysis of chlorite to kaolinite:

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10CO_2 + 5H_2O \rightarrow Al_2Si_2O_5 + 5Mg^{2+} + 10HCO_3 + H_4SiO_4 \quad (10)$$

Discussion

Amorphous silica dissolves in fresh water to the extent of 173 μmol l^{-1} (average Si concentrations of the world's largest rivers calculated by Meybeck 1979), whereas lower solubilities can be expected from crystalline forms of silica, with quartz being the least soluble of all. These minerals are released from bedrocks, mainly by physical erosion, and are transported by water. The concentration of solubilized silica in natural waters is less than the amount in equilibrium with amorphous silica. The main sources of dissolved silica in river waters are probably volcanic emanations, and solubilization by CO_2-charged waters during weathering processes of silicate minerals exposed at the Earth's surface. However, Wollast and Mackenzie (1983) researched the contribution of different rock types to chemical weathering and the sources of dissolved constituents in river water, and they concluded that 45% of these constituents originated from weathering of silicate rocks. This value is greater than that reported by Meybeck (1979) who thought that only 20% of Ca^{2+} and 40–60% of Mg^{2+} in river waters were derived from silicate weathering. These values are reported here because silica is linked to other dissolved constituents in river waters. Thus, dissolved silica represents ~9% of the salinity of average river water (Wollast and Mackenzie 1983). The composition of river water depends greatly on the nature of the terrains of the watershed, and on the ratio of chemical weathering to mechanical erosion. Krauskopf (1956) and Kennedy (1971) showed that, in most cases, a low concentration of soluble silica in river water was a result of dilution and biological uptake by diatoms; however, Drever and Zobrist (1992) considered that uptake by biota would lead to an insignificant effect on silica. Bien and others (1958) observed that adsorption of silica on suspended particles could also possibly remove silica from solution in the presence of electrolytes. In fact, dissolution of silica, either from quartz or from silicate minerals that have varied solubilization, is a very slow process, and part of the reason for the low concentrations in natural waters is the slowness of the dissolution process. Garrels and Christ (1965) reported that most river- and groundwaters contain 99.8–998 μmol l^{-1} of SiO_2. They concluded that these silica concentrations are in the range that might be expected from equilibrium with kaolinite, considering the pH and Al concentrations. The recycling behavior of silica in rocks and ocean waters, as well as factors that may influence silica fluxes, have been discussed by Wollast and Mackenzie (1983).

Transport of silica by the Garonne River

The mean concentrations of exported dissolved Si by the Garonne waters during the 1989–1992 period (Table 1; 71 μmol l^{-1} for upstream and 75 μmol l^{-1} for downstream) is much lower than those reported by Meybeck (1986) for some major rivers (Yangtse: 99.8 μmol l^{-1}; Brahmapoutra: 123 μmol l^{-1}; Ganges: 166 μmol l^{-1} and Murray: 83 μmol l^{-1}). The relationship between the discharge and the Si concentrations during the 1989–1992 study period (Fig. 3) shows a poor correlation with a tendency for Si to increase with discharge. Kennedy (1971) observed a weak correlation between Si concentrations and discharge in several studied streams. Wollast and Mackenzie (1983) considered that, on a global scale, variations in the transport rate of dissolved silica to the world's oceans is determined mainly by variations in river waters. In fact, the Si concentrations like dissolved NO_3, in the Garonne waters increase during high water periods (Semhi and others 2000).
During the 1989–1992 period, the seasonal variations of high Si concentrations in the Garonne waters are associated with high water periods (Fig. 4). Thus, the Si concentrations in the Garonne waters increased when the

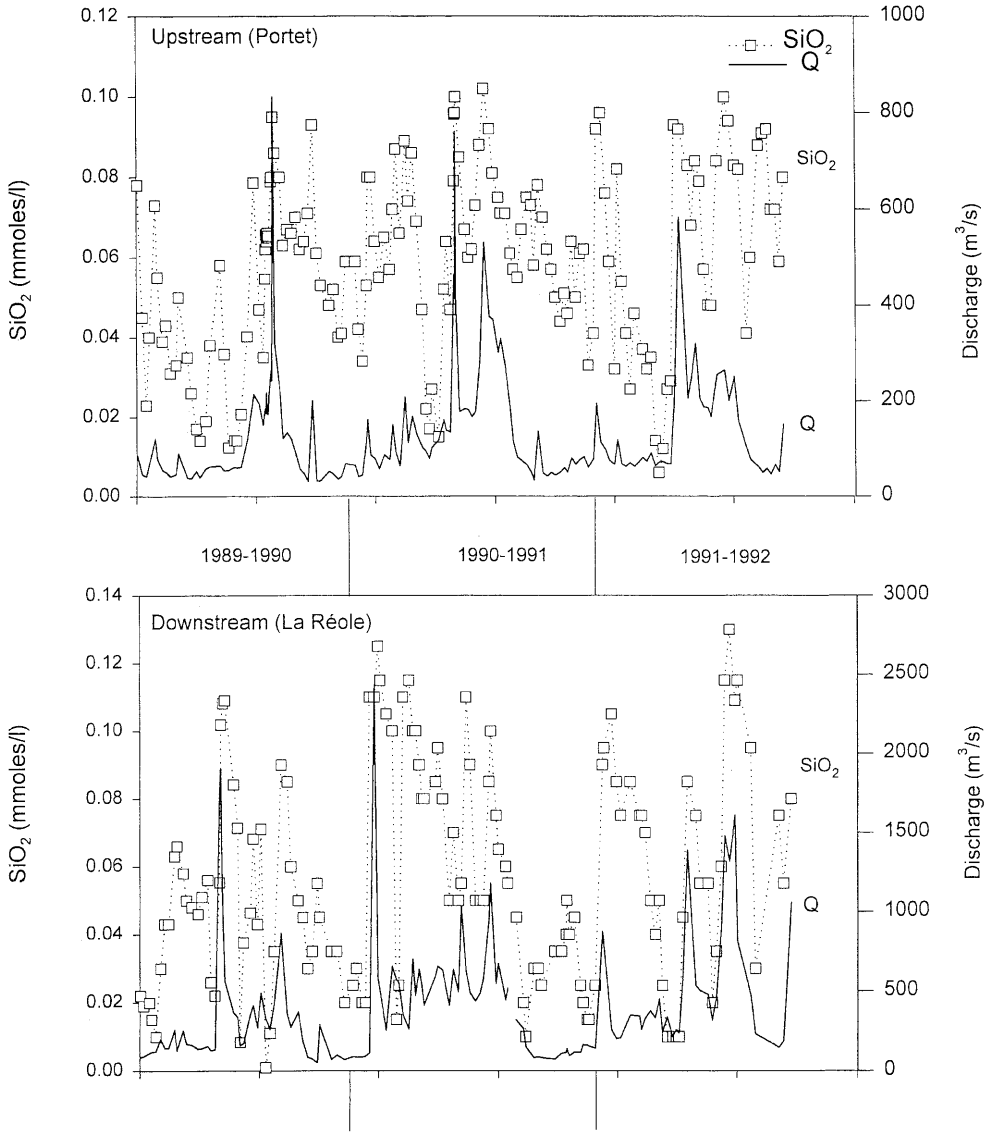

Fig. 4
Seasonal variations of daily discharge (*straight lines*) and SiO_2 concentrations (*squares* and *dotted lines*) in the waters of the Garonne River during the 1989–1992 period

discharge rates increased. This behavior can be explained by the removal of solutes from soils during high flow periods. Kennedy (1971) concluded that runoff waters percolating in soil pores were a major contributing factor to stream flows at peak discharges. This contribution is more rapid for Si than for the other dissolved elements during turbulent runoff. He also showed that 75% or more of the dissolved Si transported annually by the Mattole River (northern California) was derived from surface soils rather than from weathering of soils and rocks at depth during at least 20% of the year.

The Si budget in the Garonne waters was determined to be 1.77 t km^{-2} $year^{-1}$ in the upstream part of the river and 1.09 t km^{-2} $year^{-1}$ in the downstream part, during 1989–1992 (Table 2). The study period we chose (1989–1992) had less rain fall compared with the mean interannual discharge from 1910 to 1992. Comparison of the results obtained here with previous results obtained during more humid periods (Etchanchu and Probst 1988) with respect to the mean interannual discharge, outlines

Table 2
Annual fluxes of dissolved elements exported by the Garonne River during the 1989–1992 period (in t km^{-2} $year^{-1}$). P and B data from Probst and Bazerbachi (1986) during the 1980–1981 period; E and P data from Etchanchu and Probst (1988) during the 1971–1983 period

Study period	Upstream (Portet)		Downstream (La Réole)	
	This study	P and B	This study	E and P
Na^+	1.85	2.91	1.93	2.8
K^+	0.49	0.63	0.56	0.6
Mg^{2+}	1.38	3.3	1.51	2.6
Ca^{2+}	16.09	23.54	10.72	19.9
NO_3^{2-}	1.94	1.7	2.27	2.6
SO_4^{2-}	6.58	7.91	4.43	8
SiO_2	1.77	3.19	1.09	2.8
HCO_3^-	45.93	72.55	32.76	59
Cl^-	3.07	3.33	3.23	4.7
Q (m^3 s^{-1})	134	217	403	684

the influence of dryness on the total budgets of the Garonne waters, which is also confirmed in the transport of the other dissolved elements. The fluxes of the major dissolved elements show a net deficit in the mean flux during the period 1989–1992 coupled with a diminution of water discharge. The deficit of silica flux because of dryness, exceeds that of discharge. Thus, the ratio between the deficit in the transport of solutes and the deficit in discharge (Semhi 1996) is higher than 1 for elements that originate mainly during weathering, such as SiO_2, which is the opposite for elements that are derived from anthropogenic pollution such as NO_3^-, Cl^-, K^+ and Na^+.

Silica dynamics in the Garonne River

The chemistry of surface waters depends on weathering processes that occur in the catchment areas. To characterize the different stages of weathering, Pedro (1960, 1966) defined three predominant types of weathering processes: allitization, monosiallitization and bisiallitization. The allitization stage corresponds to the complete release of the basic cations and of Si, with only Fe and Al remaining as oxi-hydroxides (gibbsite and goethite). The monosiallitization corresponds to the complete release of basic cations and only some of the Si is removed. The remaining Si combines with alumina to produce a SiO_2/Al_2O_3 ratio of 2, corresponding to the formation of kaolinite. The bisiallitization corresponds to the neoformation of minerals with two silica layers per Al layer that have a SiO_2/Al_2O_3 ratio greater than 2. In general, tropical weathering of silicate minerals produces kaolinite as the principal alteration product, and Fe and Al hydroxides (gibbsite and goethite) (Tardy 1971), whereas temperate

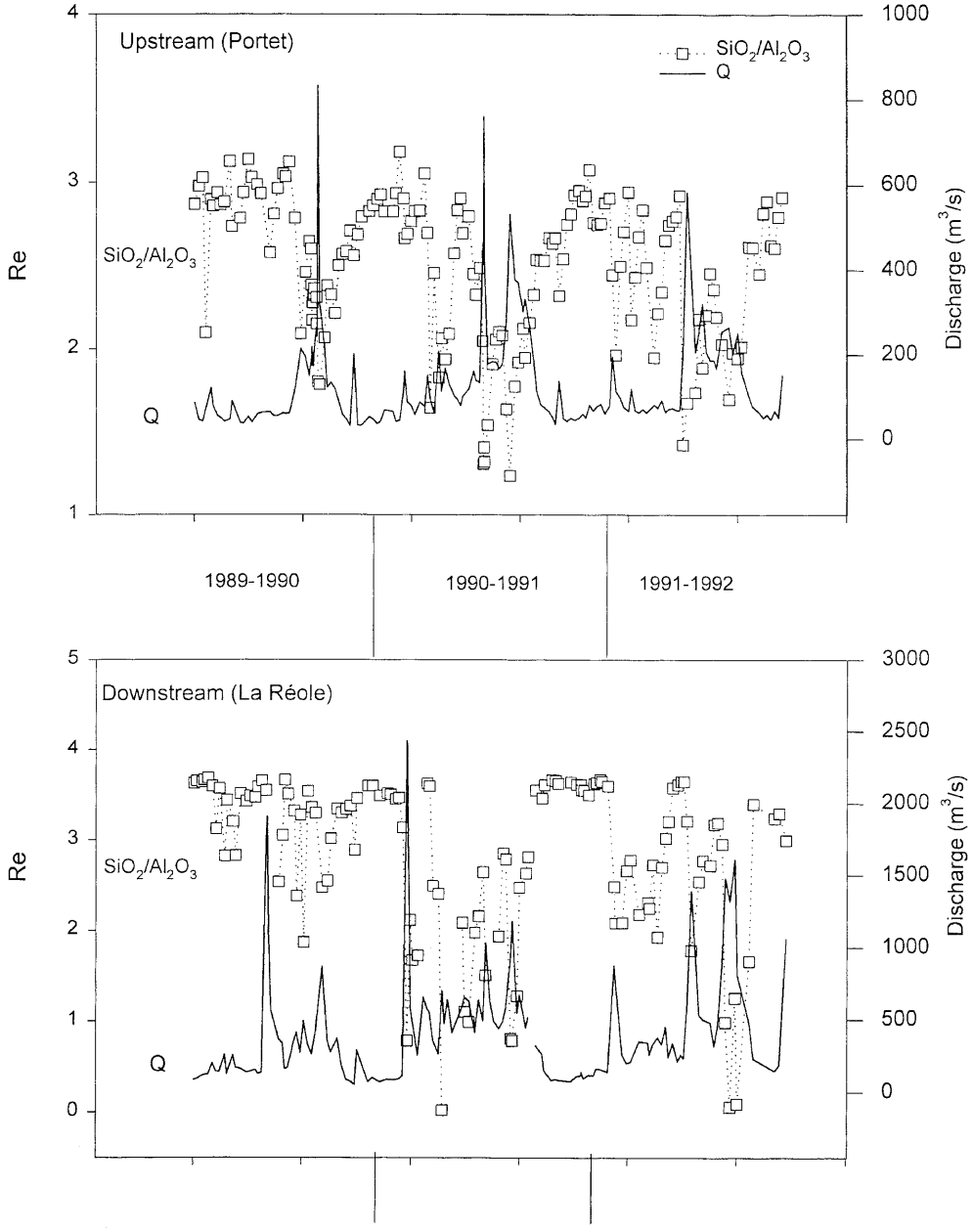

Fig. 5
Seasonal variations of daily discharge (*straight lines*) and SiO_2/Al_2O_3 ratio (=Re) (*squares* and *dotted lines*) in the Garonne waters during the 1989–1992 period

weathering results in the formation of montmorillonite. Thus, the abundance and diversity of clay minerals can reflect the chemical conditions in which they formed. The composition of a water resulting from meteoric rock weathering is the sum of the results of individual reactions. In most cases, the ions Na, Ca, K and Mg, once released during weathering, are removed in waters whereas alumina once released, remains largely in the soil:

$$Al_2O_3(\text{fixed}) = Al_2O_3(\text{released}) = K_2O(\text{removed}) + Na_2O(\text{removed}) + CaO(\text{removed})$$

