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10th INTERNATIONAL SYMPOSIUM ON ENVIRONMENTAL BIOGEOCHEMISTRY

Final Technical Report

December 15, 1990 - December 14, 1991

JUN 26 1992

Henry L. Ehrlich

Director & Treasurer

Symposia for Environmental Biogeochemistry, Inc.

c/o Department of Biology

Rensselaer Polytechnic Institute

Troy, NY 12180-3590

January 1992

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UNDER GRANT NUMBER DE-FG05-91ER61105

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MASTER

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The lecture for session 9 was "Bacterial Transformations of Organic Sulfur Compounds in Marine Environments" delivered by B.F. Taylor.

The lecture for session 10 was "Biological and Chemical Transformation of Halogenated Aliphatic Compounds in Aquatic and Terrestrial Environments" by P.L. McCarty.

The lecture for session 11 was "Methane Emissions from Northern High Latitude Wetlands: A Review and Assessment" by R.C. Harriss.

The lecture for session 12 was "Models of Terrestrial and Oceanic Sinks for Carbon Dioxide" delivered by I. Funk.

In addition to the scientific sessions, a roundtable discussion was organized on Interdisciplinary opportunities for Coordinated Research on Trace Gases, with A. Janetos as discussion leader.

Further details of the program can be found in Appendix A. Abstracts of all papers can be found in Appendix B.

The symposium was attended by 203 persons representing the USA and 19 foreign countries, including Australia, Brazil, Canada, Denmark, Finland France, Germany, India, Israel, Italy, Japan, P.R. China, Poland, Spain, Sweden, The Netherlands, the United Kingdom, The USSR, and Venezuela. The geographical distribution of attendees is detailed in Appendix C.

The registrants included 28 graduate students.

All papers on the primary theme of the symposium that pass peer review will appear in a symposium volume that will be published by Chapman and Hall, New York.

The symposium was highly successful in bringing together a representative international array of leading scientists for a thorough review of the current state of the findings to date on global change and the biogeochemistry of trace gases. It presented an integrated picture of various aspects of the topic and promoted formal and informal discussion

on the subject among the participants. The proceedings will form an important basis for directing future research.

Appendix A

THIRD ANNOUNCEMENT AND FINAL PROGRAM
OF THE
TENTH INTERNATIONAL SYMPOSIUM ON ENVIRONMENTAL BIOGEOCHEMISTRY, INC.
(ISEB 10)

San Francisco, California, U.S.A., 19 - 23 August, 1991

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W.E. Krumbein, F.R. Germany
A. Yu Lein, USSR
A. de Luca Rebello, Brazil

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R.S. Oremland, USA

NATIONAL SCIENTIFIC COMMITTEE

Chairman:

R.S. Oremland, U.S. Geological Survey, Menlo Park, California

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S. Benjamin, U.S. Geological Survey, Menlo Park, CA
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D. Chatfield, NASA Ames Research Center, Moffett Field, CA
R.J. Cicerone, University of California at Irvine
D.J. Des Marais, NASA Ames Research Center, Moffett Field, California
M. Firestone, University of California at Berkeley
R.P. Kiene, University of Georgia at Sapelo Island
K.A. Kvenvolden, U.S. Geological Survey, Menlo Park, California
P.A. Matson, NASA Ames Research Center, Moffett Field, California
P.L. McCarty, Stanford University, Stanford, California
W.S. Reeber, University of Alaska at Fairbanks
H. Singh, NASA Ames Research Center, Moffett Field, CA
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United States National Oceanic and Atmospheric Administration
United States National Science Foundation

CONFERENCE THEME:

GLOBAL CHANGE AND THE BIOGEOCHEMISTRY OF RADIATIVE TRACE GASES.

INVITATION:

Dear Colleagues,

Thank you for contributing to the scientific program of the 10th International Symposium on Environmental Biogeochemistry. In a departure from previous symposia, ISEB 10 will be devoted almost exclusively to the question of the biogeochemistry of atmospheric trace gases. Concerns about global climate change prompted this more focused conference theme. It was felt that an international organization, such as ISEB, would provide an excellent forum for discussion of the scientific dimensions of this global environmental problem.

On behalf of the U.S. National Committee of the 10th ISEB, I take pleasure in inviting you to participate in the Symposium, which will take place in San Francisco, California, USA, 19 - 23 August, 1991.

I look forward to meeting you in San Francisco.

Ronald S. Oremland
National Chairman, ISEB 10
U.S. Geological Survey, ms 465
345 Middlefield Road
Menlo Park, CA 94025
(415) 329 - 4482; FAX (415) 329 - 4463

GENERAL INFORMATION

TIME AND PLACE:

The Tenth International Symposium on Environmental Biogeochemistry will take place in San Francisco, California, 19-23 August, 1991. Sessions will be held in the Grand Ballroom of the Cathedral Hill Hotel located on the corner of Van Ness Avenue and Geary St. in San Francisco.

REGISTRATION:

The deadline for preregistration (fee: \$ 250; students, \$ 125; accompanying persons, \$ 50) has been extended to July 15, 1991. Payment is in U.S. dollars. Those wishing to preregister from overseas can do so by sending a bank check (drawn on a U.S. bank) to the ISEB 10 National Chairman. Arrangements can also be made for electronic transfer of funds from overseas. Late registration (fee: \$ 300; students, \$ 150) can be paid at the ISEB Information Desk, open from 4 to 8 PM on Saturday, 17 August, from 10 AM until 8 PM on Sunday, 18 August, and from 8 AM until 6 PM on Monday, 19 August in the Cathedral Hill Hotel. Registration forms were contained in the Second Announcement and are on page 23 of this Program.

OFFICIAL LANGUAGE:

The official language will be English.

PRESENTATIONS:

Oral - Presentation of oral papers will be limited to 20 minutes (15 min + 5 min discussion), with the exception of plenary talks, which will be for 40 minutes (35 min + 5 min discussion). Facilities will be available for slide projection (5 x 5 cm) or overhead transparencies. There will be no concurrent sessions. Oral sessions will be in the Grand Ballroom.

Posters - Poster boards are 4 ft high x 6 ft wide (1.22 m x 1.83 m). Posters for the first session (A) can be put up after 11 AM on Monday, 19 August and must be removed by 10 AM Wednesday, 21 August. Posters for the second session (B) can be put up after 11 AM on Wednesday and must be removed by 10 AM Friday. Poster sessions will be in the El Dorado Room.

PUBLICATIONS:

Full papers of both oral and poster presentations that deal with the theme of the Symposium are eligible for publication in the Proceedings, if accepted after review by the National Scientific Committee. Papers (2 copies) must be received by the Symposium Secretary by the end of the Symposium. Papers should be in CBE format (e.g., see the January issue of Applied and Environmental Microbiology).

INFORMATION DESK:

The Symposium Information Desk will be located on the second floor of the Cathedral Hill Hotel. Any correspondence for Symposium participants

should be forwarded care-of the Cathedral Hill Hotel address or phone or FAX number, indicating "Attention ISEB 10."

Cathedral Hill Hotel
Van Ness and Geary St
San Francisco, CA 94109-6986
(415) 776 - 8200
(415) 441 - 2841 FAX

Housing forms for the Cathedral Hill Hotel were contained in the Second Announcement. Reservations can be made directly with the Hotel. Indicate that you are attending ISEB 10.

TRANSPORTATION:

Ground transportation from the airport to the hotel is available on the curb outside of the terminals (taxis cost about \$ 25; super shuttles cost about \$ 10). Discount domestic airline tickets can be purchased from:

Olsen Travel Incentives (contact: Maria Quinonez)
550 Kearny St., Suite 310
San Francisco, CA 94108
(415) 362-9135; (800) 766-5736 (US and Canada)
FAX (415) 986-8551

Contact Olsen Travel Incentives if you wish to participate in the post-Symposium field trip to Mono Lake.

MEETINGS OF THE EXECUTIVE BOARD AND INTERNATIONAL COMMITTEE:

The Executive Board will meet at 7 PM on Monday evening in the Russian Hill Room. The International Committee will meet at 7 PM on Tuesday evening in rooms Telegraph Hill A and B.

SOCIAL PROGRAM:

Sunday, 18 Aug.: 10:30 AM Tailgate party and baseball game (Cincinnati Reds vs SF Giants; cost \$ 25 - payment by June 30)

7:00 PM Welcoming Reception, Japanese Pavillion

Tuesday, 20 Aug.: 10:00 AM San Francisco bus tour
8:30 PM Pub Crawl # 1

Wednesday, 21 Aug.: 9:30 PM Pub Crawl # 2

Thursday, 22 Aug.: 8:00 PM Banquet

Saturday, 24 Aug.: 10:00 AM Sausalito/Muir Woods and Luncheon (bus tour, cost \$ 50 - payment received by June 30)

Sunday, 25 Aug.: 11:00 AM Buses depart from hotel for post-Symposium trip to Mono Lake.

PROGRAM OF THE ISEB 10

Sunday, 18 August

10:30 AM Departure from Hotel lobby for tailgate party/baseball game at Candlestick Park (see the Second Announcement).

7:00 PM Welcoming Reception, Japanese Pavillion, Fourth Floor of the Cathedral Hill Hotel

Monday Morning, 19 August 1991

8:15 AM Introductory Remarks.....R.S. Orem and Land.

8:20 AM Keynote Lecture - (O-K-1) "Global Change and the Biogeochemistry of Radiative Trace Gases", R.J. Cicerone.

SESSION 1: PALEOATMOSPHERES AND PALEOCLIMATES

(Convenors: D.J. Des Marais and R.O. Hallberg)

9:00AM - (O-1-1) "Geologic History of the Biogeochemical Cycles of Carbon and Oxygen", J.C.G. Walker (Plenary Lecture).

9:40 AM Coffee Break

10:00 AM (O-1-2) "Carbon Isotopic Indicators of Atmospheric Trace Gas Concentrations in Ancient Atmospheres", D.J. Des Marais.

10:20 AM (O-1-3) "The Paleoclimate of Pangea during its Formation (Late Permian) and Disintegration (Late Jurassic)", G.T. Moore, D.N. Hayashida, C.A. Ross, and S.R. Jacobson.

10:40 AM (O-1-4) "Ice Core Records as a Key to Understanding the History of Atmospheric Trace Gases", D. Raynaud.

11:00 AM (O-1-5) "The Role of the Terrestrial Biosphere in Controlling Atmospheric Methane and Carbon Dioxide during the Last Glacial Maximum at 18 kyr", J. Servant

11:20 AM (O-1-6) "Carbon Dioxide Concentrations in Bubble Air from 1550 to 1940 AD from the GISP-2 Ice Core from Central Greenland", M. Wahlen, D. Allen, and B. Deck.

11:40 AM (O-1-7) "Long-Term Controls on Atmospheric CO₂: Implications for the Past and for the Future", J.F. Kasting.

12:00 PM Lunch Break

Monday Afternoon, 19 August

SESSION 2: GLOBAL DISTRIBUTIONS AND ATMOSPHERIC REACTIONS

(Convenors: H. Singh and I.R. Kaplan)

1:30 PM (O-2-1) "The Direct and Indirect Effects of Greenhouse Gases on Climate", D.J. Wuebbles (Plenary Lecture).

2:10 PM (O-2-2) "On the Interaction between the Biogeochemical Carbon Cycle and the Physical Aspects of the Climate System", K. Higuchi, D. Chan, C. Lin, N. Sargent, and Y.H. Chan.

2:30 PM (O-2-3) "Uncertainties in the Global Atmospheric Nitrous Oxide Budget", J.W. Elkins, J.H. Butler, and T.M. Thompson.

2:50 PM (O-2-4) "The Global Methane Cycle", M.A.K. Khalil and R.A. Rasmussen.

3:10 PM Coffee Break

3:30 PM (O-2-5) "Long-Term Trends and Seasonal Variations of Atmospheric Methane in Japan", H. Tsuruta.

3:50 PM (O-2-6) "Negative Saturation Anomalies of CH_3CCl_3 in the Open Ocean: Implications for Tropospheric OH", J.H. Butler, J.W. Elkins, T.M. Thompson, B.D. Hall, T.H. Swanson, and V. Koropalov.

4:10 PM (O-2-7) "Oxidation of Methane in the Troposphere: Assessment of Uncertainties and Impact on Calculated Global Budgets", J.M. Rodriguez, S. Fan, M.K.W. Ko, and N.D. Sze.

4:30 PM (O-2-8) "The Methane Cycle: Global Budget and Process Studies using Stable Isotopes and ^{14}C as Tracers", M. Wahlen and B. Deck.

4:50 PM (O-2-9) "A New Instrument for Precise Measurement of Atmospheric N_2O and CH_4 ", M. Loewenstein.

5:10 PM Dinner Break

Monday Evening, 19 August

7:30 - 9:30 PM SESSION 3: POSTER SESSION A

Subsessions 1, 2, 4/5, and 7.

(Conveners: S. Benjamin and R.P. Kiene)

Tuesday Afternoon, 20 August

SESSION 5: TERRESTRIAL SYSTEMS AND LAND USE CHANGE - II

(Convenors: R. Chatfield and P.A. Meyers)

1:30 PM (O-5-1) "The Influence of Tropical Biomass Burning on Climate and the Atmospheric Environment", M.O. Andreae (Plenary Lecture).

2:10 PM (O-5-2) "Global Survey of Large Historic Wildfires: Their Climatologies and Contributions to Biomass Burning", J.L. Betancourt, T.W. Swetnam, S.W. Leavitt, and D.R. Cayan.

2:30 PM (O-5-3) "Sulfur Gas Emissions from African Savannah Burning", B.C. Hguyen, N. Mihalopoulos, B. Bonsang, J.P. Putaud, C. Boissard, and J.P. Lacaux.

2:50 PM (O-5-4) "Spatial and Temporal Variations of NO Emissions from Venezuelan Savannah Soils", E. Sanhueza, C. Johansson, A. Rondon, L. Cardenas, and J. Romero.