Silica has an intermediate behavior, one part being fixed, the other removed.

$$SiO_2(\text{fixed}) = SiO_2(\text{released}) - SiO_2(\text{removed}) = 6K_2O(\text{removed}) + 6Na_2O(\text{removed}) + 2CaO(\text{removed}) - SiO_2(\text{removed})$$

The ratio between SiO_2(fixed) and Al_2O_3(fixed) in soils was used by Tardy (1969, 1971) for a quantitative reconstruction of the weathering balance as follows:

$$\text{Re} = \frac{SiO_2(\text{fixed})}{Al_2O_3(\text{fixed})} = \frac{6K_2O(\text{removed}) + 6Na_2O(\text{removed}) + 2CaO(\text{removed}) - SiO_2(\text{removed})}{K_2O(\text{removed}) + Na_2(\text{removed}) + CaO(\text{removed})}$$

The above proposals were used for the Garonne waters to characterize the geochemical variations of weathering during the 1989–1992 period. The calculations showed that the average Re ratio is 3.1 in the upstream and 3.8 in the downstream region, bisiallitization being the predominant type of weathering. These results agree with those reported by Tardy (1971) in a study of the weathering dynamics in catchments developed on silicate formations in the French Massif Central. The spatial variations of the SiO_2/Al_2O_3 ratio confirm that pronounced stages of weathering supply the river waters more downstream than upstream. Among the factors controlling the weathering rate, runoff and temperature are partly controlled by topography. The upstream part of the Garonne River is more elevated than the downstream part, which means, in turn, that the overall precipitation is higher, that the temperature is lower, and that the soils are thinner. These results agree with those of Amiotte Suchet (1995) who observed a positive correlation between SiO_2/Al_2O_3 ratios in differentiated basins and their elevation.
The seasonal variations of the SiO_2/Al_2O_3 ratio in the river waters indicate that removal of Si is accelerated during humid periods (Figs. 5 and 6), which agrees with the conclusions of Tardy (1971) and Gac (1980) in Africa. Thus, the river discharge regulates and records the weathering dynamics.

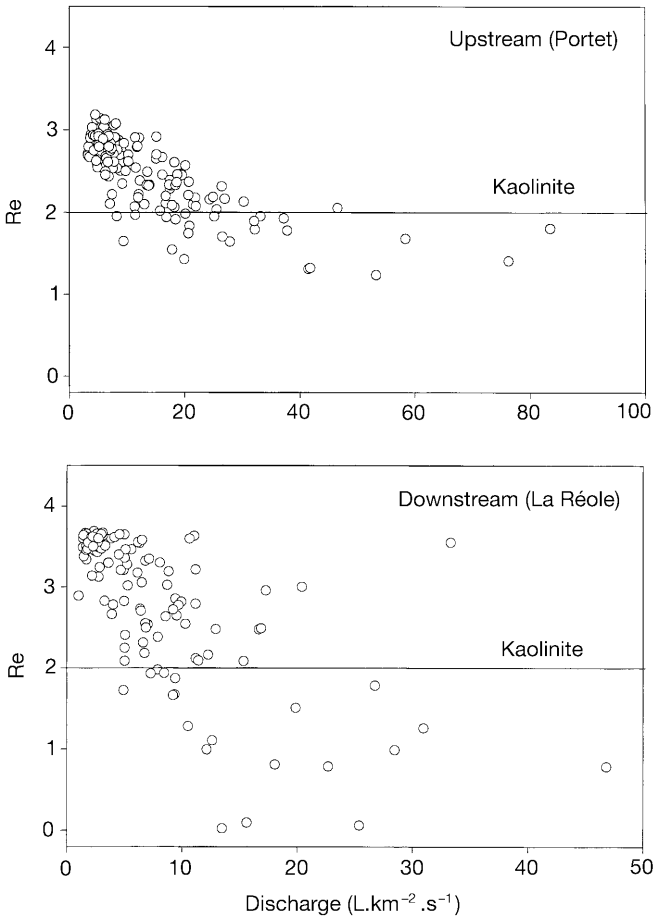

Fig. 6
Relationship between SiO_2/Al_2O_3 ratios (= Re) in waters and discharge ($m^3\ s^{-1}$) measured during the 1989–1992 period

Conclusion

High Si concentrations in the Garonne River were observed during high-water discharges. This pattern can be explained by the increased leaching of Si from soils into the river waters. The chemistry of the Garonne waters, which drain silicate and carbonate rocks, was determined by the modeling procedure MEGA, of the major dissolved elements that originate during weathering processes. Using mineralogical sources for released major elements, this modeling procedure estimates a weathering budget, and suggests that bisiallitization is the form of weathering at basin scale, and that montmorillonite is the ultimate secondary mineral in the soils. For a quantitative reconstruction of the weathering balance in the Garonne basin, we have used the ratio between the fixed SiO_2 and Al_2O_3 concentrations. The seasonal variations of this ratio in the river waters during the 1989–1992 period indicate that the mobility of silica becomes more pronounced during a period of high-water discharge.

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$\delta^{13}C$ pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges mountains, France)

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Abstract

The transfers and origins of dissolved inorganic carbon (DIC) were studied for a year in a soil–spring–stream system in the Strengbach catchment, Vosges mountains, France. This 80 ha experimental research basin is located on the eastern side of the mountains, at an altitude ranging from 883 to 1146 m.a.s.l. and is mainly covered by spruce (80%). Brown acid and podzolic soils developed on a granitic basement, and, as a result, the DIC originates solely from CO_2 generated by oxidation of soil organic matter. The ($\delta^{13}C_{DIC}$) in catchment waters is highly variable, from about −22‰ in the springs and piezometers to about −12‰ in the stream at the outlet of the catchment. In the springs, pronounced seasonal variations of $\delta^{13}C_{DIC}$ exist, with the DIC in isotopic equilibrium with the soil CO_2 that has estimated $\delta^{13}C$ of about −24‰ in winter and −20‰ in summer. These seasonal variations reflect an isotopic fractionation that seems only induced by molecular diffusion of soil CO_2 in summer. In stream water, seasonal variations are small and the relatively heavy DIC (−12‰ on average) is a result of isotopic equilibration of the aqueous CO_2 with atmospheric CO_2.

Keywords: $\delta^{13}C$; Dissolved inorganic carbon; Strengbach case study

1. Introduction

The dissolved inorganic carbon (DIC) in river water has three main sources: soil CO_2, dissolution of carbonate minerals and atmospheric CO_2 exchanged trough the air–water interface (Yang et al., 1996). On average, the contribution of soil CO_2 to the DIC in the world rivers has been estimated to be about 67% (Berner et al., 1983; Meybeck, 1987; Amiotte Suchet and Probst, 1995; Ludwig et al., 1997). In each river, the respective contribution of soil CO_2 and of carbonate mineral dissolution can only be estimated using modeling approaches (Probst, 1992; Amiotte Suchet and Probst, 1993a,b; Probst et al., 1994a,b; Amiotte Suchet and Probst, 1995; Lud-

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wig et al., 1997). On the other hand, many studies have measured the stable carbon isotope composition of the DIC, attempting to distinguish its sources in river water (Hitchon and Krouse, 1972; Mook and Tan, 1991; Tan and Edmond, 1993; Pawellek and Veizer, 1994; Cameron et al., 1995; Yang et al., 1996). Yet, despite the fact that carbon isotopic signatures of carbonate minerals and of soil CO_2 are distinctive, the variations of carbon isotope composition of riverine DIC remain quite difficult to interpret, because additional processes, such as riverine respiration and isotopic equilibration with atmospheric CO_2 play a role.

Clearly, a better knowledge of the processes that affect the isotopic composition of the DIC in the upstream parts of the river basins is needed (Pawellek and Veizer, 1994). To our knowledge, only two studies have focused as yet on isotopic composition of DIC in small watersheds: the work of Dandurand et al. (1982), for a stream draining carbonate rocks, and Kendall et al. (1992, 1995) for two streams draining predominantly silicate rocks.

In this work, we have studied the stable isotopic composition of DIC in the springs and streams of a small watershed that drains a strictly silicate basement, which means that DIC originates solely from soil CO_2. Its spatial and temporal variations during a complete hydrological cycle enable us to quantify the role of soil and atmospheric CO_2 on the isotopic composition of DIC in a small homogeneous aquatic system.

2. Materials and methods

2.1. $\delta^{13}C$ of dissolved inorganic carbon (DIC) in terrestrial aquatic systems

2.1.1. Dissolved inorganic carbon (DIC)

The DIC is composed of aqueous carbon dioxide (CO_2(aq)), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. These aqueous compounds can be in contact with gaseous carbon dioxide (CO_2 (g)) and/or carbonate minerals such as calcite ($CaCO_3$). The composition of DIC in continental water is then controlled by the chemical equilibria among these five species and is characterized at 25°C by the following equilibrium constants (Bourrié, 1976):

$$K_H = \left([H_2CO_3^*]/pCO_2\right) = 10^{-1.46} \quad (1)$$

$$K_1 = \left([H^+][HCO_3^-]\right)/[H_2CO_3^*] = 10^{-6.35} \quad (2)$$

$$K_2 = \left([CO_3^{2-}][H^+]\right)/[HCO_3^-] = 10^{-10.33} \quad (3)$$

$$K_C = [Ca^{2+}][CO_3^{2-}] = 10^{-8.47} \quad (4)$$

Note that in Eq. (1), $H_2CO_3^*$ is the analytical sum of aqueous CO_2 (CO_2aq) and of the true carbonic acid (H_2CO_3). It is generally assumed that the concentration of aqueous CO_2 is nearly identical to $H_2CO_3^*$ (Stumm and Morgan, 1981).

The concentration of each species in solution therefore depends on its pH, partial pressure of CO_2 (pCO_2) and temperature. In stream water, DIC is mainly composed of HCO_3^- ions, while in soil solutions, with usually high pCO_2 and low pH values, DIC is mainly composed of $H_2CO_3^*$.

In small watersheds, HCO_3^- ions can have two distinct origins: the soil CO_2 and carbonate mineral dissolution. Three alternatives can be considered for the origin of DIC.

For silicate weathering by carbonic acid, such as albite hydrolysis (see Eq. (5)), DIC originates solely from soil CO_2.

$$\underset{\text{albite}}{2NaAlSi_3O_8} + \underset{\text{soil } CO_2}{2CO_2 + 3H_2O} \rightleftarrows \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{solute compounds}}{2Na^+ + 2HCO_3^- + 4SiO_2} \quad (5)$$

For carbonate dissolution by carbonic acid (Eq. (6)), one-half of the DIC originates from the mineral itself and the other half from the soil CO_2.

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \quad (6)$$

For carbonate dissolution by acids other than H_2CO_3 (e.g., sulfuric or organic acids), DIC originates solely from carbonate minerals (Eq. (7)).

$$2CaCO_3 + H_2SO_4 \rightleftarrows Ca^{2+} + 2HCO_3^- + SO_4^{2-} \quad (7)$$

The two first processes are believed to predominate in rock weathering (Garrels and Mackenzie, 1971; Wollast and Mackenzie, 1983; Meybeck, 1987; Amiotte Suchet, 1995) and, at the global scale, about

two-thirds of bicarbonate ions transported by the world rivers originates therefore from soil CO_2.

2.1.2. Isotopic composition ($\delta^{13}C$) of soil CO_2

In the case of silicate rock weathering (Eq. (5)), the isotopic composition of DIC should reflect that of soil CO_2 that is produced by decomposition of soil organic matter (SOM) and by root respiration. Several processes lead the isotopic composition of soil CO_2 to be slightly different from that of SOM.

The $\delta^{13}C$ of SOM is directly related to the type of vegetation cover with an estimated average of $-26‰$ (-22 to $-30‰$) for C3 plants and $-12‰$ for C4 plants (Deines, 1980; Mariotti, 1991). This original isotopic signature of SOM is slightly enriched in ^{13}C (about 1 to 4‰) during its mineralization. As a result, the $\delta^{13}C$ of SOM is progressively heavier with increasing depth and decreasing carbon content (Mariotti, 1991; Peterschmitt, 1991; Desjardins et al., 1991, 1994).

In addition, fractionation also occurs during the decay of SOM (Rightmire and Hanshaw, 1973; Dörr and Münnich, 1980; Salomons and Mook, 1986; Cerling et al., 1991), leading to an enrichment in ^{13}C of the residual soil CO_2. This is due to the molecular diffusion of the gas through the soil pores (Craig, 1954; Dörr and Münnich, 1980; Cerling et al., 1991). Depending on the study, the enrichment ranges from 1 to 4‰, with a maximum 4.4‰ claimed by Cerling et al. (1991). Then, taking into account a $\delta^{13}C$ value for SOM of $-25‰$, the maximum $\delta^{13}C$ of soil CO_2 can be estimated to about $-21‰$.

Alternatively, soil CO_2 can sometimes originates from a mixture of atmospheric and soil air (Galimov, 1966; Rightmire, 1978; Cerling, 1984; Salomons and Mook, 1986; Cerling et al., 1991), as indicated by a negative relationship between the $\delta^{13}C$ of soil CO_2 and its associated partial pressures (pCO_2), for several soils in temperate climate and covered by C3 plants. In summer, the rate of SOM oxidation is high, inducing high pCO_2 in soils and preventing atmospheric CO_2 from penetrating the soil. As a result, the $\delta^{13}C$ of soil CO_2 is low, close to that of SOM. In contrast, the soil biologic activity is low in winter, permitting atmospheric CO_2 ($\delta^{13}C$ of about $-8‰$) to penetrate the soil, leading to an enrichment in ^{13}C. As a consequence, the $\delta^{13}C$ of soil CO_2 ranges between -20 and $-26‰$ in summer (Rightmire, 1978; Dörr and Münnich, 1980) and between -10 and $-15‰$ in winter (Cerling et al., 1991).

2.1.3. Isotopic fractionation between DIC and gaseous CO_2

The isotopic fractionation factors between the different carbonate species dissolved in continental water and gaseous CO_2 are now well known (Vogel et al., 1970; Deines et al., 1974; Mook et al., 1974; Wigley et al., 1978; Faure, 1986; Zhang et al., 1994; Szaran, 1998). In earth surface environments, fractionation is a linear function of temperature. The relationships between the isotopic enrichment factors (ε) and the temperature (T) are shown in Table 1.

Potential variations of carbon isotopic composition ($\delta^{13}C$) in an aqueous system are shown in Fig. 1. For DIC originating solely from soil CO_2, HCO_3^- ions should be enriched in ^{13}C by about 8 to 10‰ (Table 1), whereas the aqueous CO_2 should be depleted by about 1‰. In contrast, HCO_3^- ions from dissolution of carbonate rocks should not show any fractionation relative to precursor carbonate minerals. If so, for catchments covered by C3 plants ($\delta^{13}C = -26‰$), with no contamination of the soil CO_2 by atmospheric CO_2 and laying on non-carbonate rocks, the isotopic composition of DIC in

Table 1
Isotopic enrichment factors (ε) between gaseous CO_2, and dissolved carbonate species ($H_2CO_3^*$, HCO_3^- and CO_3^{2-}) as a function of temperature (in °C) (from Zhang et al., 1994)

Relationships between isotopic enrichment factors (ε, in ‰) and temperature (T, in °C)		ε in ‰	
		at 5°C	at 25°C
$\varepsilon CO_2\text{g}(H_2CO_3^*) = (0.0049 \times T) - 1.31$	(8)	−1.29	−1.19
$\varepsilon CO_2\text{g}(HCO_3^-) = (-0.1141 \times T) + 10.78$	(9)	+10.21	+7.93
$\varepsilon CO_2\text{g}(CO_3^{2-}) = (-0.052 \times T) + 7.22$	(10)	+6.96	+5.92

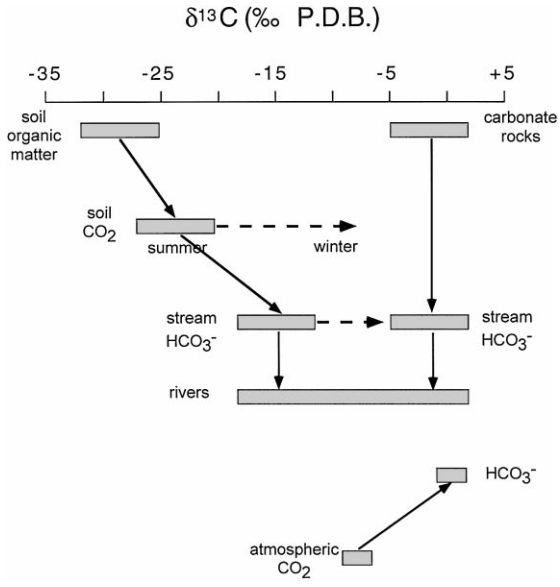


Fig. 1. Potential variations of carbon isotopic composition in aqueous systems (modified from Pawellek and Veizer, 1994).

stream water, mainly HCO_3^- ions, should vary between -16 to -19‰.

Finally, if the DIC is completely in isotopic equilibrium with atmospheric CO_2, its isotopic signature should vary between 0 and $+2$‰ (Fig. 1).

2.2. Site location

The isotopic composition of DIC in spring and stream water has been studied during one year in the Strengbach basin (Fig. 2).

The forested Strengbach catchment is located on the eastern side of the Vosges mountains (northeastern France), 58 km southwest from Strasbourg. It ranges from 883 m at the outlet to 1146 m at the top (Fig. 2). This small catchment (80 ha) lies mainly on a base poor leucogranite (the 320 My old Brézouard granite). At the top edge of the basin, a banded gneiss lies in contact with this granite (Probst et al., 1992). The fresh bedrock is overlaid with 1–10 m of saprolite. Despite the fact that the Brézouard leucogranite is somewhat affected by hydrothermal activity, no hydrothermal carbonate minerals, such as calcite, have been observed (El Gh'mari, 1995). We therefore consider all the DIC in the water of the Strengbach catchment to be derived from soil CO_2.

Brown acid soils are developed on the south facing slope, while podzolic soils cover the north facing slope. The valley bottom is occupied by a saturated area with hydromorphic soils, accounting for 2% of the catchment area. The soils are 0.8–1 m thick.

The vegetation cover is composed of C3 plants. Norway spruce (*Picea abies* L.) dominates (80% of the catchment area), and mixed silver fir (*Abies alba* L.) and beech (*Fagus sylvatica* L.) cover the rest of the area.

The Strengbach catchment has been monitored since late 1985, within the framework of the influence of acid precipitation on surface water chemistry and weathering (Probst et al., 1987, 1990a, 1992, 1994a,b, 1995). The chemistry of the stream water (Probst et al., 1992) is dominated by SO_4^{2-} and Ca^{2+} and the alkalinity is quite low (pH = 6.10 and alk = 36.0 μeq l^{-1}, on average, for the year 1994–1995).

2.3. Sampling and analytical methods

2.3.1. Soil organic matter sampling

Four representative soil profiles (two acid brown soils under Norway spruce (*P. abies* L.) and beech (*F. sylvatica* L.)), one podzolic soil (under Norway spruce) and the hydromorphic soil of the saturated area have been sampled every 10 cm, down to the bedrock.

2.3.2. Water sampling

The location of each sampling point is presented in Fig. 2. The main stream has been sampled every week at the outlet gauging station (RS) of the Strengbach catchment, from November 1994 to December 1995. During this period, the surface water from 17 other sites has been sampled 5 times. Of these sampling sites, three are located on the main stream (upstream point R1, upstream of the saturated area RAZS and the outlet the gauging station RS), four are located on secondary streams (R3, BH, RH, RUZS), six correspond to springs (CS1, CS2, CS3, CS4, SH, SG) and four are piezometers of the saturated area (PA, PD, PF, PH).

The samples were filtered in the field through a 0.45 μm Millipore membrane, applying a small underpressure with a hand-operated vacuum pump. The

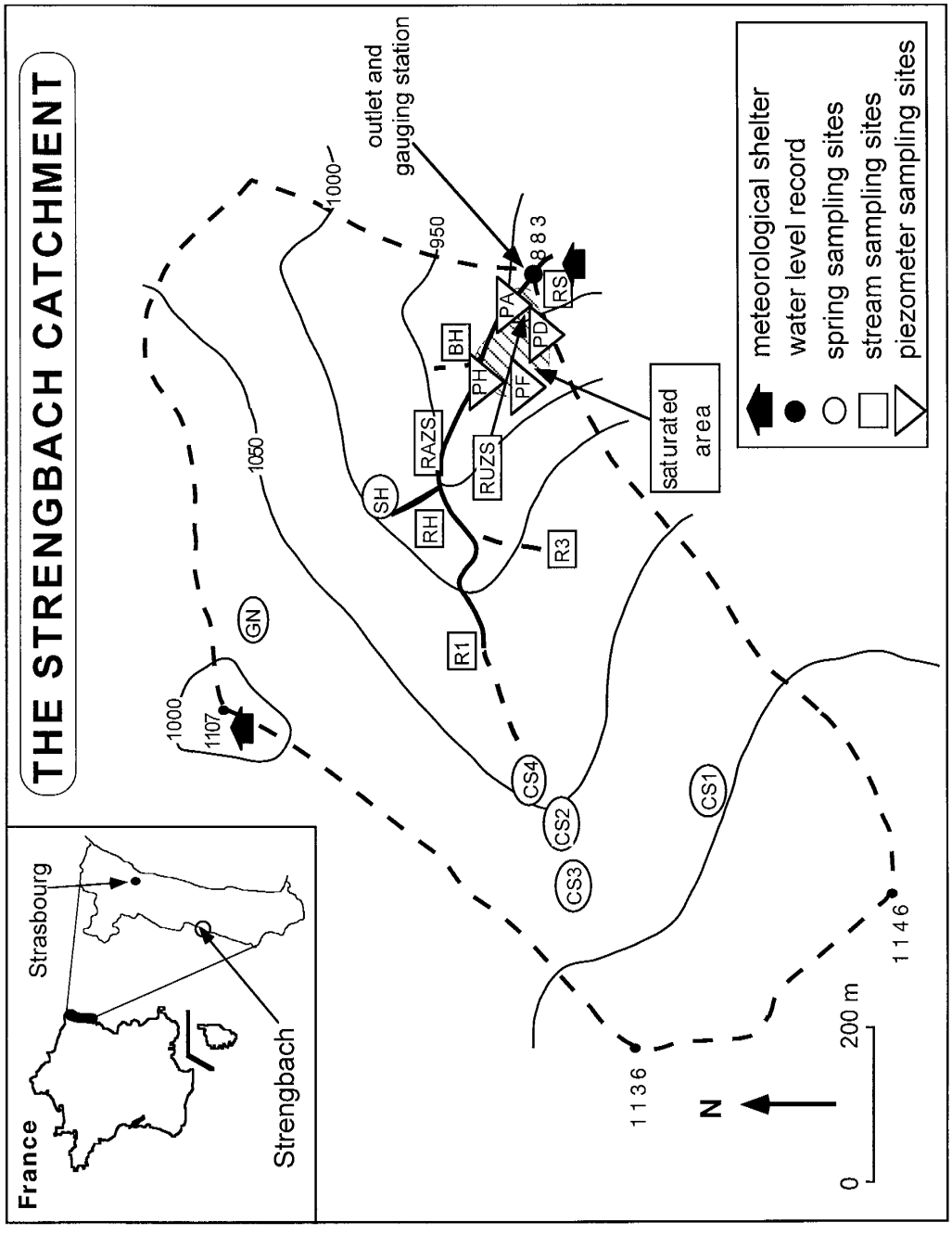


Fig. 2. Location and description of the Strengbach catchment.

membrane was pre-washed with 500 ml of deionized water. The samples for major element analysis were collected in 250 ml polyethylene bottles and those for isotopic analysis of DIC in 500 ml polyethylene bottles, poisoned with 1 ppm of $HgCl_2$ to prevent any microbial activity. Bottles were carefully sealed, taking care that no trapped air remained in contact with the sample. Finally, samples were kept between 0 and $+5$°C prior to analysis.

The $\delta^{13}C_{DIC}$ was measured at the Centre de Géochimie de la Surface, in Strasbourg, following the procedure of Kroopnick et al. (1970). Phosphoric acid (H_3PO_4) is added to the sample inside a vacuum line and the evolved CO_2 is purified and trapped with liquid nitrogen in a glass tube. The isotopic composition of this gaseous CO_2 was then measured with a VG Optima mass spectrometer. Several tests have been made for low alkalinity water, including the filtering step in the field. The resulting analytical precision was ± 0.2‰. The major elements (calcium, magnesium, potassium and sodium) were determined by Atomic Absorption Spectrophotometry, chloride, sulfate, nitrate by Liquid Ion Chromatography and alkalinity by titration with the Gran method.

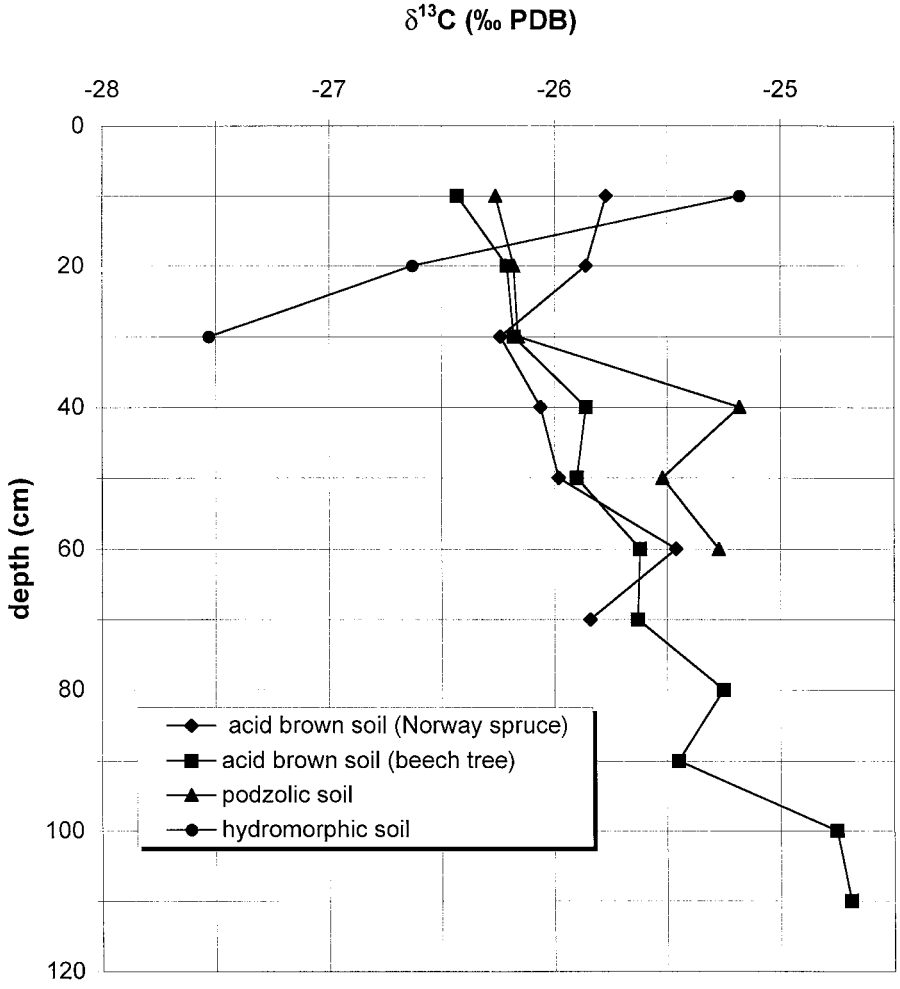


Fig. 3. Variation of $\delta^{13}C$ for the soil organic matter in the different soil profiles of the Strengbach catchment.