3:10 PM Coffee Break

3:30 PM (O-5-5) "Large-Area Estimates of Denitrification and Nitrous Oxide Flux in a Tallgrass Prairie Landscape", P.M. Groffman.

3:50 PM (O-5-6) "Production of Methane and Nitrous Oxide by Organic Soils within Northern Hardwood Forests", J.B. Yavitt and T.J. Fahey.

4:10 PM (O-5-7) "A Seasonal Study of Soil-Atmosphere Methane, Carbon Dioxide, and ^{222}Rn Flux in a Tropical Moist Forest", M. Keller and R.F. Stallard.

4:30 PM (O-5-8) "Methane Concentrations and Groundwater Flow in Peat, Glacial Lake Agassiz Peatlands, Northern Minnesota", D.I. Siegel, P.H. Glaser, and E.A. Romanowicz.

4:50 PM (O-5-9) "Nitrous Oxide and Methane Fluxes from Terrestrial Ecosystems", P. Ambus, and S. Christensen.

5:10 PM Dinner Break

Tuesday Evening, 20 August Pacific Heights/Presidio Rooms

8:00 PM ROUNDTABLE DISCUSSION: INTERDISCIPLINARY OPPORTUNITIES FOR COORDINATED RESEARCH ON TRACE GASES

(Discussion Leader: A. Janetos)

Wednesday Morning, 21 August

SESSION 6: FLUXES AND CYCLING IN AQUATIC SYSTEMS

(Convenors: M. Firestone and A. de Luca Rebello)

8:30 AM (O-6-1) "Light Hydrocarbons, Organic Acids, and Microbial Processes in Hydrothermally-Altered Sediments of the Guaymas Basin, Gulf of California", C.S. Martens, D.B. Albert, G.G. Pauly, and E.A. Canuel (Plenary Lecture).

9:10 AM (O-6-2) "Oxidation of Methane by Deep-Sea Mussels with Methanotrophic Symbionts", C.R. Fisher.

9:30 AM (O-6-3) "Determinants of Aerobic Methane Oxidation in Wetland Sediments", G.M. King and P. Roslev.

9:50 AM (O-6-4) "Methanogenesis in Gassy African Lakes: An Important Release Trigger?", W.C. Evans, L.D. White, M.L. Tuttle, and G.W. Kling.

10:10 AM Coffee Break

10:30 AM (O-6-5) "Methane Emissions from the Amazon Floodplain: Enhanced Release During Episodic Mixing of Lakes and a Habitat-Based Regional Assessment", J.M. Melack and D. Engle.

10:50 AM (O-6-6) "Methane Oxidation at Deep Methane Maxima in Coastal California Waters", D.M. Ward.

11:10 AM (O-6-7) "Marine Sources of Atmospheric Methyl Halides", K.D. Goodwin, S.L. Manley, and W.J. North.

11:30 AM (O-6-8) "Factors Affecting the Concentration of Dimethylsulfide in Seawater", R.P. Kiene.

11:50 AM (O-6-9) "Atmospheric Nitrous Oxide Fluxes from Mangrove Sediments", J.E. Corredor, J.M. Morell, and A. Aguilera

12:10 Lunch Break

Wednesday Afternoon, 21 August

SESSION 7: METALS, ORGANICS, AND DEPOSITIONAL ENVIRONMENTS

(Convenors: B. Ward and G. Stotzky)

1:30 PM (O-7-1) "Dissimilatory Reduction of Selenate to Elemental Selenium by Anaerobic Bacterial Cultures", J. Switzer-Blum, R.S. Oremland, and N. Steinberg.

1:50 PM (O-7-2) "Insight into the Mechanism of MnO_2 Reduction by Marine Bacterial Strain B111 88", H.L. Ehrlich.

2:10 PM (O-7-3) "Pyrite and Hydrogen Formation under Anaerobic Conditions", E. Drobner, G. Wachtershauser, and K.O. Stetter.

2:30 PM (O-7-4) "The Respiratory Chain Coupled to Oxidation of Fe^{2+} in Thiobacillus ferrooxidans", T. Yamanaka, T. Yano, M. Kai, H. Tamegai, and Y. Fukumori.

2:50 PM (O-7-5) "In vivo constructed PCB Degrading Strains: Degradation and Stability in Soil", J. Havel and W. Reineke.

3:10 PM Coffee Break

3:30 PM (O-7-6) "Environmental Forensic Geochemistry: Characterization of Biodegraded Petroleum Contaminants in Soil and Water to Determine Source of Pollutants and Time of Spill", I.R. Kaplan.

3:50 PM (O-7-7) "Does Organic Matter Act as a Reductant in the Deposition of Metal Ores?", P.A. Meyers, R.M. Kettler, and E.S. Ho.

4:10 PM (O-7-8) "Burial of Organic Carbon in Estuarine Zones: A Case Study in Guanabara Bay, Rio De Janeiro", A. De Luca Rebello Wagener.

4:30 PM (O-7-9) "Anthropogenic Lead in Antarctic Surface Waters", A.R. Flegal, S. Niemeyer, and H. Maring.

4:50 PM (O-7-10) "A Biogeochemical Study of Qinghai Lake Sediments", Fan Pu and Li Jinggui.

5:10 PM Dinner Break

Wednesday Evening, 21 August

7:30 - 9:30 PM SESSION 8: POSTER SESSION B

Subsessions 6, 9/10, 11, and 12.

(Conveners: L. Gaydos and R.P. Kiene)

Thursday Morning, 22 August

SESSION 9: BIOLOGICAL MECHANISMS OF FORMATION AND DESTRUCTION - I

(Conveners: W.S. Reeceburgh and S.S. Belyaev)

8:30 AM (0-9-1) "Bacterial Transformations of Organic Sulfur Compounds in Marine Environments", B.F. Taylor (Plenary Lecture).

9:10 AM (0-9-2) "Anaerobic Formation and Degradation of Dimethylsulfide and Methanethiol by New Types of Acetogenic and Methanogenic Bacteria", F. Bak and K. Finster.

9:30 AM (0-9-3) "Sulfur Cycling in Marine Microbial Mats: Distribution of Compounds and Functional Groups of Sulfur Bacteria", P.I. Visscher and H. van Gemerden.

9:50 AM (0-9-4) "Sulfur Metabolism of Benthic Marine Cyanobacteria and its possible Role in Trace Gas Exchange in Microbial Mats", L.J. Stahl.

10:10 AM Coffee Break

10:30AM (0-9-5) "Influence of Microbial Fe (III) Reduction on Methane Production in Freshwater Environments", D.R. Lovley and E.J. Phillips.

10:50 AM (0-9-6) "Biogeochemical Controls on the Carbon Isotopic Composition of Methane Produced in Anoxic Marine Sediment", M.J. Alperin, N.E. Blair, D.B. Albert, and T.M. Hoehler.

11:10 AM (0-9-7) "The Carbon Isotope Biogeochemistry of Methane Production in Anoxic Sediments", N.E. Blair, S.E. Boehme, and W.D. Carter, Jr.

11:30 AM (0-9-8) "Seasonal Variations in Methane Oxidation and Production in an Anoxic Marine Sediment", T.M. Hoehler, M.J. Alperin, D.B. Albert, and C.S. Martens.

11:50 AM (0-9-9) "Emissions of Ammonia, Nitrous Oxide, and Methane from Cattle Slurry" by O. Oenema, G.L. Velthof, and D.W. Bussink.

12:10 PM Lunch Break

Thursday Afternoon, 22 August

SESSION 10: BIOLOGICAL MECHANISMS OF FORMATION AND DESTRUCTION - II

(Convenors: R.J. Cicerone and H.L. Ehrlich)

1:30 PM (O-10-1) "Biological and Chemical Transformation of Halogenated Aliphatic Compounds in Aquatic and Terrestrial Environments" by P.L. McCarty and M. Reinhard (Plenary Lecture).

2:10 PM (O-10-2) "Consumption of Freons F-11 and F-12 in Methane-Producing Aquatic Sediments", D.R. Lovley, and J.C. Woodward.

2:30 PM (O-10-3) "HOBr Formation by Seaweeds: Impact on the Biosphere", R. Weaver and M.G.M. Tromp.

2:50 PM (O-10-4) CH_4 Production via CO_2 Reduction in a Temperate Bog: A Source of ^{13}C -Depleted CH_4 ", J.M. Landsdown, P.D. Quay, and S.L. King.

3:10 PM Coffee Break

3:30 PM (O-10-5) "Plant Hydrocarbon Emissions to the Atmosphere: What is the Linkage between Photosynthesis and Isoprene Emission?", R. Fall, A. Guenther, C. Jaeger, J. Grinspoon, and R. Monson.

3:50 PM (O-10-6) "Microbiological Transformation of Low Molecular Weight Carbon Compounds in the Deep Subsurface", S.S. Belyaev and I.A. Borzenkov.

4:10 PM (O-10-7) "Methylotrophic Bacteria: Biomarker Lipids and Controls on their Carbon Isotopic Composition", L.L. Jahnke and R.E. Summons.

4:30 PM (O-10-8) "Soil Moisture as a Regulator of the Proportions of Nitric Oxide and Nitrous Oxide Produced via Nitrification and Denitrification", E.A. Davidson.

4:50 PM (O-10-9) "Calcification, Photosynthesis, and Global CO_2 Levels", T.A. McConnaughey.

8:00 PM Symposium Banquet, Japanese Pavillion, Cathedral Hill Hotel

Friday Morning, 23 August.

SESSION 11: HIGH LATITUDE SYSTEMS

(Conveners: K.A. Kvenvolden and A. Yu Lein)

8:30 AM (O-11-1) "Methane Emissions from Northern High Latitude Wetlands: A Review and Assessment" by R.C. Harriss (Plenary Lecture).

9:10 AM (O-11-2) "The Role of Tundra and Taiga in the Global Methane Budget", S.C. Whalen and W.S. Reeceburgh.

9:30 AM (O-11-3) "Partial Pressures of Methane and N_2O in Surface and Soil Waters in Arctic Alaska: Movement of Dissolved Trace Gases from Tundra to Surface Waters to the Atmosphere", G.W. Kling, G.W. Kipput, and M.C. Miller.

9:50 AM (O-11-4) "Isotopic Characterization of Methane from Yukon-Kuskokwim Delta Tundra and Minerotrophic Fens in Northern Quebec", C.S. Martens, C.A. Kelly, W. Ussler III, and R.J. Macaffrey.

10:10 AM Coffee Break

10:30 AM (O-11-5) "Temperature and Moisture Controls over Carbon Flux in an Arctic Tundra Soil", K. Kielland and J.P. Schimel.

1050 AM (O-11-6) "Methane Emissions from Northern Wetlands, Canada", T.R. Moore, A. Heyes, R. Knowles, and N.T. Roulet.

11:10 AM (O-11-7) "Methane Emissions in Relation to Ecological Patterns in the Hudson Bay Lowlands", L.F. Klinger, P.R. Zimmerman, J.P. Greenberg, and L.E. Heidt.

11:30 AM (O-11-8) "Methane Production and Oxidation in Northern Peats", P. Crill and R. Sass.

11:50 AM (O-11-9) "Emissions of Biogenic Sulfur Gases from Northern Bogs and Fens", W.Z. de Mello, M.E. Hines, and S.E. Bayley.

12:10 PM Lunch Break

Friday Afternoon, 23 August.

SESSION 12: GLOBAL SOURCES, SINKS, AND FEEDBACKS

(Conveners: P.M. Vitousek and P. Nannipieri)

1:30 PM (0-12-1) "Models of Terrestrial and Oceanic Sinks for Carbon Dioxide", I. Fung (Plenary Lecture).

2:10 PM (0-12-2) "Biogeochemical Feedbacks from Global Warming", D.A. Lashof.

2:30 PM (0-12-3) "Oxidation of Methane by Boreal Forest Soils: A Comparison of Five Independent Methods of Oxidation Rate Measurement", S.C. Whalen, W.S. Reeburgh, and V. Barber.

2:50 PM (0-12-4) "Biospheric - Climatic Feedbacks in Methane Emissions from Northern Peatlands", N.T. Roulet, T.R. Moore, and J. Bubier.

3:10 PM Coffee Break

3:30 PM (0-12-5) "Global Methane Cycle in the Ocean", M.V. Ivanov and A. Yu. Lein.

3:50 PM (0-12-6) "Sources of Methane in China: Rice Fields, Biogas Pits, Cattle, and Industrial", Wang Ming-Xing, W. Seiler, and R.A. Rasmussen.

4:10 PM (0-12-7) "The Sensitivity of the Global Atmosphere to Changes in Anthropogenic Sources of Methane", N.G. Andronova, and I.L. Karol.

4:30 PM (0-12-8) "The Biogeochemical Sources of Isoprene Emission", J. Dignon, K.E. Taylor, and J.A. Logan.

4:50 PM (0-12-9) "An Ecosystem Approach to a Nitrous Oxide Budget for Tropical Ecosystems", P.A. Matson and P.M. Vitousek

POSTER SESSION A: MONDAY EVENING

(Conveners: S. Benjamin and R.P. Kiene)

PALEOATMOSPHERES AND PALEOCLIMATES: (PA-1)

(PA-1-1) "Climate-Induced Wetland Changes and Causes of Increasing Methane During the Past 18,000 Years", J.A. Chappellaz, A.M. Thompson, and I.Y. Fung.

(PA-1-2) "Viable Microorganisms in Permafrost as Indicator of Global Climate Changes in the Pleistocene", D.A. Gilichinsky.

(PA-1-3) "Atmospheric Records of Methane & Nitrous Oxide in Glacial Ice", M.A.K. Khalil, R.A. Rasmussen, M.J. Spencer, and P. Mayewski.

(PA-1-4) "Sodom, Gomorrah and the Lost Cities of the Plain - A Climatic Perspective", A. Nissenbaum.

(PA-1-5) "On Recent Study of Ancient Ice Air Content: The Vostok Ice Core", I.P. Semiletov.

GLOBAL DISTRIBUTIONS AND ATMOSPHERIC REACTIONS: (PA-2)

(PA-2-1) "Ozone, the Non-Linear Greenhouse Gas: How Location and Timing Emphasize Certain Source Areas", R.B. Chatfield.

(PA-2-2) "Role of Riftogenic Hydrogen in Global Budgets of Crust, Oceans and Atmosphere (A New Model of Ozone Hole Formation)", V. Syvrotkin and N. Sadovskii.

(PA-2-3) "Three-Dimensional Simulations of CFC-11 and Methylchloroform and the Inferred Distribution of Tropospheric OH", X. Tie, J. Kao, and E.J. Mroz.

TERRESTRIAL SYSTEMS AND LAND USE CHANGE: (PA-4/5)

(PA-4/5-1) "A Historical Biogeography and Environmental Analysis of the Phylloxera Disease in Northern California Viticultural Areas: The Future Impact of a Biotype on the Landscape Ecology as a Model of Land Use Planning in California", M.T. Baublitz.

(PA-4/5-2) "Effect of Nitrogen Fertilizer and Nitrification Inhibitors on Methane and Nitrous Oxide Fluxes in Irrigated Corn", K.F. Bronson and A.R. Mosier.

(PA-4/5-3) "Effect of Air Pollution on Litter Decomposition", M.F. Cotrufo, A. Virzo de Santo, A. Alfani, and G. Bartoli.

(PA-4/5-4) "Seasonal, Diurnal, and Spatial Variations in N₂O Soil Fluxes in the Venezuelan Savannah Climatic Region", L. Donoso, D. Scharffe, J. Marti, and E. Sanhueza.

(PA-4/5-5) "Extrapolation of Ecosystem Processes to Regional Scales: Development of the Regional Ecosystem Simulation System", J.L. Dungan and D.L. Peterson.

(PA-4/5-6) "Bioelement Dynamic in the Leaf and Needle Decomposition Processes in Three Evergreen Forest Ecosystems of the Duero Basin (Spain)", J.F. Gallardo, I. Hernandez, and I. Santa Regina.

(PA-4/5-7) "Respiration of Cultivated Histols in Field and Laboratory Measurements, and the Relationships between Respiration and Soil Characteristics", I. Hokkanen and J. Silvola.

(PA-4/5-8) "Nitric and Nitrous Oxide Evolution from Managed Subtropical Grassland", G.L. Hutchinson and G.P. Livingston.

(PA-4/5-9) "Use of the AVIRIS Imaging Spectrometer for Remote Estimation of Foliar Biochemical Content along the Oregon Transect", L.F. Johnson.

(PA-4/5-10) "Methane Fluxes and Nitrous Oxide Production at some Virgin and Drained Peat Sites in Finland", P.J. Martikainen, H. Nykanen, J. Silvola, and P. Crill.

(PA-4/5-11) "The Effect of Peat Substrate and Depth on Methane and Carbon Dioxide Concentrations in Swedish Mires", M. Nilsson and E. Bohlin.

(PA-4/5-12) "Methane in Flooded Soil Water and the Emission through Rice Plants to the Atmosphere", I. Nouchi, S. Mariko, Y. Harazono, and N. Owa.

(PA-4/5-13) "Methane Production and Uptake in some Terrestrial Ecosystems of the USSR", N.S. Panikov.

(PA-4/5-14) "The Characteristics and the Region Distribution Law of the Soil Environment Background Value in Gansu Province", Wang Sheng Pu and Lian Bing.

(PA-4/5-15) "Increasing CO₂ Fixation Rate Observed in *Araucaria angustifolia* from Polluted Areas in Brazil: Preliminary Results", R.L. Santelli, A. de Luca Rebello, and K. Wagener.

(PA-4/5-16) "Soil Exchange of Trace Gases in Laboratory Incubations", D.A. Schaefer and C. T. Driscoll.

(PA-4/5-17) "Biomass Burning: A Historical View Via Arctic Ice Cores", M.J. Spencer, S. Drummy, P. Mayewski, G. Holdsworth, and K. Taylor.

(PA-4/5-18) "Methane Consumption in Soils: An Intersite Comparison", R.G. Striegl, L.N. Witherbee, C.M. Tate, and I.A. McConnaughey.

(PA-4/5-19) "Assessment of Global and Regional Changes in the Biogeochemical Structure of the Agrosphere", V.N. Bashkin.

(PA-4/5-20) "Biomass Burning in Tropical Deforestation Sites. Year-to Year Practices", M.C. Pereira and A.W. Setzer.

METALS, ORGANICS, AND DEPOSITIONAL ENVIRONMENTS: (PA-7)

(PA-7-1) "The Trace Element Biogeochemical Characteristics of Depositional Organic Matter in Inland Sediments", Bei Feng, We Zheng, and Qin Tianwo.

(PA-7-2) "The Effect of Different CO₂ Concentrations upon the Embryonic Development of Sea Urchin Strongylocentrotus intermedius", R.V. Gareyeva and A.P. Nedashkovsky.

(PA-7-3) "The Integral Estimation of Extreme Environmental Conditions Before and After Chernobyl Crash", A.M. Grishchenko, I.G. Galationov, and R.V. Gareyeva.

(PA-7-4) "An up-to-now Unknown Metabolism of Metal-Mobilizing Thiobacilli: Aerobic Hydrogen Oxidation", H. Huber, E. Drobner, and K.O. Stetter.

(PA-7-5) "Heavy Metal Effect Upon the Embryonic Development of Marine Invertebrates", V.V. Malakhov, L.A. Medvedeva, and R.V. Gareyeva.

(PA-7-6) "Sources and Migration of Methane-Rich Gas in Sedimentary Rocks on the Exmouth Plateau, Northwest Australian Continental Margin", P.A. Meyers and L.R. Snowdon.

(PA-7-7) "Physiological and Biochemical Aspects of a Heavy Metal (Pb²⁺) in Agricultural Plants in a Semi-Arid Environment", K. Muthuchelian.

(PA-7-8) "Physicochemical Mechanisms of Soil Buffer Ability Towards Heavy Metal Pollution", T.V. Pampura and D.L. Pinsky.

(PA-7-9) "A Biogeochemical Study of Eggs of Back-Yard Hen from the Mangampeta Baryte Mining Area, Andhra Pradesh, India", E.A.V. Prasad and D. Niranjana Prasad.

(PA-7-10) "Coconut Tree in Biogeochemical Exploration", E.A.V. Prasad and D. Niranjana Prasad.

(PA-7-11) "Anthropogenic Change of Atmosphere Geochemistry of the Eastern European Plain", V. P. Uchvatov.

(PA-7-12) "Application of Submicroscopic Methods for Investigation of Heavy Metal Polluted Soil", J. Weber.

POSTER SESSION B: WEDNESDAY EVENING

(Conveners: L. Gaydos and R.P. Kiene)

FLUXES AND CYCLING IN AQUATIC SYSTEMS: (PB-6)

(PB-6-1) "The Change of Potassium-Saltness Ratio in the Northern Part of the Indian Ocean", V.V. Anikiev and A.P. Nedashovsky.

(PB-6-2) "Porewater Distribution and Flux of Chemical Variables in Florida Bay Sediments", T.R. Barber and P.R. Carlson, Jr.

(PB-6-3) "Sediment Deposition and the Distribution of Reduced Sulfur Compounds in Tomales Bay, California", R.M. Chambers, S. Vink, S.V. Smith, and J.C. Cornwell.

(PB-6-4) "Methane Flux from Aquatic Plants - Isotopic, Ventilation, Biomass, and Diurnal Effects", J. Chanton, G. Whiting, W. Showers, C. Kelly, C. Martens, J. Happell, and G. Gerard.

(PB-6-5) "Identifying and Quantifying Regional Sources and Air-Sea Flux of Methane in Southern California Waters", F.J. Cynar and A.A. Yayanos.

(PB-6-6) "Comparative Fluxes of Fixed Nitrogen Resulting from Contemporaneous Nitrogen Fixation and Denitrification in Tomales Bay, CA", S.B. Joye and H.W. Paerl.

(PB-6-7) "The Element Distribution in Sediments and Environment of Evolution of Qinghai Lake", Ma Bao Lin.

(PB-6-8) "Methane and Other Hydrocarbon Gases in the Floats of the Giant Kelp Macrocystis pyrifera", I.D. Lorenson, K.A. Kvenvolden, and R.S. Oremland.

(PB-6-9) "Biogeochemical Basis of Ecological Investigation of Near Sakhalin Offshore", M.N. Mansurov, V.I. Avilov, and S.D. Avilova.

(PB-6-10) "Methanogenic Activity in the Mangrove Sediment of India", R. Mohanraju, T. Ramamurthy, and R. Natarajan.

(PB-6-11) "Methane-Cycling in Eutrophic Lakes and the Corresponding Possible Global Tropospheric Emission", M. Naquib.

(PB-6-12) "Reductive Biogeochemistry of Three Alkaline- Saline Lakes", R.S. Oremland, L.G. Miller, and C.W. Culbertson.

(PB-6-13) "Environmental Biogeochemical Studies in the Cauvery River Basin, A Tropical River of Peninsular India", A. Ramanathan and V. Subramanian.

(PB-6-14) "Carbon Dioxide and Methane Fluxes from Coral Reefs and Other Lithified Marine Carbonates", F.J. Sansone, G.W. Tribble, and P.R. Haberstroh.

(PB-6-15) "Experimental Hypersaline Ponds: Carbon Isotope Gradients in

the Benthic Microbial Community", M. Schidlowski.

(PB-6-16) "The Quantification of Methane Emissions from Mountain Lakes and Wetlands Located in the Colorado Front Range", L.K. Smith and W.M. Lewis, Jr.

(PB-6-17) "Carbon and ^{14}C Budget for Organic-Rich Continental Slope Sediments of the Middle Atlantic Bight", S.E. Trumbore, R.F. Anderson, and P. Biscaye.

(PB-6-18) "A Comparison of Methane Emissions from Tropical and Boreal Wetlands: The Search For Old Methane", S.C. Tyler, G.W. Brailsford, M. Keller, and P. Crill.

BIOLOGICAL MECHANISMS OF FORMATION AND DESTRUCTION: (PB-9/10)

(PB-9/10-1) "A Comparison of Nitrogen Trace Gas Production by Autotrophic and Heterotrophic Nitrifiers", I.C. Andersen, D. Burdidge, and J. Homstead.

(PB-9/10-2) "Formation of Methylmercaptan and Dimethylsulfide from Methoxylated Aromatic Compounds in Anoxic Marine and Freshwater Sediments", K. Finster, F. Bak, and G.M. King.

(PB-9/10-3) "Microbial Response to Hydrocarbon Microseepage in the Basin, Oklahoma", D.O. Hitzman, D.C. Hitzman, and J.D. Tucker.

(PB-9/10-4) "Catabolism of Dimethylsulfide and Methanethiol by Methylo-trophic Methanogens", S. Ni and D.R. Boone.

(PB-9/10-5) "Biological Production and Consumption of Dimethylsulfide (DMS) in the Marine Photic Zone: Results of Radiolabelled Tracer Experiments", G.V. Wolfe and T.S. Bates.

(PB-9/10-6) "Winter Activity of Soils in the North and CO_2 Planetary Maximum in the Atmosphere", S.A. Zimov, S.P. Davioudov, Y.V. Voropaev, S.F. Prosiannikov, and I.P. Semiletov.

(PB-9/10-7) "Earth's Vegetation Cover Response to Changing Atmospheric CO_2 Concentration", S.A. Zimov, V.I. Chuprionin, A.P. Oreshko, and S.M. Krasnopev.

(PB-9/10-8) "On Biomodal Oscillations in Atmospheric CO_2 Concentration", S.A. Zimov and I. P. Semiltov.

HIGH LATITUDE SYSTEMS: (PB-11)

(PB-11-1) "Methane Balance in Northern Bogs", D. Ann Brown and R.P. Overend.

(PB-11-2) "Arctic and Sub-Arctic Soil Emissions: Possible Implications for Global Climate Change", T. Christensen.

(PB-11-3) "Permafrost and Gas Hydrates as Sources of Methane at High Latitudes", K.A. Kvenvolden and T.S. Collett.

(PB-11-4) "Temporal and Spatial Environmental Controls on CH₄ Emissions from Arctic Tundra", L.A. Morrissey, G.P. Livingston, and D.J. Des Marais.

(PB-11-5) "Methane in Permafrost Rocks and Its Ecological Importance", E.M. Rivkina and V.A. Samarkin.

(PB-11-6) "Methane in Tundra Soils of the Kolyma-Indigirka Lowland and its Flux to the Atmosphere", V.A. Samarkin and E.M. Rivkina.

(PB-11-7) "The Geochemistry of Methane in an Amictic, Permanently Ice-Covered Lake in Antarctica", R.L. Smith, L.G. Miller, and B.L. Howes.

(PB-11-8) pH Dependence of CH₄ and CO₂ Production in Two Contrasting Hudson Bay Lowland Wetlands", D.W. Valentine, E.A. Holland, and D.S. Schime^l.

GLOBAL SOURCES, SINKS, AND FEEDBACKS: (PB-12)

(PB-12-1) "Methane Emissions from Urban Natural Gas Delivery Systems", D.R. Blake, Tai-Yi Chen, and F.S. Rowland.

(PB-12-2) "Deuteromethanes as Potential Fingerprints of the Sources of Atmospheric Methane", E.J. Mroz.

(PB-12-3) "An Estimate of Gross Global Methane Production", W.S. Reeburgh, M.J. Alperin, and S.C. Whalen.

(PB-12-4) "Examination of the Role of Alaska's Yukon-Kuskokwim Delta Region in the Global Budgets of Methane, Ozone, and Carbon Monoxide", J.A. Ritter, C.E. Watson, J.D.W. Barrick, M.C. Shipham, B.E. Anderson, and M.A. Woerner.

the 200-2000 m layer. The possible reasons of the relative potassium impoverishment of surface waters are discussed.