3. Results

3.1. $\delta^{13}C$ values of soil organic matter

In the Strengbach catchment, the isotopic composition of SOM, the primary source of the DIC in the stream water, is typical of C3 plant covers, with $\delta^{13}C$ of -24.7 to -26.4‰ for the acid brown and the podzolic soils and a small enrichment in ^{13}C with increasing depth (Fig. 3). This ^{13}C enrichment correlates with the decrease of carbon content (Fig. 4). These results are similar to those of Balesdent and Mariotti (1996) for French soils, and typical of other soils in equilibrium with C3 plants (Andreux et al., 1990; Desjardins et al., 1991, 1994; Koutika et al., 1997 among others). This depth pattern can be interpreted as an isotopic fractionation of SOM by decomposing organisms, with the young and labile fraction (the easily mineralized SOM) depleted in ^{13}C relative to the residual SOM (Boutton, 1996). Note, however, that the hydromorphic soil of the saturated area shows different patterns. In the first 10 cm of the profile, the organic carbon is quite heavy ($\delta^{13}C = -25.2$‰), becoming lighter with increasing depth (Fig. 3). This surprising pattern can perhaps be explained by the degradation of SOM under anaerobic conditions. As reported by Wada and Ueda (1996) from a rice paddy field in Japan, aerobic bacterial

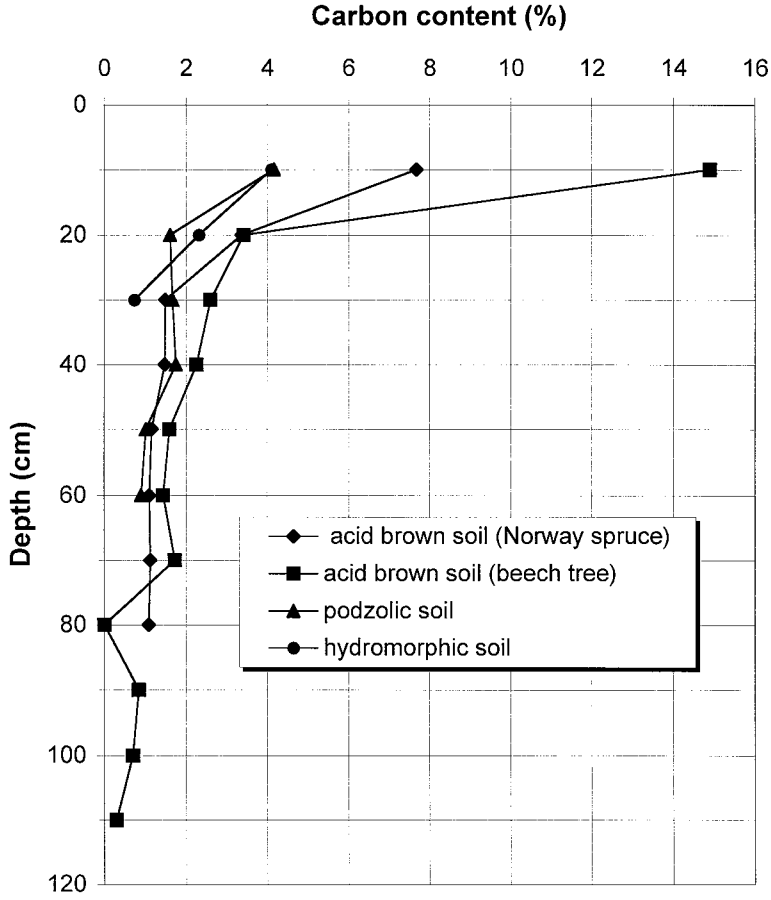


Fig. 4. Variation of carbon content of the soil organic matter in the different soil profiles of the Strengbach catchment.

decomposition of SOM produces very depleted methane ($\delta^{13}C$ around $-50‰$) but relatively enriched CO_2 ($\delta^{13}C$ from -9 to $-12‰$). Such processes lead to a decrease in the $\delta^{13}C$ of the accumulated SOM ($-29.2‰$) relative to the fresh organic matter ($-26.8‰$). Additional studies are required in order to establish to what extent the soil CO_2 could be isotopically contaminated by CH_4.

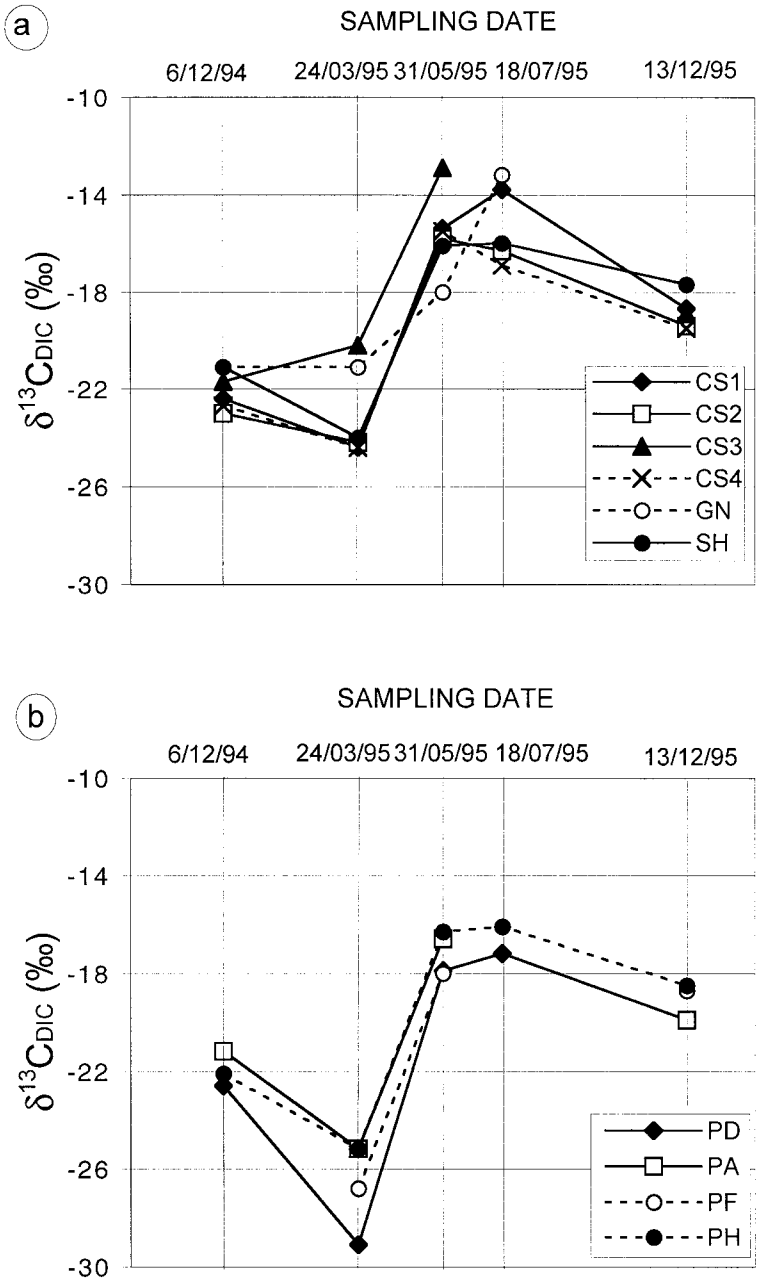


Fig. 5. Temporal fluctuations of $\delta^{13}C_{DIC}$ in the springs (CS1, CS2, CS3, CS4, GN, SH) and the piezometers (PA, PD, PF, PH) of the Strengbach catchment (see Fig. 2 for location of sampling sites).

Assuming an isotopic enrichment of +1 to +4‰ induced by molecular diffusion of CO_2 in soil pores (see above), the $\delta^{13}C$ of the soil CO_2 produced by SOM mineralization in the Strengbach catchment should range between −25 and −21‰ (between −26.5 and −21.5‰ for the hydromorphic soil of the saturated area).

3.2. $\delta^{13}C$ of DIC in spring water and piezometer

The variations of the isotopic composition of the DIC in spring water and in the piezometers of the saturated area are represented in Fig. 5. On average, the $\delta^{13}C_{DIC}$ is quite low, with mean values of −18.9 and −20.3‰ for spring water and piezometers, respectively (Table 2). This is the result of higher concentrations of $H_2CO_3^*$, isotopically equilibrated with light soil CO_2, relative to HCO_3^- ions. Nevertheless, the $\delta^{13}C_{DIC}$ values shows significant, station independent, seasonal variations (Fig. 5). In winter 1994/95, the $\delta^{13}C_{DIC}$ values vary on average between −26.6 and −23.2‰, that is in the estimated range of the soil CO_2. Subsequently, in the late spring and in summer, DIC becomes enriched in ^{13}C, with mean values ranging between −16.7 and −15.1‰. The following 1995 winter, shows return to more negative values (−19.3‰ on average), but not a recover to the values of December, 1994.

Note also that the $\delta^{13}C_{DIC}$ values in piezometers are generally more depleted than those of the spring water (Table 2). This perhaps can be related to the isotopic composition of the soil organic matter and soil gases in the saturated area, considering that the proportions of DIC species ($H_2CO_3^*$ vs. HCO_3^-), are similar in spring and in piezometers. Whatever the explanation, the enrichment in ^{13}C (about 7–8‰) between winter and summer samples, is also recorded in piezometers as well.

3.3. $\delta^{13}C$ values of DIC in stream water

DIC in stream water is clearly enriched in ^{13}C (Fig. 6) with a yearly average of −11.8‰. Note however that, in contrast to springs and piezometers, no clear seasonal variations are indicated. In general, the $\delta^{13}C_{DIC}$ ranges between −13.8‰ and −9.3‰

Table 2
Average values and ranges of $\delta^{13}C_{DIC}$, HCO_3^- concentrations and pCO_2 in springs and piezometers for 5 sampling campaigns

Sampling date	Number of sample			$\delta^{13}C_{DIC}$		HCO_3^- (meq l^{-1})		log pCO_2 (atm.)	
	Piezo	Springs		Pz	Sp	Pz	Sp	Pz	Sp
6/12/94	3	6	Mean	−22.0	−22.0	0.050	0.062	−2.92	−3.01
			Min	−22.6	−23.0	0.009	0.022	−3.15	−3.11
			Max	−21.2	−21.1	0.098	0.131	−2.79	−2.89
24/03/95	4	6	Mean	−26.6	−23.2	0.052	0.033	−2.22	−2.41
			Min	−29.1	−24.4	0.010	0.006	−2.62	−2.71
			Max	−25.2	−20.2	0.102	0.080	−1.79	−2.18
31/05/95	4	4	Mean	−17.2	−15.6	0.063	0.055	−2.85	−3.00
			Min	−18.0	−18.0	0.021	0.043	−3.29	−3.06
			Max	−16.3	−12.9	0.119	0.086	−2.58	−2.91
18/07/95	2	5	Mean	−16.7	−15.1	0.114	0.052	−2.97	−2.99
			Min	−17.2	−16.9	0.109	0.016	−3.01	−3.17
			Max	−16.1	−13.2	0.119	0.114	−2.92	−2.86
13/12/95	4	5	Mean	−19.3	−18.8	0.030	0.034	−3.13	−3.16
			Min	−19.9	−19.5	0.000	0.005	−3.29	−3.60
			Max	−18.5	−17.7	0.083	0.049	−2.97	−2.99
Total	17	26	Mean	−20.3	−18.9	0.062	0.047	−2.82	−2.91
			Min	−29.1	−24.4	0.000	0.005	−3.29	−3.60
			Max	−16.1	−12.9	0.119	0.131	−1.79	−2.18

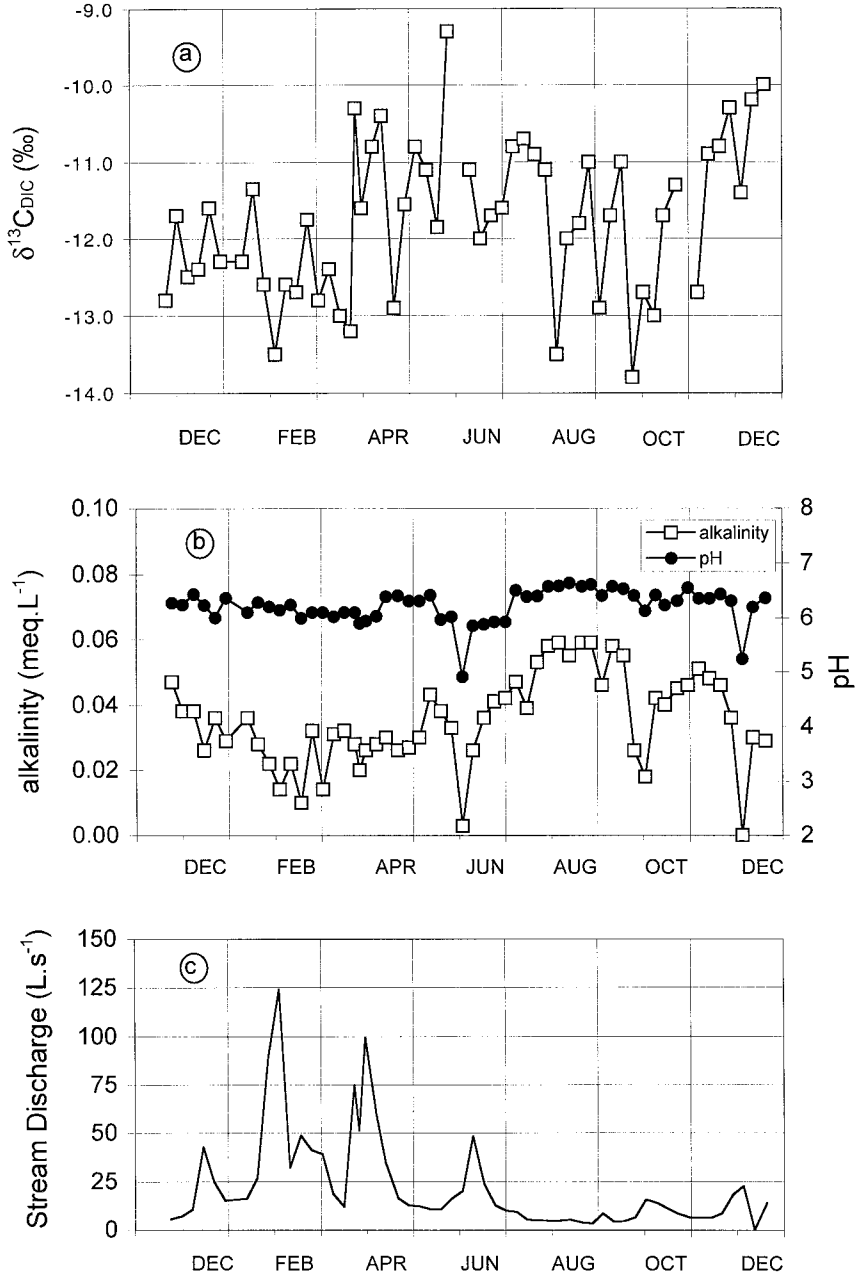


Fig. 6. Weekly fluctuations (22/11/94 to 13/12/95) of (a) $\delta^{13}C_{DIC}$, (b) alkalinity and pH and (c) stream discharge in the Strengbach stream at the outlet from the catchment (site RS).