O-9-2 ANAEROBIC FORMATION AND DEGRADATION OF DIMETHYLSULFIDE AND METHANETHIOL BY NEW TYPES OF ACETOGENIC AND METHANOGENIC BACTERIA. **FLAK¹** AND **K. FINSTER²**. 1) Max-Planck-Institut für Terrestrische Mikrobiologie, Marburg, FRG; 2) Department of Ecology and Genetics, University of Aarhus,

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10th International Symposium
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*Third Circular
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Global Change and the Biogeochemistry
of Radiative Trace Gases

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Wolf Vishniac Award Manuscripts	July 15
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Abstracts

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Global Change and the Biogeochemistry
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O-4-7 SOIL RESPIRATION IN RELATION TO VEGETATION COVER AND MICROTOPOGRAPHY IN THREE DRAINED PEATLAND SITES. JUKKA ALM AND JOUKO SILVOLA. Department of Biology, University of Joensuu, P.O. BOX 111, SF-80100 Joensuu, Finland

Mire ecosystems consist of vegetation patches of various scales. Plant species forming tussocks and hummocks provide different environments for microorganisms and roots than those growing in lawns. This study focuses on the effects of microsite characteristics on soil respiration. Carbon dioxide production is accelerated when virgin peatland is reclaimed for forestry. CO₂ evolution from three peatland sites was monitored after the drainage by infrared gas analyzer (IRGA) and dynamic chamber technique. Variation in the data was assigned to three factors. The effects of nutrition status and temperature were statistically extracted and the remaining variation construed by microsite characteristics. On oligotrophic sedge pine mire, the variation in CO₂ exchange could not be clearly explained by differences in microtopography or dominant vegetation. However, on more fertile sites the effect was more evident. On mesotrophic sedge pine mire and spruce swamp, the soil respiration was higher in tussock and stump vicinity environments than in hummocks or lawns. The phenomenon was less traceable into vegetation patterns, presumably because of the rapid ongoing succession after drainage that resulted in spreading out of hummock species to lawn habitats during the study period.

O-9-6 BIOGEOCHEMICAL CONTROLS ON THE CARBON ISOTOPIC COMPOSITION OF METHANE PRODUCED IN ANOXIC MARINE SEDIMENT. M. J. ALPERIN (1), N. E. BLAIR (2), D. B. ALBERT (1), AND T. M. HOEHLER (1). (1) Curriculum in Marine Sciences, University of North Carolina, Chapel Hill, NC, 27599-3300, USA. (2) Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC, 27695-8208, USA.

The carbon isotopic composition of methane produced in anoxic sediment is controlled by four principle factors: (a) the pathway of methane formation (i.e. CO₂ reduction, acetate fermentation, or decomposition of "non-competitive" compounds), (b) the isotopic composition of methanogenic substrates, (c) the isotope fractionation factors for methane production, and (d) isotope fractionation associated with methane oxidation. The importance of each factor was evaluated by monitoring carbon isotope ratios in methane produced by a well-defined sediment microcosm. Anoxic marine sediment from Cape Lookout Bight, NC, was placed in a Pyrex, headspace-free enclosure and allowed to incubate for 120 days. Sediment samples were removed at weekly intervals and analyzed for CH₄, CH₃COOH, SCO₂, and SO₄²⁻ concentrations as well as δ¹³C-CH₄ and δ¹³C-SCO₂. In addition, methane production rates from CO₂ and acetate, methane oxidation rates, and sulfate reduction rates were measured using radio-tracer techniques. Methane did not accumulate during the initial period when sediment contained sulfate, indicating little methane production from "non-competitive" substrates. Following sulfate depletion, methane accumulation in the sediment microcosm proceeded in three distinct phases. The first phase was characterized by acetate accumulation to concentrations >5 mM. During this period, methane production rates from CO₂ and acetate were approximately equal and the isotopic composition of methane ranged from -75 to -85‰. In the second phase, the acetate pool experienced a precipitous decline to concentrations >20 μM. During this period, acetate fermentation was the dominant

methanogenic pathway and the methane produced was isotopically heavy (-25‰). Acetate concentrations remained low through the third phase and methane production was dominated by CO₂ reduction. The isotopic composition of methane produced during this period was ca. -60‰. Conversion of ¹⁴C-CH₄ to ¹⁴C-CO₂ concurrent with methane production was detected throughout the period of methane accumulation, at rates equivalent to 2 to 10% of the net methane production rate. Isotope fractionation associated with this oxidation may play a secondary role in modifying the isotopic signature of the methane. Results from this laboratory study suggest that microbial interactions at the sulfate-methane transition zone affect both the relative importance of different methanogenic pathways and the isotopic composition of the methanogenic substrates. Both these factors could create variations in the isotopic composition of methane produced in seasonally variable marine sediments.

O-5-9 NITROUS OXIDE AND METHANE FLUXES FROM TERRESTRIAL ECOSYSTEMS. P. LAMBUS and S. CHRISTENSEN, Institute of Population Biology, Copenhagen University, Denmark.

Time series for N₂O and CH₄ fluxes are obtained from an agricultural soil (sandy loam), two forest floors (Spruce and Beech; sand and sandy loam respectively) and three grass covered soils (fen coastal and sandy grasslands respectively). Thirty 25 cm length by 10 cm diameter PVC tubes were driven 20 cm into the soil at 2 - 5 meter intervals along toposquences at each site. The stationary cylinders are covered with a lid and two gas samples are withdrawn from the headspace at a 20 - 30 min interval. The gas samples are stored in evacuated crimp seal vials, until analysis by gas chromatography. Fluxes of N₂O and CH₄ has been determined monthly since December 1989 (n=8-10) and August 1990 (n=2-5) respectively. The sandy soils (Spruce and grassland) showed the lowest N₂O emission, with a net average production below 2.4 μg N dm⁻² d⁻¹. N₂O production in the four other sites varied between 3.8 and 5.6 μg N dm⁻² d⁻¹, lowest in the fen and highest in the agricultural soil. The highest rates, up to 40 μg N dm⁻² d⁻¹, were found at lower positions in the coastal grassland and in the fen, the only sites showing a pronounced spatial variability at the mesoscale. At each sampling the chambers were ranked with respect to N₂O fluxes. The average rank values identified certain chambers as stable "cold" or "hot" N₂O producers; except for the sandy grassland, where none of the average ranks differed significantly from 15.5, the median value. Disturbed soil samples from the forest bottoms and the sandy grassland, incubated under reduced oxygen, produced N₂O 1000 times faster than *in situ* N₂O production. C₂H₂ amended slurries implied denitrification as the main process producing N₂O, except for the higher elevations in the Spruce forest, where a slightly negative C₂H₂ effect indicated that nitrification could have formed some N₂O. In most cases, except the lower position in the Spruce toposquence, N₂O production appeared to be NO₃ limited. All areas consumed CH₄ at average rates between 0.3 and 2.9 μg C dm⁻² d⁻¹. The highest CH₄ consumption was found in the Spruce forest and in the sandy grassland, the two areas having the lowest nitrous oxide production, thus indicating a connection between CH₄ consumption and N₂O production. CH₄ flux was significantly correlated (r=-0.30**) with N₂O flux in the Spruce forest. Occasionally a very high CH₄ production, up to 40 μg C dm⁻²

d⁻¹ could be detected from chambers at lower positions, especially in the fen and the coastal grassland.

PB-9/10-1 A COMPARISON OF NITROGEN TRACE GAS PRODUCTION BY AUTOTROPHIC AND HETEROTROPHIC NITRIFIERS. I. C. ANDERSON, D. BURDIGE, AND J. HOMSTEAD, Old Dominion University, Department of Oceanography Norfolk, Virginia, USA., and M. A. POTH, USDA Forest Service, Riverside, California, USA.

Soil microorganisms have been shown to be important sources to the atmosphere of the nitrogen trace gas species, nitric oxide (NO) and nitrous oxide (N₂O). Present evidence suggests that autotrophic nitrifiers such as *Nitrosomonas europaea* are the primary producers of NO and N₂O in aerobic soils, whereas denitrifiers such as

Pseudomonas sp. or *Alcaligenes sp.* are responsible for most of the NO and N₂O emissions from anaerobic soils. Recently it has been shown that *A. faecalis*, a bacterium common in both soil and water, is capable of heterotrophic nitrification as well as denitrification. The work presented here was undertaken to determine whether heterotrophic nitrification might be as important a source of NO and N₂O as autotrophic nitrification. We compared the responses of *N. europaea* and *A. faecalis* to changes in pO₂ and to the presence of typical nitrification inhibitors. Head space samples were injected into a modified luminol, NO₂ detector for analysis of NO and into a gas chromatograph with electron capture detector for analysis of N₂O. For determination of pO₂, cultures sparged with various mixtures of air and N₂ were continuously circulated through a tee fitted with an O₂ microelectrode. Maximal production of NO and N₂O occurred at low pO₂'s in both *N. europaea* (pO₂ = 0.3%) and in *A. faecalis* (pO₂ = 2 - 4%). In *N. europaea* most of the NH₄⁺ oxidized was converted to NO₂ with NO accounting for 2.6% and N₂O for 1% of the end product. In *A. faecalis* maximal production of NO occurred at a pO₂ of 2 and N₂O at a pO₂ of 4. At these low pO₂'s there was net nitrite consumption. Nitric oxide production normalized to 10⁶ cells per day was 20.9 ng NO-N for *N. europaea* and 17 ng NO-N for *A. faecalis*. Nitrous oxide production was 7.9 ng N₂O-N for *N. europaea* and 94.5 ng N₂O-N for *A. faecalis*. Phenylacetylene which effectively suppressed both NO and N₂O production by *N. europaea* partially reduced N₂O emissions by *A. faecalis* but had no effect on NO production. N-serve was only partially effective at these low pO₂'s in both organisms. Under anaerobic conditions *A. faecalis* was able to denitrify nitrite but not nitrate. Production of NO and N₂O by nitrite reduction under anaerobic conditions was 0.12 ng NO-N and 6.65 ng N₂O-N per 10⁶ cells per day. Once much of the nitrite was consumed the NO and N₂O produced were further reduced to N₂. Given the rates of NO and N₂O production reported here, these results suggest that heterotrophic nitrification may be a significant source of both NO and N₂O in aerobic to near-anaerobic soils and water.

O-5-1 THE INFLUENCE OF TROPICAL BIOMASS BURNING ON CLIMATE AND THE ATMOSPHERIC ENVIRONMENT. M.O. ANDREAE, Max Planck Institute for Chemistry, Biogeochemistry Department, P.O. Box 3060, D-6500 Mainz, Germany.

The historical, economical, and environmental aspects of biomass burning are briefly outlined. The use and extent of agricultural burning and its geographical distribution are discussed. The emissions of gases and aerosols to the atmosphere are estimated based on field and laboratory measurements. The atmospheric reactions of these emissions, their transport and deposition, and their impact on global climate and environmental quality are assessed.

O-12-7 THE SENSITIVITY OF THE GLOBAL ATMOSPHERE TO CHANGES IN ANTHROPOGENIC SOURCES OF METHANE. N.G. ANDRONOVA and I. L. KAROL, Main Geophysical Observatory Karbyshev Street, 7 Leningrad 194018, USSR

The global atmosphere is represented simply by interactions near their equilibrium values of temperature and seven components: methane, carbon monoxide, tropospheric ozone, stratospheric ozone, total ozone, hydroxyl and water vapor. A linearized system of interactions is defined and the value of its parameters are estimated from analyses of empirical data and model experiments for annually averaged conditions. The properties of the system are studied by the Cause-and-Effect Analysis (CEA) technique. The CEA technique enables the identification and visualization of the pathways from the system's external parameters to its internal variables and all of the system's feedbacks, and allows the quantitative estimation of the sensitivity of any internal variable to a change in any external parameter. Here we consider a change in anthropogenic methane sources to be the external forcing for the global atmosphere, and take the anthropogenic methane sources equal to 60% of the total methane source. It is shown that the properties of the atmosphere depend on: (1) the intensity of the interaction between hydroxyl and tropospheric ozone; (2) the ratio of the intensity of the chemical regulation of hydroxyl content by methane and carbon monoxide to other hydroxyl sinks not included in the system; and (3) the intensity of the interaction between temperature and water vapor. It is also shown that an increase in the anthropogenic methane source results in increases in methane, ozone and temperature in the troposphere (positive sensitivities), and a decrease in tropospheric hydroxyl (negative sensitivity). Quantitatively, a 1% increase in the anthropogenic methane source leads to a 0.2% increase of ozone, an 0.008°K increase in temperature, a 0.4% decrease in hydroxyl, and a 1.7% increase in methane. Because the methane concentration can be considered as the "output" for this particular external forcing or "input", the last result can be interpreted as a net amplification by the set of atmospheric feedbacks such that a 1% perturbation in the input is amplified by a factor of 1.7 at the output.

PB-6-1 THE CHANGE OF POTASSIUM-SALINITY RATIO IN THE NORTHERN PART OF THE INDIAN OCEAN. V.V. ANIKIEV, A.P. NEDASHKOVSKY, Pacific Oceanological Institute of the Far Eastern Branch, USSR Academy of Sciences, Vladivostok, USSR.

In November-December 1989, at 5 stations of the northern part of the Indian Ocean the precision measurements of potassium-salinity ratios were carried out at the horizons from 5 to 2000 m. In the surface layer 0-100 m there was revealed the decrease of potassium-salinity ratio in

the 200-2000 m layer. The possible reasons of the relative potassium impoverishment of surface waters are discussed.

O-9-2 ANAEROBIC FORMATION AND DEGRADATION OF DIMETHYLSULFIDE AND METHANETHIOL BY NEW TYPES OF ACETOGENIC AND METHANOGENIC BACTERIA. E. BAK¹ AND K. FINSTER². 1) Max-Planck-Institut für Terrestrische Mikrobiologie, Marburg, FRG; 2) Department of Ecology and Genetics, University of Aarhus, Aarhus, Denmark.

Intense formation of dimethylsulfide (DMS) was observed in anaerobic marine and freshwater enrichment cultures supplemented with methoxylated aromatic compounds (3,4,5-trimethoxybenzoate or syringate). After transfer into fresh medium, however, DMS production ceased and the originally expected *Acetobacterium* species developed. Growth of *Acetobacterium* sp. in further subcultures was not accompanied by formation of volatile organic sulfur compounds. However, by direct dilution of anoxic mud samples in liquid media, undescribed nonmotile rod-shaped bacteria were obtained which degraded the methoxylated aromatic compounds with concomitant formation of DMS. Two strains, a freshwater species (strain TMB4) and a marine species (strain SA2), were subsequently isolated in pure culture. Both strains grew in defined sulfide-reduced medium and degraded the aromatic compounds to acetate and DMS. Small amounts of methanethiol (MT) were formed as intermediate. The volatile organic sulfur compounds were derived from the methoxy-carbon and the inorganic sulfide added as reductant to the medium. The principle biochemical mechanism leading to DMS and MT production has not been elucidated. Both isolates grew also with gallate, phloroglucinol, or pyrogallol without producing DMS or MT. By their overall physiological capabilities both strains resemble the obligate anaerobic *Pelobacter acidigallici*. The release of DMS and MT during demethoxylation reactions by strains TMB4 and SA2 represents a new mode by which volatile organosulfur compounds can be formed under anoxic conditions. Moreover, strain TMB4 and SA2 were able to degrade methoxylated aromatic compounds directly to acetate, a process which previously was believed to proceed in two steps involving *Acetobacterium* (demethoxylation) and *Pelobacter* (cleavage of the hydroxylated aromatic ring).

To investigate the anaerobic microbial degradation of methylated sulfur compounds, enrichments and dilution series supplemented with MT were inoculated with anoxic mud samples. In enrichment cultures MT was first rapidly consumed. In subcultures, however, MT consumption ceased after 3-4 transfers. In contrast, in dilution series (dilution steps 10^3 - 10^5) MT consumption started only after a lag phase of 3 weeks but continued also in subcultures. From a dilution series inoculated with saltmarsh sediment a coccoid methanogenic bacterium (strain MTP1) was isolated that grew in defined mineral medium with MT as sole source of energy and carbon. Strain MTP1 disproportionated MT to methane and carbon dioxide according to the following equation:

$$\Delta G^\circ = -36.9 \text{ kJ mol}^{-1}$$

Besides, the strain grew readily with DMS, mono-, di-, and trimethylamine, or methanol. Acetate was utilized slowly. On formate the isolate produced CH_4 without significant growth. During growth with MT minor amounts of DMS were formed but were consumed again within the growth period. Strain MTP1 tolerated MT in concentrations of 30-40 mM. Under optimal conditions the strain had a doubling time on MT of about 14h. Per mole of MT about 3 g dry

cell mass were formed. Strain MTP1 is the first obligate anaerobic bacterium isolated so far that is able to grow with methanethiol.

PB-6-2 FOREWATER DISTRIBUTION AND FLUX OF CHEMICAL VARIABLES IN FLORIDA BAY SEDIMENTS. T.R. BARBER AND P.R. CARLSON, JR. Florida Marine Research Institute, St. Petersburg, Florida, USA.

Rapid, widespread, and unexplained mortality of the seagrass *Thalassia testudinum* is occurring in Florida Bay, a highly productive, subtropical marine lagoon at the southern tip of the Florida peninsula. Over 270 km² (18%) of the dense seagrass beds of Florida Bay have been affected. The purpose of this study was to investigate the influence of *Thalassia* die-off on the biogeochemistry of the carbonate-mud sediments in Florida Bay. The depth distributions of porewater pH, ΣCO_2 , CH_4 , and H_2S in sediments inhabited by *Thalassia* and in an adjacent dead patch were measured four times during 1990. Benthic flux measurements of methane were made, and the calculated sediment-water exchange coefficient was used to estimate the flux of sulfide out of the sediments. The biogeochemical signal produced from the decomposition of freshly dead below ground biomass was not detectable within one year of the die-off event. In this study, methane was quantitatively consumed during the winter. Porewater concentrations and sediment-water fluxes of methane increased during the year. The shape of the methane profile suggests methane is produced in the zone of sulfate reduction; methanogens may be utilizing non-competitive substrates exuded from the roots and rhizomes. The calculated diffusive flux of sulfide from the sediments is always larger in the live zone than the dead, except in winter where there is no statistical difference. The ratio of ΣCO_2 : H_2S approaches the theoretical stoichiometry of 2 only during the spring; *Thalassia* may influence porewater chemistry by supplying oxygen to the sediments and/or by removal of dissolved CO_2 . Important factors controlling the distribution of sulfide are: the quantity and quality of dissolved organic matter exuded from the below ground biomass, the availability of surplus photosynthetic oxygen, and the influence of temperature on microbial activity. Paradoxically, the high concentrations of sulfide, supported by the exuded dissolved organic matter, may overwhelm the ventilation system of the *Thalassia* community, exposing the roots and rhizomes to hypoxia and sulfide toxicity.

PA-4/5-19 ASSESSMENT OF GLOBAL AND REGIONAL CHANGES IN THE BIOGEOCHEMICAL STRUCTURE OF AGROECOSPHERE. V.N. BASHKIN. Institute of Soil Science and Photosynthesis, Pushino, Moscow region, USSR.

At present the sustainable development of the agroecosphere is impossible without the conservation of natural biogeochemical cycling of various elements both on regional and global levels. The intensive application of agrochemicals for the achievement of maximal yield, however, accompanied by a transformation of biogeochemical cycles into agrogeochemical ones, characterizing by sufficiently lesser sustainability. As a consequence, there is the dilemma of a food or ecological crisis, which solution can not be made on the base of traditional approaches to agriculture. These situations are actual, both for developed countries and developing ones. So, the overstep of agriculture on the industrial foundation led to the sharp enhancement of energy and resource use, agrochemical application growth and disturbance of biogeochemical structure, accompanied by pollution and acidification of soil, water and bottom sediments. In the agroecosphere and biosphere there is the huge excess of many elements and in particular N, its excessive

accumulation is about 9 million t/yr (up to 120 kg/ha in intensive agricultural region) in spite of sharp enhancement of NO_x evolved due to denitrification. Simultaneously, the residues of pesticides, microelements and heavy metals accumulate, synergetic and antagonistic relationships appear. An accumulation of various pollutants takes place in bottom sediments that leads to water pollution. Most trophic chains are altered, but these alterations differ, depending on the level of anthropogenic pressure in various biogeochemical provinces. In accordance with this, the alteration of physiological parameters of human organism take place. For example, we found more stable relationships between fertilizer rates, cholesterol content and changes of blood lipid structure of people living permanently in nonchemozemic biogeochemical provinces in comparison with chemozemic ones. As a consequence, it is necessary to overstep from constant guidelines of pollutants in various media to their slipping (regional) values, grounded from biogeochemical and normal human physiology positions. It is established that the solution to all these problems is possible using geoinformation and expert-modeling systems to manage the huge information fluxes in hierarchy organized landscapes. To avoid the irreversible changes in the biogeochemical structure of the agroecosphere, it is necessary to work out the parameters of ecologically optimal bioproductivity. Under these conditions, the agrochemical rates must be included into limits of natural deviation of biogeochemical cycles of various elements without their disturbance. The practical consequence of the theory of ecologically optimal bioproductivity of agroecosphere on the local level is ecological-agrogeochemical regionalization of agrolandscapes. Such a regionalization exists on the ground of biogeochemical landscapes and their conjugations in soil-geochemical catenes as elementary structural units. An example, it is worked out the regionalization of the agricultural area of the Moscow region, with division of zones of a real danger of surface and ground water pollution by residues of N and P fertilizers as well pesticides. On the base of mathematical analysis the prediction of disturbance of N and P biogeochemical cycles exist and the possibility of agrolandscape pollution is shown. It is recommended to decrease the level of agrochemical application. Using geoinformation and expert-modeling systems the parameters of ecologically optimal bioproductivity of various agrolandscapes are carried out.

PA-4/5-1 AN HISTORICAL BIO-GEOGRAPHY AND ENVIRONMENTAL ANALYSIS OF THE PHYLLOXERA DISEASE IN NORTHERN CALIFORNIA VITICULTURAL AREAS: THE FUTURE IMPACT OF A BIOTYPE ON THE LANDSCAPE ECOLOGY AS A MODEL OF LAND USE PLANNING IN CALIFORNIA AGRICULTURE. MICHAEL T. BAUBLITZ. Lawrence Berkeley Laboratory, Berkeley, CA 94720.

Based on a preliminary survey, it is recognized that there are forthcoming changes in viticultural practices, especially in fumigation of the various soils, which are increasingly directed away from traditional sulfur compounds and toward biological alternatives; this raises the important question of whether the reduction of chemical uses has been a factor in the severe comeback of the phylloxera disease which now takes the form of a biotype (mutated form) after years of consistent treatment in the areas of once resistant rootstock and are causing the demise of aged vineyards of the Napa and Sonoma viticultural areas. It raises the question about the effects of the prolonged drought as a factor in plant (and soil-root) stress and the increasingly aged vines as being more susceptible to disease or its comeback in times of drought. The future integrity as well as the unique historic-cultural legacy of California's prime vineyards is now at stake as new pressures of urbanization pose a critical debate for planners when it costs \$10,000 an acre to replant diseased vineyards.

What this problem now entails may soon open up new opportunities for genetic engineering intervention in targeting areas infected by disease by innovating new rootstock which is both resistant to disease and drought in such a manner that the new rootstock is best suited to the local micro-climate/micro-environment(s) and hence planted in restricted locales in recognition of the "terroir" of the region or area (incorporating the French concept of optimum growing conditions for specific varieties in one area designated as best suited to viticultural practice). This means adding greater genetic/variety diversity to the landscape instead of great expanses of one single planting (a "monoculture" concept) which may well have been a factor in the spread of disease (vector) and is added testimony to the risks of heavily relying on a single vine on aged rootstock, which in the face of drought conditions becomes susceptible to disease. Hence, a challenge for bio-engineers and viticulturists in the innovation of both disease and drought resistant rootstock with respect to landscape ecology and microclimate which are optimally suited to growing certain vines.

This study will also represent an ecological land use planning model for the future of California agriculture in general, with the information gained from an ongoing environmental survey compiled and analyzed in terms of "geographic information system" (GIS) which can be made applicable to land use planners, agriculturists, and bio-geographers alike. Together, these disciplinarians can focus on the future growth bio-geographers alike. Together, these disciplinarians can focus on of a viable industry and way of life in notable geographically defined wine-growing areas (regions) known to the rest of the world as one of the greatest treasures of such an economically vital resource and aesthetic landscape.

O-10-6 MICROBIOLOGICAL TRANSFORMATION OF LOW MOLECULAR CARBON COMPOUNDS IN DEEP SUBSURFACES. BELYAEV S.S., BORZENKOV, I.A., Institute of Microbiology, USSR Academy of Sciences, Moscow, USSR.

Bacterial transformation of low molecular carboxyl compounds were studied in stratal waters of oil fields of Tatariga. Oil occurs in sand-aleurite layers of Upper Devonian sedimentary deposits at a depth of 1700 m. The temperature of oil strata is 30-40°C. The fields were worked out using flooding with fresh river water. Through injection wells dissolved oxygen entered the oil strata and then was consumed very quickly during aerobic bacterial processes. Redox conditions of the near bottom zone were changed considerably. When surface water was injected, Devonian relic brines were diluted and the spectrum of stratal water mineralization became wider. At one of the areas studied, mineralization varied from 16 to 292 g/l; at another, from 2.6 to 34.6 g/l.

The activity of microbiological processes was studied comparatively in near bottom zones of injection well and oil-bearing strata of the areas mentioned above. The intensity of inclusion of bicarbonate, acetate, and methanol in bacterial cell composition and the intensity of bacterial methanogenesis from bicarbonate, formate, methylamine and acetate were determined by radioisotope method using substrate labelled by ¹⁴C.

As regards changes in redox conditions the intensity of inclusion of carbon of low molecular compounds in organic matter of bacterial cells was maximal from 4.69 to 33.09 mg C l⁻¹ day⁻¹ (mean value - 22.15 mg C l⁻¹ day⁻¹). In stratal water this value ranged from 0.1 to 14.56 mg C l⁻¹ day⁻¹ at mean value 5.04 mg C l⁻¹ day⁻¹ for the area

with high stratal water mineralization and $6.01 \text{ mg C l}^{-1} \text{ day}^{-1}$ for low-mineralized water. The ratio of intensities of acetate to bicarbonate cells inclusion in organic matter showed the prevalence of autotrophic processes of bacterial carbon and for near bottom zone (0.86).

Mean value of methanogenic intensity in the near bottom zone of injection well was $4.33 \text{ mg CH}_4 \cdot \text{l}^{-1} \cdot \text{day}^{-1}$. At the area with freshened stratal water this value decreased to $1.01 \text{ mg CH}_4 \cdot \text{l}^{-1} \cdot \text{day}^{-1}$, and in high mineralized water to $0.19 \text{ mg CH}_4 \cdot \text{l}^{-1} \cdot \text{day}^{-1}$. In the studied ecosystems bicarbonate was the main substrate for the bacterial methanogenesis. Acetate was the second most important substrate for methanogenesis, although in several cases the contribution of formate to methanogenesis was considerable. The contribution of methylamine to the process of methanogenesis increased as stratal water salinity became higher.