and, although it tends to be more depleted in winter than in the spring and summer, the trend is not significant. For the upper part of the main stream and for secondary stream water, more depleted $\delta^{13}C_{DIC}$ values have been observed (up to −19.6‰). This overall downstream enrichment in ^{13}C is evident across the entire catchment (Table 3). The most depleted $\delta^{13}C_{DIC}$ values were recorded in the stream

Table 3
Average values and ranges of $\delta^{13}C_{DIC}$, HCO_3^- concentrations, pCO_2 and pH in stream water for each sampling site, as calculated from the measurements of the 5 sampling campaigns (sampling sites are listed in increasing order of the estimated distances from springs)

Sampling site		$\delta^{13}C_{DIC}$ (‰ PDB)	HCO_3^- (meq l^{-1})	log pCO_2 (atm.)	pH
R3	Mean	−17.3	0.000	n.c.	5.00
	Min	−18.5	0.000	n.c.	4.89
	Max	−16.6	0.000	n.c.	5.25
RUZS	Mean	−17.2	0.019	−2.79	5.83
	Min	−19.6	0.000	−2.91	5.63
	Max	−15.8	0.049	−2.73	6.24
BH	Mean	−10.6	0.092	−2.86	6.58
	Min	−12.4	0.058	−2.95	6.27
	Max	−9.3	0.114	−2.69	6.79
R1	Mean	−15.9	0.025	−2.86	6.01
	Min	−17.3	0.015	−2.93	5.81
	Max	−14.4	0.035	−2.82	6.19
RH	Mean	−13.4	0.042	−2.90	6.23
	Min	−15.6	0.018	−3.04	5.84
	Max	−11.4	0.058	−2.77	6.62
RAZS	Mean	−11.7	0.026	−2.99	6.17
	Min	−13.3	0.016	−3.09	5.92
	Max	−10.7	0.035	−2.90	6.38
RS	Mean	−10.9	0.035	−2.94	6.21
	Min	−12.5	0.020	−3.09	5.90
	Max	−10.0	0.053	−2.78	6.44

draining the upper horizons of the saturated area (RUZS), which is consistent with measurements in the piezometers of the same area.

4. Factors controlling the $\delta^{13}C$ values of DIC

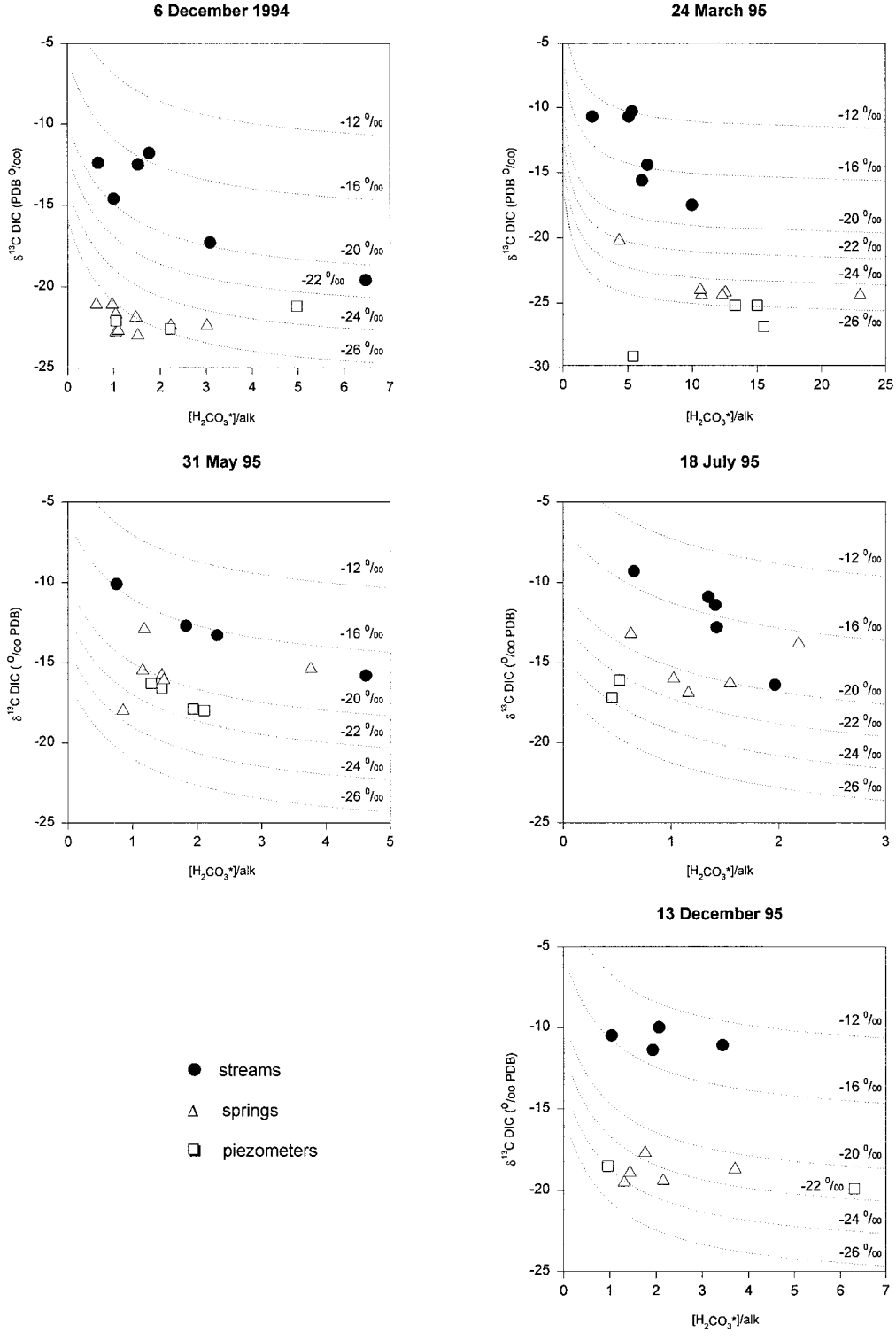
4.1. Influence of the CO_2 partial pressure (pCO_2)

The $\delta^{13}C_{DIC}$ values of a given sample can be expressed as a function of the concentrations of aqueous CO_2 ($[H_2CO_3^*]$) and of bicarbonate ions ($[HCO_3^-]$), together with their respective $\delta^{13}C$ values ($\delta^{13}C_{H_2CO_3^*}$ and $\delta^{13}C_{HCO_3}$), in the manner (Stumm and Morgan, 1981):

$$\delta^{13}C_{DIC} = \left([H_2CO_3^*] \times \delta^{13}C_{H_2CO_3^*} + [HCO_3^-] \times \delta^{13}C_{HCO_3^-}\right) / \left([H_2CO_3] + [HCO_3^-]\right) \quad (11)$$

At isotopic equilibrium, $\delta^{13}C_{H_2CO_3^*}$ and $\delta^{13}C_{HCO_3^-}$ are constant and determined by the isotopic composition of soil gaseous CO_2. Thus, the variation of $\delta^{13}C_{DIC}$ is only controlled by the proportions of $H_2CO_3^*$ and HCO_3^- in the solution.

The relationships between the $\delta^{13}C_{DIC}$ in surface water of the Strengbach catchment and the ratio $([H_2CO_3^*]/[HCO_3^-])$ are plotted in Fig. 7 for the five sampling dates. In the same diagram, we have plotted the theoretical variations of $\delta^{13}C_{DIC}$ in equilibrium with different isotopic composition of soil CO_2, as calculated from Eq. (11) and from the isotopic enrichment factors expressed in Eqs. (8) and (9) of Table 1. Two distinctive groups of points can be clearly observed: (i) the springs and piezometers, in apparent isotopic equilibrium with a ^{13}C depleted gaseous CO_2, and (ii) the stream water, in apparent isotopic equilibrium with ^{13}C enriched gaseous CO_2. Within these two groups, at a given sampling date, the $\delta^{13}C_{DIC}$ values appear to be more or less con-


6 December 1994
24 March 95
31 May 95
18 July 95
13 December 95
δ13C DIC (PDB °/oo)
δ13C DIC (°/oo PDB)
[H2CO3*]/alk
-12 °/oo
-16 °/oo
-20 °/oo
-22 °/oo
-24 °/oo
-26 °/oo
streams
springs
piezometers

trolled by the relative ratio of $H_2CO_3^*$ to HCO_3^-. Note nevertheless, that the trends of points often cross the theoretical curves, which should indicate that the isotopic composition of the gaseous phase is spatially changing. Such changes are feasible for spring water and piezometers, while, for stream water, non-equilibrium conditions between the gaseous phase and the solution are a more likely alternatives. Indeed, as it can be seen in Table 3, $\delta^{13}C_{DIC}$ values generally increases with increasing distance from springs. This is probably a result of isotopic exchanges between stream DIC with atmospheric CO_2, which occurs together with the evasion of dissolved CO_2 to the atmosphere.

4.2. Influence of soil respiration rates

Comparing the plots for the different sampling dates (Fig. 7), it can be noted that for springs and piezometers the $\delta^{13}C_{DIC}$ seems to be in equilibrium with a gaseous phase which changes with season. In December and March, the DIC appears to be in equilibrium with highly ^{13}C depleted gaseous CO_2 (-25 to -27‰), whereas, in May and July, it seems to be in isotopic equilibrium with CO_2 that has $\delta^{13}C$ around -20‰. This suggests that in winter, soil CO_2 has an isotopic signature similar to that of vegetation, without any fractionation or contamination by atmospheric CO_2, while in summer, the soil CO_2 is fractionated by $+4$ to $+5$‰. These observations are in disagreement with these of Solomon and Cerling (1987) and Cerling et al. (1991) with ^{13}C depleted soil CO_2 accompanying high pCO_2 in summer and atmospheric ^{13}C enrichment and low pCO_2 in winter.

In the Strengbach case, the seasonal variations of $\delta^{13}C$ of the soil CO_2 are better explained by ^{13}C enrichment (up to $+4.4$‰) that is induced by molecular diffusion of gaseous CO_2 throughout the soil pores (Craig, 1954; Dörr and Münnich, 1980; Cerling, 1984; Cerling et al., 1991). This process is more pronounced in summer than in winter, in accord with observations of Dörr and Münnich (1980) and Davidson (1995). In winter, respiration rate being almost equal to zero, molecular diffusion and accompanying isotope fractionation are non-existent. As a result, the isotopic composition of CO_2 is similar to that of the precursor SOM.

4.3. Isotopic equilibration of stream DIC with atmospheric CO_2

Seasonal variations of the $\delta^{13}C_{DIC}$ in the stream at the outlet of the catchment (Fig. 6), are small. We have no explanation for these small oscillations (± 2‰ around -12‰), since we did not observed any clear relationships between the isotopic signal and other parameters, such as the stream discharge, the pH, alkalinity (Fig. 6), pCO_2 in the water, or the concentration of dissolved organic carbon (DOC) that could be partly oxidized in the water.

Fig. 7 shows that the DIC in the stream, in contrast to springs, is not in isotopic equilibrium with the soil CO_2. The general enrichment in ^{13}C of the DIC is caused by the evasion of the isotopically light aqueous CO_2 into the atmosphere and by isotopic equilibration with the atmospheric CO_2 as well. The latter can be modeled by Eq. (11) and by the isotopic fractionation factors expressed as a function of the temperature in Eqs. (8) and (9) (Table 1). The theoretical variations of $\delta^{13}C_{DIC}$ values in the stream can thus be calculated with water temperature weekly recorded in the Strengbach catchment. In our calculations, we have also used the monthly mean $\delta^{13}C$ of the atmospheric CO_2 calculated from the data recorded at Schauinsland, Black Forest, Germany (Levin et al., 1994), about 50 km southeast of the basin. This locality is at a similar altitude and has comparable vegetation cover.

We have calculated two theoretical values of $\delta^{13}C_{DIC}$ with the following assumptions: (i) The entire stream DIC is in isotopic equilibrium with the atmospheric CO_2 (the total equilibrium working hypothesis), and (ii) only the aqueous CO_2 ($H_2CO_3^*$) is in isotopic equilibrium with the atmospheric CO_2 (the partial equilibrium working hypothesis). The resulting theoretical $\delta^{13}C_{DIC}$ are represented in Fig. 8, together with the observed $\delta^{13}C_{DIC}$ values. This

Fig. 7. Evolution of $\delta^{13}C_{DIC}$, vs. $[H_2CO_3^*]$/alkalinity ratio during sampling campaigns, compared to the theoretical evolution of the $\delta^{13}C_{DIC}$ in isotopic equilibrium with different soil CO_2 phases (calculated from Eqs. (8), (9) and (11), see text for explanation).