0-5-2 GLOBAL SURVEY OF LARGE HISTORIC WILDFIRES: THEIR CLIMATOLOGIES AND CONTRIBUTIONS TO BIOMASS BURNING. **J.L. BETANCOURT**, U.S. Geological Survey, Tucson, AZ, USA; **T.W. SWETNAM** & **S.W. LEAVITT**, Lab. of Tree-Ring Research, Univ. of Arizona, Tucson, AZ, USA; **D.R. CAYAN**, Scripps Institution of Oceanography, La Jolla, CA, USA.

Enhanced carbon uptake by temperate forests, due to stimulation of photosynthesis by CO_2 enrichment, may explain discrepancies between interhemispheric atmospheric CO_2 budgets and measurements of CO_2 partial pressures in surface ocean waters¹. A disturbing outcome of global warming could be increased probabilities for persistent droughts, massive diebacks and widespread forest fires², with instantaneous releases of both old and newly-sequestered carbon into the atmosphere. Though wildfires are an important source of radiatively and chemically active gases in the atmosphere, neither their climatologies (i.e., their predictability) nor their contributions to biomass burning are well understood. There can be little doubt that catastrophic fires emanate from large-scale variations in the climate system that promote drought on a subcontinental scale. For example the total area burned annually across the southern USA closely tracks the Southern Oscillation (SO), with maximum acreage burned during the positive SO or La Nina phase³⁻⁴. This is in contrast to Indonesia and Australia, where the largest fires commonly occur during the negative SO phase or El Nino conditions. Carbon gas emissions from single, catastrophic fires contribute significantly to annual fluxes from biomass burning. Over a 3-day period in October 1871, forest fires affecting 1.5 million ha in the Great Lakes states of Michigan and Wisconsin emitted an estimated 100 TgC, nearly the current total annual emissions from fires in temperate forests⁵. The Great Black Dragon Fire of May 1987, which burned over 5 million ha in Siberia and Mongolia, produced about 79 TgC during a 3-week period⁶. Hence, large forest fires yield relatively high variances in annual carbon gas emissions that can be attributed to large-scale climatic anomalies. We will use composite maps of anomalies in daily 100-mb heights available since 1947 and monthly sea level pressures since 1899 to describe climatologies associated with a number of large fires in the 20th century. An understanding of fire climatologies will be coupled with estimates of gas emissions to evaluate how global warming might alter fire regimes to impact atmospheric chemistry.

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0-9-7 THE CARBON ISOTOPE BIOGEOCHEMISTRY OF METHANE PRODUCTION IN ANOXIC SEDIMENTS. **N.E. BLAIR**, **S.E. BOEHME** and **W.D. CARTER, JR.**, Department of Marine, Earth and Atmospheric sciences, North Carolina State University, Raleigh, NC 27695-8208, USA.

The carbon isotopic composition of methane from temperate marine and freshwater sediments varies by as much as 10 per mil seasonally. Isotopic measurements of the methanogenic precursors, CO_2 and acetate, isolated from the anoxic marine sediments of Cape Lookout Bight, NC, have been made to determine the source of the seasonal variations. The $\delta^{13}\text{C}$ value of the acetate ranged from -17.6 per mil in the sulfate reduction zone to -2.8 per mil in the underlying methanogenic sediment. The ^{13}C enrichment downcore appears to be associated with the dissimilation of acetate to CO_2 and CH_4 . The fractionation factors for that process have been estimated to be 1.032 ± 0.014 and 1.036 ± 0.019 for the methyl and carboxyl groups, respectively. The $\delta^{13}\text{C}$ values of the dissolved inorganic carbon range from 0 per mil at the surface to +8 per mil at depth with a subsurface minimum as light as -12 per mil at 3-6 cm depth. The downcore ^{13}C -enrichment is attributed to the isotopic fractionation associated with CO_2 -reduction. Changes in the relative rates of acetate dissimilation and oxidation within the methanogenic zone have been cast as the key pivot point in a model which describes the seasonal variation in methane $\delta^{13}\text{C}$ values. Those changes ultimately control the relative importance of the acetate dissimilatory and CO_2 -reduction pathways. Migration of the methanogenic zone along the isotope gradient in the dissolved inorganic carbon pool within the sediment also contributes to the seasonal variation at the marine site. Investigations at White Oak River, NC suggest that the latter factor is less important in freshwater settings.

PB-12-1 METHANE EMISSIONS FROM URBAN NATURAL GAS DELIVERY SYSTEMS. **DONALD R. BLAKE**, **TAI-YI CHEN** and **F. SHERWOOD ROWLAND**, Department of Chemistry, University of California, Irvine.

The importance of methane as a greenhouse gas has become increasingly clear in recent years. Current annual emissions of methane into the atmosphere exceed the removal rate by approximately 50 teragrams. Most sources of methane are biogenic and have been studied more than the geogenic or anthropogenic sources. Recent studies of the carbon-14 content of atmospheric methane suggests that the nonbiogenic emissions are about 1/3 of the total. If this is the case then current source estimates severely underestimate the importance of anthropogenic methane emissions to the atmosphere. The focus of this study was to determine whether natural gas leakage from delivery systems might be a significant source of atmospheric methane. The study was divided into two categories one in which we collected 20 samples or less in many U.S., Middle Eastern and European cities. The purpose of this study was to

determine what excess methane levels were observed in the cities and guide us in choosing a smaller number of cities to more rigorously study. Background levels of methane for the particular latitudes were subtracted from the various city methane values to yield excess mixing ratios. The range of excess values encountered during this snapshot global study was 50 - 1500 ppbv. Estonia and Soviet Armenia were the two cities in which methane excess levels were greater than 1000 ppbv while Austria was at the low end of the range. In addition to methane measurements the air samples were assayed for numerous nonmethane hydrocarbons from which estimates of the natural gas contribution to the excess methane levels can be made. A suite of halocarbons were also measured from which CFC-12 excess levels were used to estimate methane emission rates from that urban study, in which we collected more than 500 samples, focused on the western U.S. Using CFC-12 usage figures for those cities we estimate annual methane emissions from the U.S. to be $10 \pm$ teragrams.

O-7-1 DISSIMILATORY REDUCTION OF SELENATE TO ELEMENTAL SELENIUM BY ANAEROBIC BACTERIAL CULTURES. J. SWITZER BLUM, R.S. OREMLAND AND N. STEINBERG. U.S. Geological Survey, Menlo Park, California, 94025, USA.

Selenium oxyanions in drainage waters from irrigated regions of the western USA pose serious environmental problems. The dissimilatory reduction of selenium oxyanions by bacteria present in sediments has been shown to be a widespread and very active phenomenon. However, the bacteria involved in this reduction have only been poorly characterized. An enrichment culture grew in defined minimal medium with acetate as the electron donor and either selenate or nitrate as the electron acceptors. No growth occurred without an electron acceptor. Growth on selenate resulted in its disappearance from the medium, the transient appearance of selenite, and the progressive reddening of the medium due to formation of Se^0 . Cell densities reached 3×10^8 cells/ml on selenate. Similarly, growth on nitrate resulted in its removal from the medium, the transient appearance of nitrite, and a final cell density of about 6×10^8 cells/ml. When grown with both 20 mM nitrate and selenate in the medium, nitrogen oxyanions were attacked first and completely depleted from the medium before selenium oxyanions were metabolized.

Pure cultures were obtained from the enrichment by streaking agar plates containing defined mineral media with acetate as the electron donor, selenate as the electron acceptor, and an atmosphere of $\text{N}_2/\text{H}_2/\text{CO}_2$ in an anaerobic chamber. After 5-10 days, red colonies were visible. Isolated colonies were picked and transferred to liquid media. The isolate was a gram-negative, motile vibrio (1.5 - 2 μ length). The isolate grew best, with concomitant Se^0 formation, in media containing lactate or pyruvate as electron donors and supplemented with yeast extract. No growth was observed on acetate unless H_2 was also present.

PA-4/5-2 EFFECT OF NITROGEN FERTILIZER AND NITRIFICATION INHIBITORS ON METHANE AND NITROUS OXIDE FLUXES IN IRRIGATED CORN. K.E. BRONSON AND A.R. MOSIER. USDA-ARS, Fort Collins, CO., USA.

Agricultural systems contribute a large proportion of the global emissions of methane (CH_4) and nitrous oxide (N_2O) to the atmosphere. Nitrogen fertilizer strongly influences the flux rates of these gases in agroecosystems. Methane and N_2O fluxes were measured in an irrigated corn (*Zea mays* L.) field throughout a cropping system. Fertilizer treatments included 0 and 218 kg urea-

Nitrogen (N) ha^{-1} as well as applications of the nitrification inhibitors (NI's) nitrapyrin and encapsulated calcium carbide. Brief periods of CH_4 emissions were observed after irrigations, with no effect of N or NI's. Uptake of CH_4 was highest in the unfertilized plots and lowest in the plots that received N and NI's. Nitrous oxide emissions were 16 times greater in urea-fertilized plots compared to unfertilized soils. Applying NI's with urea decreased N_2O emissions 43 to 71%.

PB-11-1 METHANE BALANCE IN NORTHERN BOGS. D. ANN BROWN, AECL Research, Whiteshell Laboratories, Pinawa, Manitoba, Canada and R.P. OVEREND. Solar Energy Research Institute, 1617 Cole Blvd., Golden, Colorado, U.S.A.

Waterlogged peat soils of northern wetlands cover nearly 5% of the terrestrial surface. The top layer of a peat bog, (acrotelm), is an open matrix of decaying vegetation where water from precipitation can flow across the surface. The main body of the bog (catotelm), is almost impermeable to water and to gas, so rainfall does not penetrate it.

Methane in these wetlands is produced from decaying plant biomass by a consortium of anaerobic bacteria. The plant polymers, (eg. cellulose), are first depolymerized, then broken down into sugars; these are then fermented to volatile fatty acids, alcohols, carbon dioxide and hydrogen. It is these latter two that are the substrates for methanogenic bacteria. Methane can then be further metabolized, both aerobically and anaerobically, to carbon dioxide by methanotrophic bacteria.

Methane samples were extracted on a square grid spacing at three depths from Mer Bleue, an ombrotrophic bog near Ottawa, Canada. The concentrations of methane were found to be spatially variable. Laboratory incubations have shown that, although methane production occurs throughout the peat profile, it is quite heterogeneous, since there are two populations of methanogenic bacteria. One is found mainly near the surface in the acrotelm and is strongly active; the other occurs in the catotelm and may be two orders of magnitude less active.

Laboratory peat columns show that, as the concentration of methane increases, the moisture content and hydraulic conductivity decrease. These changes did not occur in a sterilized column of peat. A mass balance determination at the end of the experiment showed that 17% of the active column to be gaseous. Methane is only sparingly soluble in water and most of the methane produced in bog is trapped within the peat matrix. Carbon dioxide, though quite soluble, is also present in the gas phase. This volume of gas makes the peat unsaturated with regard to water. The gas also blocks the pore space, which in turn prevents water flow, thus reducing the hydraulic conductivity. The conductivity in unsaturated soils is much less than that in saturated ones, and although peat bogs are considered to be saturated, evidence suggests otherwise. The result is that little water or gas is able either to enter or to escape the catotelm.

A methane balance is probably conserved within bogs, except for an occasional "burp" when the atmospheric pressure is low and the pressure within the bog is sufficient to allow gas to be vented. In the aerobic acrotelm, dissolved methane is oxidized by methanotrophic

bacteria to carbon dioxide, using oxygen as the electron acceptor. Preliminary results indicate that, in the catotelm, there are also methanotrophic bacteria that oxidize the methane anaerobically, possibly using water as the electron acceptor. The methanogen and methanotroph organisms seem to be symbiotically interdependent, possibly in a predator/prey relationship since it has not yet been possible to separate the cultures and maintain their viability. Although methane does accumulate slowly in the catotelm, this accumulation appears to be limited.

As methane is conserved, any major loss of mass from the bog must be in the form of hydrogen or carbon dioxide. Hydrogen is a small molecule that can easily diffuse through the peat matrix, whereas dissolved carbon dioxide can be transported both by diffusion and by advection. If these ideas, based on results by us and co-workers at Agriculture Canada are correct, they imply that, so long as bogs remain undisturbed, little methane will escape. However, once the bog is disrupted by man for mining, agriculture or silviculture, or even possibly by climatic change, methane will be released and vented to the atmosphere, where it will act as a greenhouse gas.

O-2-6 NEGATIVE SATURATION ANOMALIES OF CH_3CCl_3 IN THE OPEN OCEAN: IMPLICATIONS FOR TROPOSPHERIC OH. J.H. BUTLER, J.W. ELKINS, T.M. THOMPSON, B.D. HALL. Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA. T.H. SWANSON. Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA. V. KOROPALOV. Institute of Applied Geophysics, Moscow, USSR.

We recently have observed extensive negative saturation anomalies for CH_3CCl_3 in the mid-Pacific Ocean. These measurements were made as part of the third Soviet-American Gas and Aerosol Experiment (SAGA-3), conducted in the central and west Pacific Ocean from February through April, 1990. Saturation anomalies, corrected for physical effects, were largest at the equator, where upwelling and biological activity were greatest, but present virtually everywhere in our sampling range of 20°N to 15°S. The mean saturation anomaly for all of our CH_3CCl_3 data was -12%, suggesting that the ocean may be a significant sink. Extrapolation of our results to the global ocean suggests that consumption of CH_3CCl_3 in surface waters could account for 6% of the loss of atmospheric CH_3CCl_3 , with a possible range of 17% to 15%, depending upon the actual distribution of these anomalies. This translates to a partial residence time of 110 y for atmospheric CH_3CCl_3 relative to oceanic consumption. These anomalies are supported to some extent by known hydrolysis rates for CH_3CCl_3 , although we cannot rule out the possibility of biological processes playing a part. Because the oceanic sink has not been considered in calculations of tropospheric OH concentration from the distribution and growth rate of CH_3CCl_3 in the atmosphere, our findings may have a significant impact on these calculations. This, in turn, would affect the calculated atmospheric lifetimes of compounds that react with OH in the troposphere, including CO, CH_4 , non-methane hydrocarbons, methyl halides, and hydrochlorofluorocarbons (HCFC's).

PB-6-3 SEDIMENT DEPOSITION AND THE DISTRIBUTION OF REDUCED SULFUR COMPOUNDS IN TOMALES BAY, CALIFORNIA. R.M. CHAMBERS¹, S. VINK², S.V.

SMITH², AND J.C. CORNWELL³. ¹Tiburon Center, SFSU, San Francisco, CA, ²Dept. of Oceanography, University of Hawaii, Honolulu, HI, ³Horn Point Environmental Labs, University of Maryland, Cambridge, MD, USA.

The distributions of reduced sulfur compounds in sediment cores from salt marsh and subtidal environments in Tomales Bay were determined using standard extraction procedures. Chromium reducible sulfur (CRS), operationally defined as the elemental sulfur and pyrite pool, was typically larger than the acid-volatile (AVS) pool, defined as iron monosulfides; free sulfides were detected in salt marsh sediments but not in subtidal sediments. Sandy subtidal sediments contained much less sulfur than muddy sediments, most of which occurred as pyrite. Further, deep subtidal muds (> 1 m) were enriched in sulfur relative to shallow muds (< 1 m), suggesting historical changes in sediment diagenesis. Sediment dating using Pb-210 and Cs-137 methodologies, however, was not able to distinguish distinct historical horizons, due probably to 1) intense sediment mixing by bioturbation, and 2) high rates of sedimentation in the past one hundred years. Although changes in land-use patterns in the surrounding watershed influence sedimentation rate in Tomales Bay, it does not appear that depth distributions of reduced sulfur compounds reflect these changes.

PB-6-4 METHANE FLUX FROM AQUATIC PLANTS-- ISOTOPIC, VENTILATION, BIOMASS & DIURNAL EFFECTS. JEFFREY CHANTON¹, GARY WHITING², WILLIAM SHOWERS³, CHERYL KELLEY⁴, CHRISTOPHER MARTENS⁴, JAMES HAPPELL¹, GHISLAIN GERARD¹. 1. Department of Oceanography, Florida State University, Tallahassee, FL 32306. 2. NASA Langley Research Center, Hampton VA 23665. 3. North Carolina State University, Raleigh, NC 27695 4. University of North Carolina, Chapel Hill, NC 27599.

Emergent aquatic plants play an important role in the interaction of the biosphere and troposphere by serving as direct conduits between reducing and oxidizing atmospheres. Living with their roots in flooded anaerobic sediments and soils requires aquatic plants to maintain effective gas transport systems for delivering oxygen to their roots. A byproduct of oxygen delivery to the rhizosphere is the release of methane to the atmosphere. In addition to serving as active and passive gas transporters, plants can increase methane emission by providing substrates for methanogenic bacteria through the production of leaf litter and root exudates. Plants can also reduce potential methane emission by the delivery of oxygen to their roots thus fueling aerobic methane oxidation.

Methane oxidation consumes the lighter carbon isotope of methane ($^{12}\text{CH}_4$) preferentially, leaving the residual methane enriched in the heavy isotope ($^{13}\text{CH}_4$). We hoped to quantify the importance of methane oxidation in vegetated systems by measuring the difference in the isotopic composition of methane within plant stems and within sediments. It was our hypothesis that isotopic enrichment of methane within plant stems would be proportional to the quantity of methane oxidized within the rhizosphere. We assumed that the isotopic composition of methane within plant stems would be identical to that released by the plants.

Methane concentrations within the stems of the aquatic macrophytes generally varied in concentration between 100 ppm to 1200 ppm in *Carex*, from 0.2 to 4.0 % in *Arctophila*, from 0.5 to 1.9 % in *Peltandra*, and from 0.5 to 4.0 % in *Pontederia*. In all of these plants, methane within plant stems was ^{13}C enriched relative to sedimentary methane by values of from 2 to 15 ‰. However, our assumption that the isotopic composition of methane within the plant

stems would be the same as that released by the plants proved to be wrong. The isotopic composition of methane emitted by the plant canopy was similar in isotopic composition to sedimentary methane. Our current hypothesis is that the ^{13}C enriched plant stem methane is due to the more rapid diffusion of $^{12}\text{CH}_4$ relative to $^{13}\text{CH}_4$ out of leaves to the air, which causes the heavier methane to "back up" within the plant stem. Calculations based on the relationship between gas phase diffusion coefficients and the inverse square root of the reduced mass of the diffusing substance and its matrix (air) suggest a maximum fractionation of -19‰ for methane diffusing in air. All of the plants listed above primarily rely upon molecular diffusion in the transport of gases into and out of the rhizosphere.

If our hypothesis is correct, then plants which rely upon pressurized ventilation for gas transport, rather than molecular diffusion, should not exhibit ^{13}C enrichments in plant stem methane relative to sedimentary methane. Such has been found to be the case for the aquatic macrophytes *Nymphaea*, *Typha*, *Nelumbo*, and *Menyanthes*. However, preliminary data will be discussed which show isotopic fractionations associated with release of methane by pressurized plants. However, in all cases, the isotopic composition of methane emitted by plants has not been consistent with significant methane oxidation in the rhizosphere.

Variations of methane flux as a function of biomass, and diurnal variations of gas emission as a function of plant ventilation system will also be discussed.

PA-1-1 CLIMATE-INDUCED WETLAND CHANGES AND CAUSES OF INCREASING METHANE DURING THE PAST 18,000 YEARS. J.A. CHAPPELLAZ(*), A.M. THOMPSON(+) AND I.Y. FUNG(*). (*) NASA Goddard Institute for Space Studies, New York, New York, USA. (+) NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

Measurements of methane concentration in ice-cores from Greenland and Antarctica show a doubling from glacial (350 ppbv) to interglacial (650 ppbv) periods and another large increase from ~1700 AD up to the present day. At present atmospheric methane is approximately 1700 ppbv and is increasing 1%/yr. We are investigating the roles of changing emissions of CH_4 and other trace gases and climate on the CH_4 cycle. Both sources and sinks for these different eras are being estimated. We are using NASA/GISS global data bases to derive relationships between wetlands - the major natural CH_4 source - and vegetation type, topography and soil moisture. These relationships are being used with the output of the GISS GCM to obtain an estimated change of the wetland areas and revised methane sources for the conditions of the Last Glacial Maximum and pre-industrial Holocene. These in turn are being used in a photochemical model to calculate atmospheric methane abundances and to check for self-consistency with the revised source function. In addition, the photochemical model is being used to evaluate the role of non-methane factors in chemical and climate-induced changes in OH, the free radical that determines the methane photochemical lifetime. These include variations in CO , NO_x , O_3 and climatic parameters, temperature, water vapor and stratosphere - troposphere exchange. Both wetlands variations and changes in OH abundance are responsible for methane changes from the Last Glacial Maximum through the pre-industrial Holocene. Since that time, anthropogenically driven source changes in CH_4 , CO and NO_x have dominated the increase in atmospheric methane.

PA-2-1 OZONE, THE NON-LINEAR GREENHOUSE GAS: HOW LOCATION AND TIMING EMPHASIZE

CERTAIN SOURCE AREAS. ROBERT B. CHATFIELD. NASA Ames Research Center, Moffett Field, CA 94035, USA.

Tropospheric ozone is often omitted in considerations of the biologically related greenhouse gases, even though the projected radiative effects of the increase of tropospheric ozone are commensurate with those methane and nitrous oxide. As an oxidant, its trends are also intimately related to OH and consequently the sink term for methane. One reason for this omission is likely the complex and non-linear nature of ozone chemistry. This makes estimates of present and future global budgets more intricate than for the simple biogenic emissions.

The most significant intricacies are becoming understood and named. I present some globally significant examples of these. A regional two-dimensional tropospheric photochemical model is applied to typical situations of hydrocarbon and NO_x emission from biomass burning in tropical South America and Africa. The relative importance of African burning for large-scale ozone levels is demonstrated. The simulation also shows that nitrate deposition pattern from the burning shows related differences. The relevant meteorological and source-distribution effects are concisely illustrated.

PB-11-2 ARCTIC AND SUB-ARCTIC SOIL MISSIONS: POSSIBLE IMPLICATIONS FOR GLOBAL CLIMATE CHANGE. TORBEN CHRISTENSEN. Scott Polar Research Institute, University of Cambridge, Lensfield Rd., Cambridge CB2 1ER, England.

Arctic and sub-Arctic tundra soils contains about 30% of the carbon stored in the solid globe. Large amounts of this organic material is presently frozen in the permafrost. Greenhouse warming, predicted to be profound in the Arctic, will result in melting of permafrost and increasing rates of decomposition in the tundra soil. The tundra has, until recently, been seen as a small sink of CO_2 and a substantial source of CH_4 . The aim of this study is to evaluate how this flux pattern will respond to the predicted climate warming over the next century.

Detailed time series measurements of CO_2 and CH_4 fluxes will start at tundra sites near Toolik Lake, Alaska, early June, 1991. Subsequently, environmental parameters, temperature, moisture, character and concentration of the organic matter, and pH, will be measured. Field manipulations of temperature, moisture and ambient CO_2 and CH_4 concentrations will be carried out to provide a better understanding of the factors controlling the balance between CH_4 production and oxidation in tundra soils. The manipulation studies are also designed to give indications on the magnitude of a potential carbon loss from tundra regions under a climate warming scenario.

The data collected from the field work will be parameterised in cooperation with the British Meteorological Office in order to develop a one-dimensional model of CO_2 and CH_4 exchange between tundra soils and the atmosphere. Eventually the plan is to incorporate this model into the Meteorological Office GCM.

O-K-1 GLOBAL CHANGE AND THE BIOGEOCHEMISTRY OF RADIATIVELY ACTIVE TRACE GASES. RALPH L. CICERONE. Geosciences Department, University of California, Irvine, California, USA.

The composition of the atmosphere is changing worldwide; specifically, the concentrations of many trace gases are increasing rapidly and globally while the stratospheric ozone layer is being

depleted. Two projected consequences of these changes are: 1.) an altered global climate due to an increased greenhouse effect, and 2.) increased intensities of ultraviolet light at earth's surface.

How do these phenomena arise and what are the key chemical and biogeochemical pathways? A framework for viewing these questions will be presented and the principles that underly the natural greenhouse effect and ozone-layer behavior will be reviewed.

Gases that exhibit the correct properties to be effective greenhouse gases include carbon dioxide, methane, water vapor, nitrous oxide, ozone and chlorofluorocarbons (CFC's). Certain gaseous sulfur compounds also can affect climate; the gases are converted to sulfur-containing particles that interact with visible (as opposed to infrared) radiation. Estimates of the relative sizes of the present and possible future climatic perturbations due to each of these substances will be presented. Similarly, the ozone layer is strongly influenced, although in different ways, by methane, nitrous oxide, methyl chloride and methyl bromide, as well as by the synthetic CFC's. Accordingly, biogeochemical processes that control atmospheric amounts of these gases, mainly terrestrial and marine sources and sinks, must be quantified and understood as must perturbations to the biogeochemical cycles of C, N, S, Cl and Br.

O-4-3 METHANE OXIDATION IN THE SOIL SURFACE LAYER OF A FLOODED RICE FIELD. R. CONRAD, and F. ROTHFUSS. Max-Planck-Institut für Terrestrische Mikrobiologie, D-3550 Marburg, FRG.

The flux of CH_4 from intact soil cores of a flooded rice field in Italy was measured under aerobic and anaerobic incubation conditions. The difference between anaerobic and aerobic CH_4 flux apparently was due to CH_4 oxidation in the oxic soil surface layer. This conclusion was supported by measurement of the vertical CH_4 profile in the upper 2 cm layer, and of the V_{max} of CH_4 oxidation in slurried samples of the soil surface layer. About 80% of the CH_4 was oxidized during its passage through the soil surface layer. CH_4 oxidation was apparently limited by the concentration of CH_4 and/or O_2 in the active surface layer. Addition of ammonium to the water layer on top of the soil core reversibly increased the aerobic CH_4 fluxes due to inhibition of CH_4 oxidation in the soil surface layer.

O-6-9 ATMOSPHERIC NITROUS OXIDE FLUXES FROM MANGROVE SEDIMENTS. J.E. CORREDOR, J.M. MORELL AND A. AGUILERA. Department of Marine Sciences, University of Puerto Rico, Mayaguez, P.R. 00709

As a contribution to the global nitrous oxide budget, fluxes of this gas from mangrove sediments subjected to secondary sewage emissions and from unimpacted pristine areas were measured using bell jar incubations and GC/ECD analysis. Head space analysis of dissolved nitrous oxide in adjacent waters, were also performed. On the whole, eutrophied mangrove sediments constitute a net source of nitrous oxide to the atmosphere with mean emission rates of $219 \text{ nmole/m}^2/\text{h}$. Rates are lower at the landward fringe where organic inputs are low and salinity stress is high, highest in the transition zone between black and red mangrove communities characterized by high organic substrate availability, and again low at the seaward fringe. In sediments of nearby Phosphorescent Bay, there is net uptake of nitrous oxide along the landward, salinity-stressed fringe ($-231 \text{ nmole/m}^2/\text{h}$), but positive efflux ($109 \text{ mole/m}^2/\text{h}$) within the mangrove forest. Water column measurements reflect supersaturation of nitrous oxide at mean levels of 280% at both sites. Eutrophic intertidal

mangrove environments represent a heretofore unrecognized source of this radiative trace gas to the atmosphere.

PA-4/5-3 EFFECT OF AIR POLLUTION ON LITTER DECOMPOSITION. M.E. COTRUFO, A. VIRZO DE SANTO, A. ALFANI, G. BARTOLI. Dipartimento di Biologia Vegetale, Università di Napoli "Federico II", Napoli, Italia.