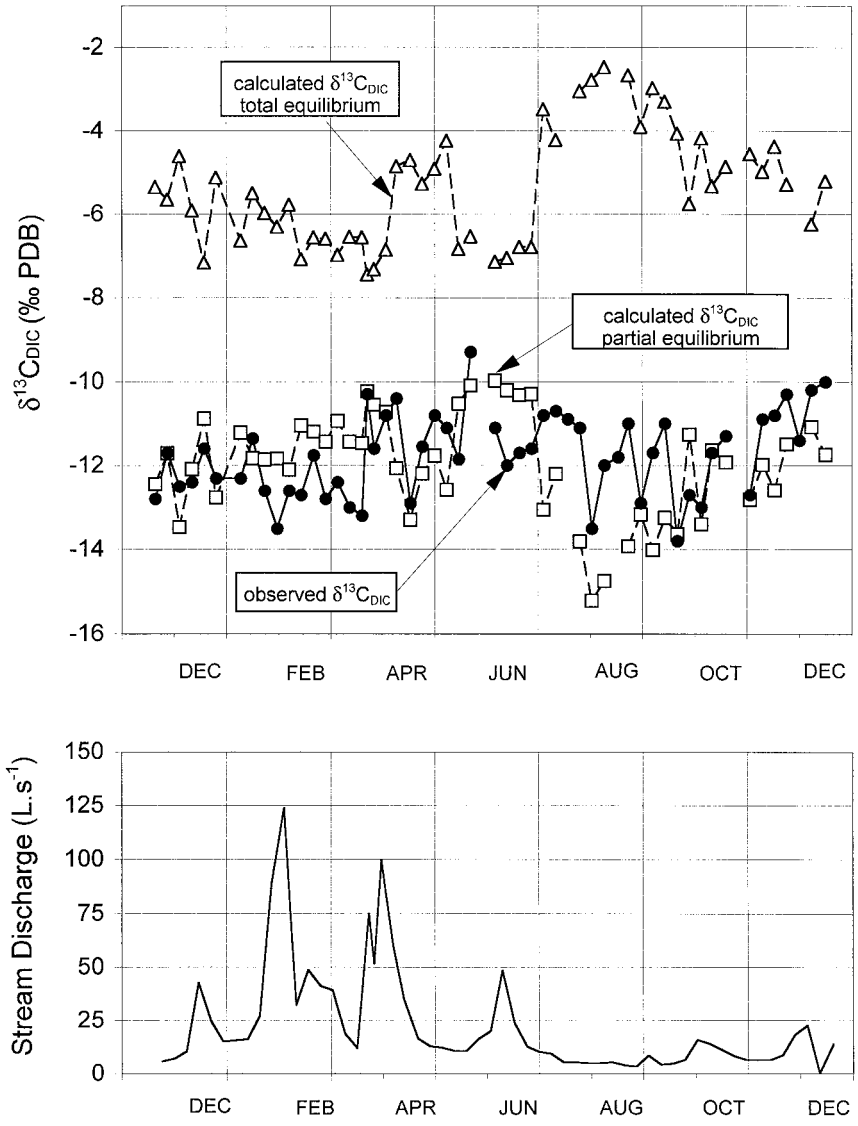


Fig. 8. Temporal fluctuations of $\delta^{13}C_{DIC}$ in the Strengbach stream at the outlet of the catchment December 1994 to December 1995), compared to theoretical predictions of the $\delta^{13}C_{DIC}$ (calculated from Eqs. (8), (9) and (11) and considering total or partial isotopic equilibrium with atmospheric CO_2, see text for explanation).

comparison shows clearly that the partial equilibrium hypothesis is much more consistent with the observations, suggesting that the isotopic exchange between aqueous CO_2 ($H_2CO_3^*$) and atmospheric CO_2 is easier and/or faster than that between bicarbonate ions (HCO_3^-) and atmospheric CO_2. However, this calculated $\delta^{13}C_{DIC}$ is somewhat overestimated for high flow periods (in winter or in June for example) and underestimated for low flow period (in summer). Two hypothesis could explain these differences: (i) the isotopic exchange with atmosphere could be enhanced during low flow periods because of a longer residence time of the water in the stream, whereas a shorter residence time during high flow period would lead to minimize isotopic exchange; (ii) the contribution of the saturated area (bringing

light DIC) relative to the rest of the catchment is higher during high flow periods than during low flow periods. Idir et al. (1998) have estimated that the saturated area contributes to 20–30% of the stream discharge at the outlet of the catchment for flood periods. Nevertheless, there are no additional evidence to support either hypothesis.

5. Conclusions

The isotopic composition of the dissolved inorganic carbon (DIC) in the stream at the outlet of the Strengbach catchment is rather uniform, with a mean $\delta^{13}C_{DIC}$ value of $-11.8‰$, despite the fact that the DIC in the Strengbach surface water originates from the soil CO_2 and ultimately from the decay of soil organic matter. The DIC in the spring water is in equilibrium with the soil CO_2, with $\delta^{13}C$ varying from $-20‰$ in the summer to $-26‰$ in winter. This could be a result of, mainly, isotopic fractionation induced by enhanced molecular diffusion of CO_2 through the soil pores in summer due to high respiration rates.

In contrast, the stream DIC is not in isotopic equilibrium with a any specific gas phase, and the ^{13}C enrichment of the stream DIC can reflect evasion of lighter aqueous CO_2 into the atmosphere, coupled with a partial isotopic equilibration with the atmospheric CO_2. Isotopic data suggest that it was the aqueous CO_2 (not all DIC) that equilibrated with atmospheric CO_2. These results clearly show that isotopic composition of the DIC can be significantly affected by atmospheric contamination, without attaining an equilibrium, and this has to be taken into account in interpretation of the riverine $\delta^{13}C_{DIC}$.

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^{13}C composition of dissolved organic carbon in upland forested catchments of the Morvan Mountains (France): Influence of coniferous and deciduous vegetation

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Stream water;
Soil organic matter;
Soil solution

Summary One of the main environmental changes caused by human activities is that of land use. These changes influence the quantity and quality of the dissolved organic matter (DOM) fluxes through the vegetation–soil–stream system. The aim of this work is to evaluate the influence of the substitution of native deciduous forests by well managed coniferous forests on dissolved organic carbon (DOC) fluxes and their associated carbon isotopic composition ($\delta^{13}C_{DOC}$). DOC fluxes and $\delta^{13}C_{DOC}$ were monitored for 2 years in the streams of four similar upland forested catchments in the Morvan Mountains (France). Mean annual DOC concentrations and fluxes were 2–4 times lower in streams in catchments with predominant coniferous vegetation than in those with deciduous vegetation. $\delta^{13}C_{DOC}$ values were lower by 0.5–1.0‰ in the stream under deciduous vegetation (−28.3‰ to −30‰) than in the other streams (−27.1‰ to −29.5‰). Furthermore, stream DOC was ^{13}C depleted compared to the isotopic composition of the soil organic matter (SOM). This ^{13}C depletion was higher under deciduous cover where SOM was enriched in ^{13}C with increasing depth, producing ^{13}C depleted solute fraction. Under coniferous cover, no significant isotopic differentiation was observed between the solute and solid phase in the soil. Our results show that the $\delta^{13}C_{DOC}$ in stream is marked by the vegetation cover because of differences in the degradation pathway and dynamics of SOM. Besides, it

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means that the substitution of deciduous forests by coniferous plantations may significantly modify the chemical composition of DOC in streams.

Introduction

Dissolved organic matter (DOM) is an important component of aquatic ecosystems where it has different functions. It is a significant source of carbon and energy in stream ecosystems (Tipping et al., 1997; Ludwig et al., 1996; Maurice and Leff, 2002) and it filters solar UV radiations (Dahlen et al., 1996; Zhuo and Jones, 1997). It also supports the mobility of pollutants such as trace metals and hydrophobic organic compounds (Cabaniss and Shuman, 1988; Piccollo, 1994). The easiest means to estimate DOM concentration is to measure dissolved organic carbon (DOC) concentrations. DOC composes about 20% of the 1×10^{15} g of carbon that is annually transferred by rivers from the continents to the oceans (Meybeck, 1993; Ludwig et al., 1996, 1998). This DOC (or DOM) mainly comes from the degradation of organic matter in the soil (Bishop and Pettersson, 1996; Ludwig, 1996; Hongve, 1999) and, to a lesser degree, from the contribution of biological processes occuring in the stream (Meybeck, 1993). DOC transfer is influenced by climate (Moore, 1989a,b; Grieve, 1994; Ludwig, 1996; Tipping et al., 1997; Fillion-Guigues, 1998; Worrall et al., 2004), soil type (Dawson et al., 2001; Grieve and Marsden, 2001), vegetation cover (Moore, 1989a,b; Hongve, 1999; Ross et al., 1999; Neal et al., 2005) and microbial activity (Aiken et al., 1985).

One of the most visible environmental changes caused by human activity is that of land use. It strongly influences both the quantity and the quality of DOM fluxes through the vegetation–soil system toward rivers and oceans. In rural and mountainous areas of most industrial countries, various changes in land use have affected landscapes over the last century: hedge removal, tree felling and increase in fallow lands. The most common practice was the substitution of native or more or less abandoned deciduous forests by well managed coniferous plantations of spruce and Douglas fir. These changes affected soil organic matter (SOM) dynamics (Guellec, 1982; Andreux et al., 2002), especially the rate of litter decomposition and microbial activity (Lévèque et al., 1998; Berg, 2000). As a consequence, the nature of dissolved compounds in soil and stream water can be strongly modified (Martin, 1979; Lelong et al., 1988; Rosén et al., 1996).

As the chemical composition of DOM is difficult to elucidate, its natural carbon isotopic composition ($^{13}C/^{12}C$) appears to be an interesting tool to monitor DOM in stream and soil solutions. This tool has been mainly used for tracing the fate and turnover of solid SOM in cases with sharp transition from C3 to C4 vegetation (Balesdent and Wagner, 1988; Desjardins et al., 1994 among others) and vice versa (Schwartz et al., 1986; Martin et al., 1990). At the scale of river basins, some studies have used the stable isotope composition of DOC to determine the origin and fate of organic carbon in river water (Raymond and Bauer, 2001; Bianchi et al., 2004; Ziegler and Brisco, 2004). In these studies, DOC from SOM dissolution has generally been assumed to have the same isotopic signature as SOM and a possible isotopic differentiation between DOC and SOM was never considered.

There is some evidence that the isotopic composition of soil DOC could vary with time and space and that it may not exactly reflect the isotopic composition of SOM, even in watersheds with only C3 plants. The ^{13}C composition of SOM changes during its decay because ^{12}C is preferentially used by decomposers, resulting in an enrichment in ^{13}C of the remaining SOM (Andreux et al., 1990; Martin et al., 1990; Desjardins et al., 1994; Balesdent and Mariotti, 1996; Boutton, 1996; Koutika et al., 1997 among others). Because of these processes, soil organic constituents can be ^{13}C-enriched by 1.5–4.3‰ relative to homogenous plant constituents (Lichtfouse et al., 1995). This enrichment may be controlled by factors such as the quality of the initial material (Agren et al., 1996), the degree of its degradation (Blair et al., 1985) and the diversity of decomposers (Andrews et al., 2000). As a result, soil CO_2 and DOC produced during the decomposition should be depleted in ^{13}C compared to SOM. Moreover, as inferred from the analyses of Agren et al. (1996) showing that the ^{13}C enrichment of SOM is stronger when it comes from deciduous species, CO_2 and DOC should be more depleted in ^{13}C in soils under deciduous vegetation than under coniferous vegetation. However, concerning soil CO_2, it is often observed that its isotopic composition is nearly the same as that of the SOM it comes from (Amundson et al., 1998; Andrews et al., 2000). Concerning DOC, to our knowledge, no studies have attempted to evaluate the spatial and temporal variations in its stable isotope composition in soils and upland streams. Investigating the isotopic composition of DOC in a soil–water system and determining how it is related to the isotopic composition of SOM is a key point in understanding the variability of the isotopic signature of DOC in stream and river water. In addition, such observations should provide very useful information in tracing DOC production, degradation and transfer in hydrosystems using stable carbon isotopes.

This work aims at evaluating the influence of the substitution of deciduous forest by coniferous plantations on fluxes and isotopic composition of DOC in temperate forest ecosystems. This paper specifically addresses the question of changes in the isotopic composition of DOC in relation to the origin and degradation of the solid organic matter. It also attempts to assess whether the isotopic changes in soil DOC are revealed by the spatial and temporal variations of the isotopic signature of stream DOC in small forested watersheds.

Materials and methods

The concentration and the isotopic composition of DOC were monitored bi-monthly for two years in the streams of four small forested catchments in the Morvan Mountain (France) for which the only variable parameter is the vegetation cover: two catchments are covered by conifers, one catchment is mainly occupied by a native deciduous forest and one is covered by a mixed (deciduous and coniferous) cover. Spatial and

temporal variations in the isotopic composition of the stream DOC were compared to those of solid and water soluble organic material from the vegetation—soil system.

Study area and site description

The four catchments (Fig. 1) are located in the Natural Regional Park of Morvan, in Burgundy (Centre-East France). These small catchments (less than 1 km^2, see Table 1) are all located in the same geographic area between 425 and 675 m a.s.l, and exhibit the same characteristics of soil, climate and geology. The bedrock is formed by the alkaline granite of ''La Pierre qui Vire''. The soil is a humus-rich acid brown soil (dystric Cambisol, Dekkers et al., 1998) of variable thickness (from 0.4 to 1 m), with a low pH and a sandy loam texture. The climate is continental, with oceanic influence. It is characterized by quite large precipitation

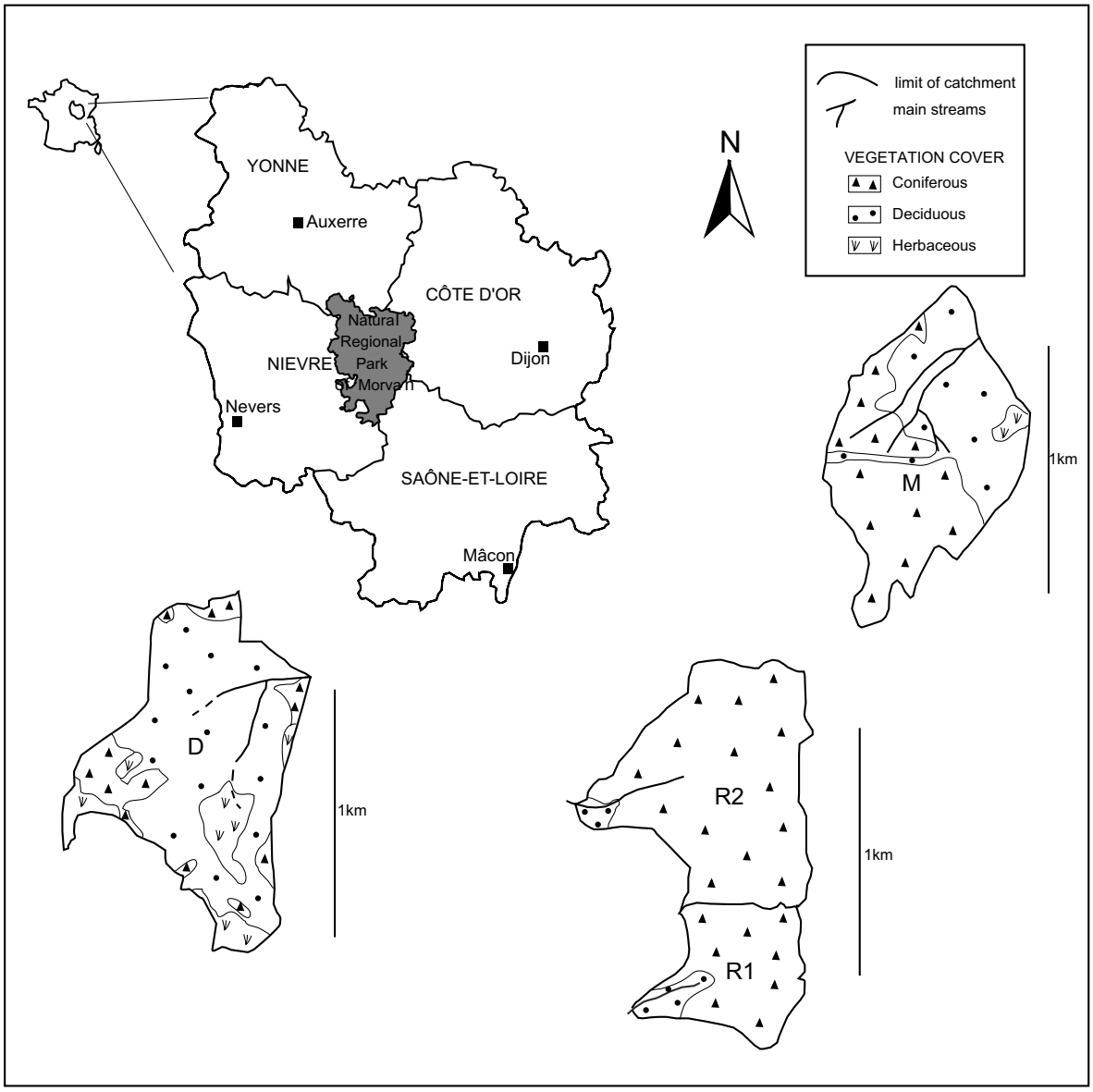

Figure 1 Site location and vegetation cover of the four studied catchments (see also Table 1 for more information).

Table 1 Vegetation cover and morphological characteristics of the four studied catchments

Catchment	Main vegetation cover	Area (ha)	Slope (%)	Altitude (m a.s.l.)		
				Maximum	Minimum	Average
D	Deciduous: oak and beech	77.8	11.36	665	562	636
M	Mixed: oak, pine, spruce and douglas	62.8	8.31	500	425	471
R1	Coniferous: spruce and douglas fir	28.6	7.24	567	499	551
R2	Coniferous: spruce and douglas fir	69	7.98	561	483	537

(1300 mm/y on average over the 1990–2000 period) and contrasting temperatures (2.5 °C in January and 19 °C in August with an annual mean of 16.5 °C over the same period).

In contrast to this homogeneity, the four watersheds have different vegetation. Two catchments (R1 and R2) were planted with conifers after clear-cutting of the original forest 40 years ago (Fig. 1). Catchment R1 is dominated (83% of its area) by a coniferous forest composed of spruce and Douglas fir. Catchment R2 is less homogeneous, with a 40 years old coniferous forest on 61% of its area and a younger (10-year-old) Douglas fir stand on 32% of its area. In both catchments, the rest of the area is occupied by a mixed forest and by a hydrophilic deciduous vegetation along the stream. By contrast, catchment D is covered by the original deciduous forest of oak and beech on 70% of its area (Fig. 1). The rest of the area is occupied by grassland (16%) and several small young coniferous planting (14%). Finally, catchment M has a rather mixed composition with a forest of oaks and 15% of pines on 46% of its area, a 40-year-old plantation of spruce and Douglas fir on 52% of its area, and a small herbaceous cover on the rest of the area.

Sampling and analytical methods

Plant, litter and soil material sampling

In order to characterize the isotopic composition of organic matter in the different compartments of the catchments, solid organic material was sampled. Two soil profiles representative of each vegetation cover (native oak and beech forest vs. douglas fir plantation) were sampled as followed: the litter and five to six soil layers of 10 cm each were collected and brought to the laboratory. One soil profile was located under oaks in the deciduous tree area of catchment M. The second one was located in a 40 years old plantation of spruce and Douglas fir in catchment R1. The litter material was separated into two layers: (i) material of the year and (ii) decomposing material of previous years. Fresh elements of the vegetation cover (leaves or needles and twigs) were also collected in the vicinity of the soil pits for analyses. Soil samples were dried, sieved at 2 mm, separated with a sample divider and homogenised by grinding. The litter material was dried, manually sorted to eliminate pieces of branches, and finally milled.

Stream water, litter and soil solutions sampling

Four litres of stream water was sampled and stream discharge was measured bi-monthly from February 1999 to February 2001, at the outlet of each catchment.

Extraction of solution was performed on the litter layer and on the humus-rich layer (0–5 cm) sampled under each kind of vegetation. Litter solutions were obtained by stirring samples for 18 h in 5 volumes of deionised water with a magnetic rod. On the humus-rich soil samples, the moisture was brought to 60% using de-ionised water and soil solutions were collected by a low tension method under nitrogen at 1000 hP pressure for 4 h.

Stream, litter and soil solution samples were filtered through 0.45 μm Millipore membranes pre-rinsed with deionised water and stored in the dark at 4 °C as soon as possible after collection. All the dissolved inorganic carbon (aqueous CO_2, HCO_3^- and CO_3^{2-}) was removed by acidification of the collected waters with HCl, decreasing its pH to values lower than 3.

About 2 l of each acidified sample was freeze-dried for the determination of the isotopic composition of the DOC. The resulting powders, with various colours and textures, were then homogenised by grinding in an agate mortar.

Analytical methods

Stream DOC concentrations were determined on the acidified samples using a Shimadzu TOC 5000 analyser. All solid samples (plant, litter and soil material, freeze-dried solutions) were analysed for C and N contents by dry combustion using a Carlo Erba analyser. Stable isotope composition was determined using a Micromass Isochrom EA continuous flow mass spectrometer with an internal precision of 0.2 ‰, calibrated with a isotope standard of graphite with a δ^{13}C value of −16.1‰ (±0.2‰). Each sample was measured three times and the result was an average of this replicate. To avoid ''size effects'', weights of samples were adapted to contain approximately the same quantity of carbon.

Results

Isotopic composition of organic matter in the catchments

Table 2 shows the isotopic composition of organic matter in different parts of the vegetation–soil system of each catchment. All values were typical of C3 vegetation and related soils (Deines, 1980), with δ^{13}C values ranging between −31.0 and −25.1‰. Fresh organic matter (twigs and leaves) from the deciduous vegetation (catchments D and M) showed a small depletion in ^{13}C of 0.4–0.5‰, compared to that of the same materials (twigs and needles) from the coniferous vegetation (catchments R1 and R2).

Conversely, in the litter compartment (Table 2), δ^{13}C values did not show such differences. Due to the mineralisation of labile organic matter (Desjardins et al., 1994), the decomposing litter material was enriched in ^{13}C compared to fresh

Table 2 δ^{13}C values (‰) of organic matter in fresh aerial material, litter and soil layers sampled in the four catchments

Catchment	Fresh aerial materials		Litter	Soil					
	Twig	Leaf/Needle		−5 cm	−15 cm	−25 cm	−35 cm	−45 cm	−55 cm
D			−28.0	−26.6	−26.5	−26.3	−26.2	−26.1	−25.7
M[a]	−28.7	−31.0	−27.2	−26.3	−26.2	−26.0	−25.8	−25.5	−25.1
R1			−26.3	−26.5	−26.2		−26.5		−26.2
R2	−28.3	−30.5	−27.7	−26.3	−26.5	−26.3	−26.4	−26.3	

[a] On catchment M, litter and soil profile have been sampled in a deciduous vegetation area.

aerial parts, with $\delta^{13}C$ values ranging between −26.3 and −28.0‰.

In the four soil profiles, the $\delta^{13}C$ values of SOM ($\delta^{13}C_{SOM}$) increased slightly (not more than 1.0 delta unit) with increasing depth as reported by many authors (e.g. O'Brien and Stout, 1978; Andreux et al., 1990; Balesdent and Mariotti, 1996; Amiotte-Suchet et al., 1999). However, this ^{13}C enrichment did not show the same pattern in each of our studied soil profiles (Table 2). In the first centimetres, no clear difference in $\delta^{13}C$ values between profiles was found, which could be related to the homogenisation of organic matter during its incorporation in the soil mineral fraction. Then, between −5 and −55 cm, an enrichment of about 1‰ was noticed under deciduous cover (profiles of catchment D and M), whereas no enrichment was observed under coniferous cover (profiles of catchments R1 and R2).

Isotopic composition of dissolved organic carbon in stream water

DOC contents of stream water

Figure 2 shows the variations of the specific stream discharge and DOC concentrations from February 1999 to February 2001 in the four catchments. The stream discharge followed the same seasonal variations in the four catchments, with high water levels in winter and spring and low water levels in summer. However, higher values of specific stream discharge were reached in catchment D compared to the three other catchments, together with stronger flow amplitude. This is probably because catchment D was located at a slightly higher altitude and had steeper slopes (Table 1).

DOC concentrations (Table 3 and Fig. 2) varied from 1.8 to 4.4 mg l^{-1} on average and reached a maximum of 13 mg l^{-1} on catchment M. These values are typical of stream water draining small forested catchments (Moore, 1989a,b; Schiff et al., 1990; Tipping et al., 1997). There was no clear relationship with stream discharge (Fig. 2a), contrary to statements by Grieve (1990) or Tipping et al. (1997). However, the same temporal variations were observed on the four catchments. The DOC concentrations were generally higher during the growing period (May to October) than during the dormant period (November to April), as already observed in other forested catchments (Moore, 1989b; Grieve, 1994; Ludwig, 1996; Tipping et al., 1997; Kaiser et al., 2001a) or in catchments with peaty soils

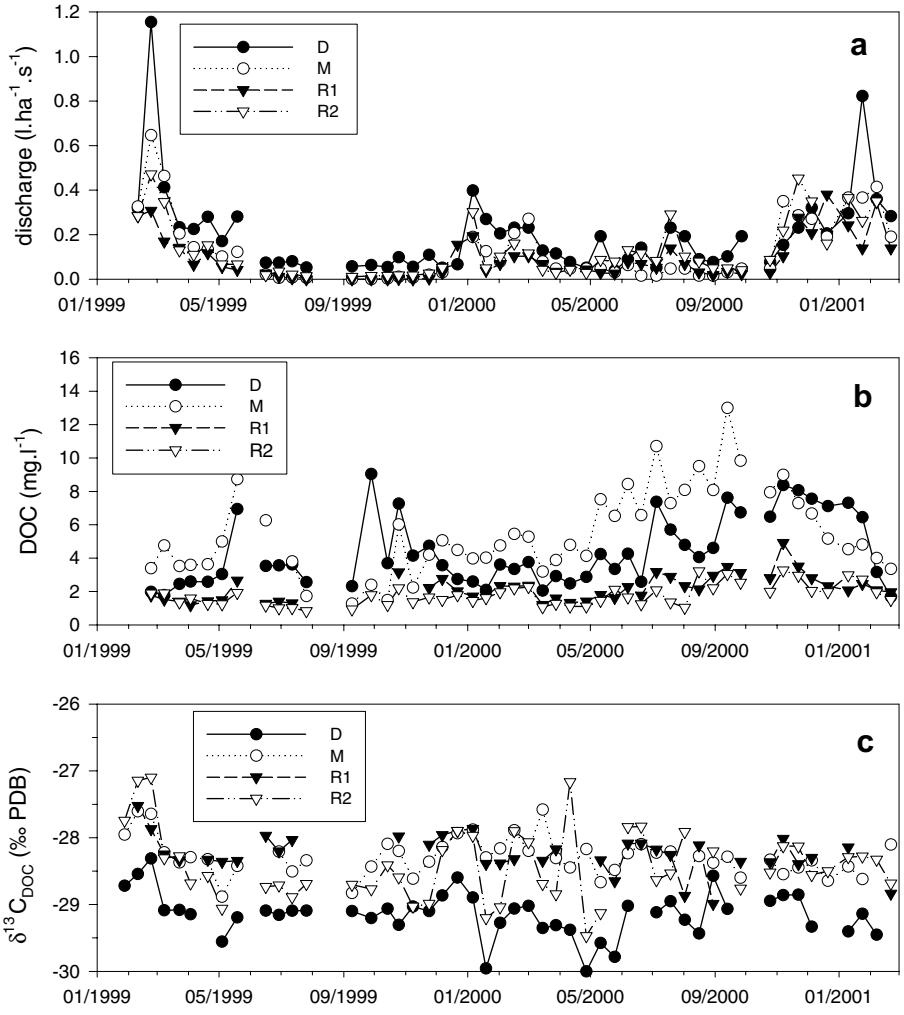

Figure 2 Seasonal variations of (a) the stream discharge, (b) the concentrations of the dissolved organic carbon (DOC) in streamwater and (c) the isotopic composition of stream DOC ($\delta^{13}C_{DOC}$) at the outlet of the four catchments.

Table 3 Average concentration (mg l^{-1}), annual fluxes (kg ha^{-1} y^{-1}) and $\delta^{13}C$ values (‰) of Dissolved Organic Carbon (DOC) in streamwater at the outlet of the four catchments

		D	M	R1	R2
DOC concentrations (mg l^{-1})	wm	3.9	4.4	1.9	1.8
	min	1.7	1.3	1.2	0.8
	max	9.0	13.0	4.9	3.3
	sd	2.1	2.5	0.8	0.6
DOC fluxes (kg ha^{-1} y^{-1})	m	25.7	21.0	9.4	6.2
	min	4.1	0.5	0.3	0.1
	max	167.3	104.0	54.3	25.7
	sd	28.2	21.4	11.9	6.9
$\delta^{13}C$ (‰)	m	−29.1	−28.3	−28.2	−28.4
	min	−30.0	−28.9	−29.0	−29.5
	max	−28.3	−27.6	−27.5	−27.1
	sd	0.3	0.3	0.3	0.5

wm: discharge weighted mean; m: arithmetic mean; min: minimum value; max: maximum value; sd: standard deviation.

(Grieve, 1991). Many authors (Christ and David, 1996; Tipping et al., 1997; Anderson et al., 2000; Kaiser et al., 2001a among others), explained this seasonal contrast mainly by the increase in DOC production in soils during the summer, as a result of the enhancement of SOM degradation under humid and warm conditions. As an indication of this climatic influence, DOC concentrations were lower during the dry summer of 1999 than during the rainy summer of 2000 (Fig. 2b).

Even though a general temporal trend could be observed, the average DOC concentrations and fluxes differed from one catchment to another. First of all, mean annual DOC concentrations (Table 3) were higher in the streams under deciduous (D) or mixed (M) vegetation (3.9–4.4 mg l^{-1}, respectively) than in those under coniferous (R2 and R1) vegetation (1.8–1.9 mg l^{-1}, respectively). Moreover, the value ranges were much higher under deciduous (from 1.3 to 13.0 mg l^{-1} in the stream of catchment M) than under coniferous vegetation (from 1.2 to 4.9 mg l^{-1} in the stream of catchment R1). Thus, seasonal variations were very slight in the streams in catchments R1 and R2 (Fig. 2b). In the same way, mean DOC fluxes were 2–3 times higher in catchments D and M than in catchments R1 and R2 (Table 3). These differences in average DOC concentrations and fluxes were statistically analysed using a non parametric multiple comparison procedure (Kruskal–Wallis test and Dunn's post-test). It showed that differences between average values were not significant ($p > 0.01$) for catchments D and M on one hand and for catchments R1 and R2 on the other hand. It also showed that average values were very significantly different ($p < 0.01$) between catchments under deciduous or mixed vegetation (D and M) and catchments under coniferous vegetation (R1 and R2).

These relationships between DOC concentrations and fluxes and the vegetation cover could be explained by the ability of litter material from deciduous trees to produce higher quantities of soluble organic matter. For example, Hongve (1999) calculated that about 13% of an initial amount of deciduous litter was converted into dissolved organic matter, against only 2% for coniferous litter.

$\delta^{13}C_{DOC}$ variations in stream water

The ^{13}C abundance of DOC ($\delta^{13}C_{DOC}$) in stream water of the four catchments ranged from −30‰ to −27.1‰ (Fig. 2c), which reflects the original isotopic composition of SOM (see Table 2). Although these $\delta^{13}C_{DOC}$ values were highly variable, no clear seasonal trend was observed. As regards the spatial variability of $\delta^{13}C_{DOC}$, values for catchment D were always more negative than those of other catchments (Fig. 2). This difference was highly significant ($p < 0.001$, Kruskal–Wallis test followed by Dunn's multiple comparison test). For catchment D, $\delta^{13}C_{DOC}$ varied between −28.2‰ and −30‰, whereas DOC was slightly richer in ^{13}C in the three other streams (M, R1 and R2) with $\delta^{13}C_{DOC}$ values ranging from −27.1 ‰ to −29.5‰ (Table 3).

Isotopic composition of dissolved organic carbon in litter and soil solutions

The isotopic composition of DOC was measured in seepage water, i.e. in soil solutions and in litter solutions. Seepage solutions were extracted from the litter layer and from the 0–5 cm soil layer sampled under coniferous vegetation (in a 40 years old Douglas plot of catchment R1) and under deciduous vegetation (in an adult beech + oak plot of catchment M). The results are synthesized in Figure 3 where the isotopic composition of DOC is compared to that of the solid fractions shown in Table 2. Under the beech and oak forest (Fig. 3a), the solutions were always more depleted in ^{13}C than in solid sources of litter and soil. Conversely, under coniferous vegetation (Fig. 3b), the litter and its litter solution had the same isotopic composition while the soil solution was very slightly enriched in ^{13}C compared to its solid sources. As a result, soil DOC was richer in ^{13}C in coniferous catchments than in deciduous catchments.

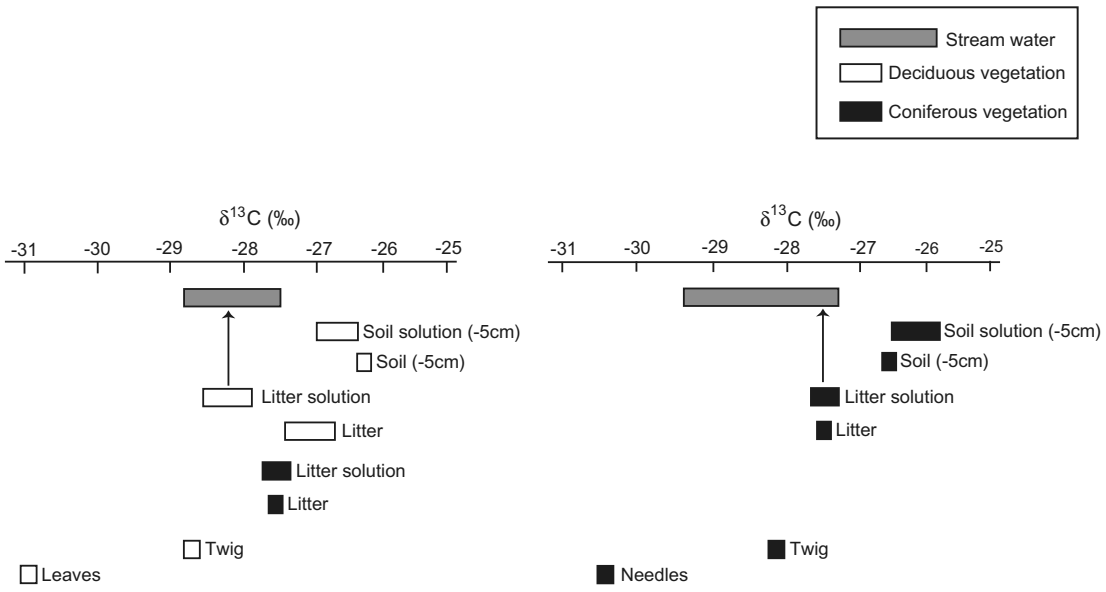

Figure 3 Carbon isotopic composition ($\delta^{13}C$) of solid and dissolved organic matter in the different compartments of catchments M and R1. In catchment M (scheme (a), mixed vegetation), isotopic composition of solid and dissolved organic matter of the litter and the upper soil layer have been measured on material sampled under oak trees. For comparison, isotopic composition of organic matter of litter from coniferous vegetation (catchment R1) has been represented on this scheme.

Discussion

Our study showed that the substitution of deciduous cover by coniferous vegetation in the Morvan region strongly modified DOC concentrations and fluxes as well as the DOC composition. Mean annual DOC concentrations were 2 times lower in streams of coniferous catchments than in those under deciduous vegetation. Moreover, because of runoff differences, mean annual DOC fluxes were 3–4 times lower at the outlet of coniferous catchments than under deciduous cover.

The quality of the DOC seemed also to be affected by vegetation changes, as revealed by the isotopic composition of dissolved and solid organic matter in different compartments of each system.

First of all, the isotopic composition of fresh plant material did not significantly differ between vegetations. Even though it was richer in ^{13}C by 0.5‰ for Douglas fir compared to deciduous cover (Table 2), its variability seemed to be greater for one plant of the same species than between plants of different species. In fact, the highest $\delta^{13}C$ difference (about 2.3‰, see Table 2) appeared in the same kind of vegetation (between aerial parts, namely twigs and leaves or needles). This could be related to differences in their biochemical composition as already mentioned by Leavitt and Long (1986). Meanwhile, Andreux et al. (1990) and Schleser (1992) did not observe any isotopic difference between green leaves and twigs. The average value of −31.3‰ that they calculated was similar the values observed in our study on leaves and needles. The ^{13}C depletion of 0.5‰ we observed between deciduous and coniferous trees has already been mentioned even with higher ranges, by other authors. For example, Stuiver and Brazinas (1987) tabulated data from the literature and found an average ^{13}C depletion (i.e. decrease in $\delta^{13}C$) of 3‰ in deciduous trees, compared to conifers at all latitudes. In a similar study, Leavitt and Newberry (1992) showed that *Acer Saccharinum* is consistently 1.1‰ more ^{13}C depleted than pine species in nearby stands. This is mainly explained by the large number of factors controlling carbon isotope composition of the bulk live vegetation, such as: temperature, light intensity, moisture availability, partial pressures of O_2 and CO_2, source of CO_2 assimilated during photosynthesis and spatial variability in populations and species composition (Leavitt and Long, 1986; Stuiver and Brazinas, 1987; Bird et al., 1996; Edwards et al., 2000). All these factors may be controlled by vegetation cover. As in the present case the selected catchments were characterized by the same geographical parameters (climate, altitude, location...),it can be considered that only the vegetation cover differed and could therefore be the main factor of ^{13}C discrimination. The small isotopic enrichment in ^{13}C we observed in spruce fresh organic matter compared to deciduous trees could be explained by a higher water-use efficiency which leads to higher $\delta^{13}C$ values, as observed by Farquhar et al. (1989) for species placed in the same environmental conditions.

However, this isotopic difference tends to disappear when fresh organic material falls to the ground. Organic matter from litter showed a more degraded and depleted material with more homogeneous $\delta^{13}C$ values varying between −26.3 and −28.0‰ (Table 2). The $\delta^{13}C$ differences between litter materials seem rather due to the degree of litter decay than to the composition of the initial plant materials. This homogenisation is confirmed in the first centimetres of the soil where $\delta^{13}C$ values of soil organic matter ($\delta^{13}C_{SOM}$) showed almost no difference between vegetation covers. Nevertheless, the evolution of $\delta^{13}C_{SOM}$ with increas-

ing depth varies from one vegetation to another. Under deciduous vegetation, SOM was enriched in ^{13}C by about 1‰ between −5 and −55 cm, whereas, under coniferous vegetation no significant variations were observed (Table 2). This is in agreement with the statement of Agren et al. (1996) who proposed that the slowdown of SOM degradation coming from coniferous covers leads to a small ^{13}C enrichment of the degraded materials.

The evolution of the isotopic composition ($\delta^{13}C_{DOC}$) of the dissolved organic matter (DOM) from litter and soil layers is very consistent with these patterns. Indeed, under deciduous cover, litter and upper soil layer solutions were depleted in ^{13}C compared to the solid material (Fig. 3a). Thus, an apparent fractionation is noticed between the organic solute fraction and the solid fraction. In other words, the ^{13}C enrichment of SOM with increasing depth can be related to the corresponding release in solution of a ^{13}C-depleted organic matter. Under coniferous vegetation, lower rates of organic matter degradation lead to a minimisation of such apparent isotope fractionation between the dissolved and the solid fraction, and no significant $\delta^{13}C$ variation with increasing depth was observed. This can be interpreted in terms of changes in the chemical composition the DOM. Our observations are similar to those of Kaiser et al. (2001a) who determined that DOC in seepage water was enriched in ^{13}C under Pine forest (−26 to −26.5‰) compared to seepage water under Beech forest (−26.5 to −27.5‰). This difference corresponded to variations in the chemical composition of DOM: under Pine forest, the production of carbohydrates was lower than under Beech, whereas the production of lignin derivatives and aliphatic material was higher under Pine than under Beech.

The $\delta^{13}C$ values of DOC in stream water reflected this apparent fractionation as shown by $\delta^{13}C_{DOC}$ values in the stream water which were systematically lower by one unit in catchments under deciduous vegetation (catchment D) than in the other catchments (see Table 3). This would mean that the isotopic signature of stream DOC is rather controlled by the way the organic matter is degraded in the system than by the differences in the isotopic composition of this organic matter. In our study, the $\delta^{13}C_{DOC}$ in stream is marked by the vegetation cover because the degradation pathway and dynamics of organic matter differ from one vegetation to another.

Insofar as our laboratory leachates are representative of natural soil solutions, we can try to relate stream DOC to soil DOC using their respective isotopic composition. Our results (Fig. 3) showed that, in catchment M, DOC exports could be partly the result of the mixing of litter and soil leachates from both plant sources. However, the isotopic composition of DOC from soil and litter solutions (−28.2‰ ± 0.3 and −26.7‰ ± 0.3, respectively) did not explain the lowest $\delta^{13}C_{DOC}$ values (around −28.8‰) that have been observed in the stream of catchment M and certainly not the even much lower values observed in the stream of catchment D (down to −30.0 ‰). In the same way, in coniferous catchments (R1 and R2), most of the $\delta^{13}C_{DOC}$ values observed in the stream (from −28.8 to −29.5 ‰) were not justified by the isotopic composition of the top soil (−26.1‰ ± 0.3) and litter layers (−27.5‰ ± 0.3). This would mean that, in the coniferous catchment, and to a lesser extend in the deciduous catchments, the DOC that was produced during litter decomposition contributed to a small part of DOC exports by stream water. Finally, another source or process producing DOC with more negative values has to be identified. Such source could be located deeper in the soil. Indeed, in these soils with a sandy and loamy texture, water leaving the forest floor passes through the deeper layers where DOC from the upper layers is sorbed, desorbed or even mineralised (Qualls and Haines, 1992; Kaiser and Zech, 1997; Michalzik et al., 2001, 2003 among others). Theses processes probably affect the isotopic composition of the soil DOC, as suggested by Schiff et al. (1990) and Ludwig et al. (2000) who have shown that the $\delta^{13}C$ values of DOC became more and more negative (a depletion of 1−3.5‰) as the water percolated from the upper organic-rich layers toward the deeper mineral layers. Thus, strongly depleted DOC in our stream water could be explained by physico-chemical processes in the deeper soil layers. However, this is in disagreement with the results of Kaiser et al., 2001b) who have shown that the $\delta^{13}C$ of DOC increased with increasing depth because of selective sorption of the ^{13}C depleted hydrophobic fraction.

As a consequence, temporal variations of $\delta^{13}C_{DOC}$ in the four streams may be controlled by the respective contributions of sub-surface layers (litter and organic rich soil layers) and deeper mineral soil layers. However, no seasonal trends or correlation with stream discharge and DOC concentrations could be observed, preventing us from strengthening this hypothesis. It remains that stream $\delta^{13}C_{DOC}$ exhibits negative or positive shifts which occur simultaneously in the four streams (Fig. 2), suggesting that these variations are induced by the same processes.

Conclusion

In the above study, the isotopic composition of the stream DOC was not the same as of its soil sources, because of an isotopic differentiation which may occur between the solute and the solid phase in the soils. The stream DOC was always ^{13}C depleted compared to the isotopic composition of SOM. This ^{13}C depletion was higher in the deciduous catchment where SOM was enriched in ^{13}C with increasing depth, producing ^{13}C depleted solute fraction. In coniferous catchments, the ^{13}C depletion of the stream DOC was smaller, the DOC exports were lower and no significant isotopic differentiation was observed between solute and solid phase in the soil. This implies that, even though the vegetation changes do not clearly influence the isotopic composition of the bulk organic matter from litter and soil compartments, it leads to a 1‰ difference in the stream $\delta^{13}C_{DOC}$. Furthermore, this difference could be related to the way the soil organic matter is degraded.

Our results show that the composition of DOC in stream water is influenced by the degradation pathway and dynamics of organic matter in the vegetation−soil system. Besides, it means that the substitution of deciduous forests by coniferous plantations may significantly modify the chemical composition and properties of DOC in streams.

Finally, even though the isotopic composition of DOC seems to be an interesting means of identifying DOC sources, as recently proposed by Ziegler and Brisco (2004), further investigations have to be carried out to characterize

the processes and factors which control the $\delta^{13}C$ of the DOC produced in soils.

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