Decomposition of *Quercus ilex* leaf litter, collected in a polluted site inside the city of Naples (Giardini Jolanda) and in a control site (the Astroni Park) out of the city, was studied by a microcosm experiment. Nitrogen, carbon and sulphur were determined by an automatic N,C,S analyzer (Carlo Erba); heavy metals were measured by atomic absorption (SpectrAA 20, Varian). Fungal biomass was estimated by measuring hyphal length with the intersection technique. Respiration was assayed by CO_2 evolution.

Heavy metal concentration was higher in the leaves of the polluted site with about threefold values for Fe, Zn, Cu, Cr, Ni and about sevenfold values for Pb. The soil of Giardini Jolanda also showed significantly higher heavy metal concentration than the soil of Astroni. As compared to the leaves of the polluted site, the leaves of the control site showed somewhat higher N concentration (2.1% and 1.8% respectively) and lower C/N ratio (27 and 31 respectively). S/N ratio of 0.062 in the leaves of the polluted site indicated sulphur load.

Litter mass loss, respiration, and fungal biomass were measured at intervals during the experimental period. During the first two months, control leaves showed decomposition rates twice as high as polluted leaves; while in the following two months control and polluted leaves differed by a factor 1.5. Litter mass loss did not increase significantly during the last period of study (4th- 10th month) and reached 42% and 29% of the initial weight respectively in control and polluted leaves. Respiration rates decreased with time; the difference between control and polluted leaves was very high during the first two months, with the lowest values for the polluted leaves; no difference occurred in the following period. Fungal biomass increased during litter decay and was higher in the control leaves during the whole study period. Lower fungal biomass was found in the soil of the polluted site.

It was concluded that heavy metals accumulated in the leaves prior to shedding have a long term impact on the subsequent decomposition of the litter.

O-11-8 METHANE PRODUCTION AND OXIDATION IN NORTHERN PEATS. PATRICK CRILL, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA and RON SASS, Department of Ecology and Evolutionary Biology, Rice University, Houston, Texas, USA.

Simply quantifying the current source strength of atmospheric methane (CH_4) source from northern wetlands is essential but is inadequate in itself. In order to understand the potential of the changing climate to affect the carbon partitioning between boreal soils and the atmosphere, an understanding of the microbiological processes that ultimately control the flux is necessary. We developed and utilized a syringe incubation technique to measure CH_4 production in peats collected from wetlands in Minnesota, Alaska and Quebec to begin to quantify and understand the biological processes of the CH_4 cycle.

Samples from Itasca county, Minnesota were collected from forested and unforestod ombrotrophic bogs in late February. The production rates measured in the peats collected in winter were very much lower than the CH_4 flux rates measured in the same bogs during warmer months indicating that the methanogenic organisms were substrate and/or population limited. However, the temperature

response ($E_a' = 150-170$ kJ/mol) of CH_4 production was statistically the same as that observed for CH_4 flux measured during the spring/summer which suggested that the same processes were acting on the incubation samples and that the bacterial populations were not growing significantly during the experimental time frame of approximately three weeks.

The Schefferville, Quebec samples were collected from two bryophyte dominated fens near the beginning of the growing season. Unlike the Minnesota samples, the Quebec peats produced as much as an order of magnitude more CH_4 than what was necessary to account for the observed effluxes. The addition of acetate, a common substrate, did not enhance production. In this case the methanogenic communities were well established and not substrate limited and oxidative processes strongly mediated fluxes.

Near Bethel, Alaska, organic-rich soils were collected from macrophyte dominated wetlands throughout much of the short growing season. Here again production exceeded flux indicating that significant rates of CH_4 oxidation are a common feature of northern wetlands that mediates the total release. Biomass and CH_4 concentration data were also recorded and CH_4 production could be correlated to biomass production in these environments.

PB-6-5 IDENTIFYING AND QUANTIFYING THE REGIONAL SOURCES AND AIR-SEA FLUX OF METHANE IN SOUTHERN CALIFORNIA WATERS. E. L. CYNAR and A. A. YAYANOS. Scripps Institution of Oceanography, La Jolla, California, USA.

The oceans are thought to be a minor source of CH_4 when compared to other environments such as rice paddies and the rumen. The estimates of the flux of CH_4 from the oceans, however, are based on little data and an inadequate understanding of seasonal and regional variability. This report describes preliminary results from an ongoing investigation of the distribution of CH_4 in the waters of the Southern California Bight; the research is centered on identifying, discriminating, and quantifying the various sources of methane and estimating the air-sea flux of methane for this region over the period of data collection (22 months). Preliminary results suggest that near-shore methane-rich waters resulting from hydrocarbon seeps are the dominant source of methane observed at stations more than 700 km from shore. In addition to hydrocarbon seeps, biological production and oxidation of CH_4 are suggested. The estimated flux of methane to the atmosphere from this region is 20-30 fold greater than previously assumed. This report will provide new data for estimating the role of a regional marine environment in the global biogeochemical cycling of methane.

O-10-8 SOIL MOISTURE AS A REGULATOR OF THE RELATIVE PROPORTIONS OF NITRIC OXIDE AND NITROUS OXIDE PRODUCED VIA NITRIFICATION AND DENITRIFICATION. E. A. DAVIDSON. Woods Hole Research Center, P.O. Box 296, Woods Hole, MA, 02543, USA.

It is well known that soil moisture and soil aeration affect rates of NO and N_2O production by nitrifying and denitrifying bacteria. However, the response to variation in soil moisture is highly nonlinear, and several complex regulatory mechanisms are involved. This paper reviews our current understanding of these mechanisms and characterizes the nonlinear relationships between soil moisture and N gas emissions. Experiments using acetylene as an inhibitor of nitrification in intact soil cores from two different ecosystems, a temperate grassland and a seasonally dry tropical forest, consistently

show that NO emissions exceed N_2O emissions and that both gases are emitted primarily by nitrifying bacteria when soil moisture is below field capacity (i.e., when macropores are air-filled). In contrast, when macropores fill with water, denitrification becomes a more important process and N_2O emissions exceed NO emissions. It is suggested that soil moisture parameters can be used to predict ratios of NO -to- N_2O . If this mechanistic approach to understanding factors affecting the relative proportions of NO and N_2O production via nitrification and denitrification can be combined with a similar mechanistic understanding of factors affecting the rates of N cycling processes in general, then a broad-scale predictive model of N trace gas emissions appears feasible.

O-11-9 EMISSIONS OF BIOGENIC SULFUR GASES FROM NORTHERN BOGS AND FENS. W. Z. DE MELLO¹, M. E. JONES¹ AND S. E. BAYLEY². Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA,¹ and Department of Botany, University of Alberta, Edmonton, Alberta, Canada².

Sulfur gases are important components of the global cycle of S. They contribute to the acidity of precipitation and they influence global radiation balance and climate. The role of terrestrial sources of biogenic S and their effect on atmospheric chemistry remain as major unanswered questions.

Experiments have been conducted in wetlands in New Hampshire, and at the Experimental Lakes Area (ELA) in Ontario. Emissions were determined using Teflon enclosures, gas cryotrapping methods and gas chromatography with flame photometric detection. Dynamic (sweep flow) and static enclosures were employed.

Emissions of dimethyl sulfide (DMS) dominated S gas fluxes from all sites. In New Hampshire, DMS fluxes were $>1.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ in early summer, 1989 when temperatures were warm and the water table was 5 cm below the vegetation surface. These rates are several-fold faster than average oceanic rates of DMS emission. Despite continued warm temperatures, a rapid drop in the water table resulted in a 6-fold decrease in DMS emissions in late July. In 1990, a new beaver dam kept water levels above the surface of the fen for the bulk of the season and S gas emissions were much lower than during 1989. Concentrations of methane and DMS in surface waters co-varied closely until the water table dropped below the surface. Emissions of DMS were highest in the most oligotrophic areas. Using static chambers, we observed that these fens are sinks for atmospheric COS .

Similar measurements were made at the ELA in July, 1990. Mire 239 was irrigated with sulfuric and nitric acids to simulate acid rain. Emissions of DMS dominated the S gases and fluxes followed a smooth diel pattern and were higher in the acidified areas. Emissions were also much higher in the oligotrophic regions compared to the minerotrophic ones. Despite the wide differences in S gas fluxes (20-fold), it was difficult to determine if acidification or variations in trophic status were most responsible for differences in S gas emissions. DMS dissolved in the surface of the water table (situated ~25 cm below the vegetation surface) did not vary throughout the fen. Estimates of S gas flux using dissolved concentration data were significantly lower than directly measured fluxes. This discrepancy may have been due to enhanced diffusivity of S gases from water sequestered during capillary action by *Sphagnum* mosses. Measurements using only dissolved concentrations of S gases may grossly underestimate fluxes when the water table is below the vegetation surface.

Highest S gas emissions (DMS) occurred in the most oligotrophic regions of mires despite the fact that these locations would be

expected to have the smallest S input. Our preliminary data from Alaska to the northeastern USA suggest that DMS emissions correlate with atmospheric S depositions. If this is true, then scaling up using remotely sensed information would be greatly facilitated. However, hydrologic variations influence emissions by perhaps orders of magnitude.

O-1-2 CARBON ISOTOPIC INDICATORS OF ATMOSPHERIC TRACE GAS CONCENTRATIONS IN ANCIENT ATMOSPHERES. D.J. DES MARAIS, Ames Research Center, Moffett Field, CA 94035.

The stable carbon isotopic compositions of sedimentary organic matter and carbonates are useful indicators of trends in the sizes of crustal carbon reservoirs. The globally averaged difference in $^{13}\text{C}/^{12}\text{C}$ values between marine organic and carbonate carbon reflects the isotopic discrimination associated with the production, decomposition and burial of organic matter. Isotopic selectivity during photosynthetic carbon fixation is lessened by a more restricted supply of carbon in the ocean-atmosphere system. The globally-averaged absolute $^{13}\text{C}/^{12}\text{C}$ values of organic and carbonates, relative to the known average crustal $^{13}\text{C}/^{12}\text{C}$ value, can be related to the relative rates of burial of organics and carbonates during a given geologic interval. A trend of increasing $^{13}\text{C}/^{12}\text{C}$ values for organic matter between 2.5 and 0.8 billion years (Ga) ago suggests that carbon isotopic discrimination associated with photosynthesis was lessened. This trend is consistent with a decline in atmospheric CO_2 concentrations of at least one order of magnitude. The trend towards increasing $^{13}\text{C}/^{12}\text{C}$ values for both organics and carbonates during this interval indicates that rates of organic burial increased, relative to that of carbonates. This trend is consistent with a simultaneous increase in crustal and atmospheric reservoirs of oxidized species, including molecular oxygen. Thus, carbon isotopes might have documented the rise of oxygen from the status of trace gas to that of a major atmospheric constituent. The trends indicated for carbon dioxide and free oxygen have major implications for biological evolution, especially regarding pathways for carbon assimilation by bacteria, algae and plants.

O-12-8 THE BIOGEOCHEMICAL SOURCE OF ISOPRENE EMISSIONS. JANE DIGNON, KARL E. TAYLOR. University of California Lawrence Livermore National Laboratory, Livermore, California 94550, and JENNIFER A. LOGAN, Harvard University, Dept. of Earth and Planetary Sciences, Cambridge, MA 02138.

Terrestrial vegetation is an important source of non-methane hydrocarbons in the atmosphere. Isoprene (C_5H_8) has long been known to be a major constituent of the trace gases emitted to the atmosphere by vegetation. The biogeochemical cycle of isoprene is considered important in atmospheric chemistry because of its role in tropospheric ozone and OH photochemistry. Tropospheric ozone is harmful to both plant and animal life, and may also contribute to a warming of the earth's atmosphere due to its properties as a greenhouse gas. Isoprene is also a sink for the OH radical in the continental boundary layer. Reaction with OH is the primary removal path for a variety of greenhouse gases such as CH_4 and HCFCs. Understanding the global budget of isoprene will contribute to the current knowledge of ozone and OH, and their respective radiative and biogeochemical implications. We have developed a global inventory of isoprene emissions distributed at a $1^\circ \times 1^\circ$ degree resolution including model calculated variations with latitude, and daily temperature and sunlight conditions. This discussion will include the assumptions made in deriving the source model as well as its

uncertainties. Comparisons are made of this inventory with other global and regional estimates.

PA-4/5-4 SEASONAL, DIURNAL AND SPATIAL VARIATIONS OF N_2O SOIL FLUXES IN THE VENEZUELAN SAVANNAH CLIMATIC REGION. L. DONOSO¹, D. SCHARFFE², I. MARTI¹ AND E. SANHUEZA¹. ¹ I.V.IC., Apartado 21827, Caracas 1020 A, Venezuela. ² M.P.I. für Chemie, Postfach 3060, 6500 Mainz, F.R.G.

Atmospheric nitrous oxide is a greenhouse gas which also plays an important role in the catalytic destruction of the stratospheric ozone. Current budgets indicate that a large fraction (~60%) must be produced by biogenic processes in soils. The estimated sources have large uncertainties due mainly to the sparse information available concerning the spatial and temporal variability of the N_2O soil fluxes, especially in tropical ecosystems.

Soil N_2O fluxes have been measured at several locations at the Venezuelan savannah climatic region: a grassland savannah (Chaguarama), a woodland savannah (Chaguarama), a semideciduous forest (Guri), a scrub-grassland savannah (Guri) and a trachipogon savannah (Calabozo). N_2O fluxes were measured using enclosed chambers inserted in the soil. The accumulated N_2O was analyzed directly with a gas chromatograph equipped with an electron capture detector. In general, the results show that in the savannah region relatively lower emissions (-2.6 to 15×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$) are produced, in comparison with the emissions found in the Amazon rain-forest region (2.1 to 26×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$).

An important seasonal variation in the N_2O fluxes is observed, with larger emissions during the rainy season (wetter soils seems to promote larger emissions); at the Guri savannah site even a net daily consumption was found during the 1989 dry season; larger consumption rates were recorded during nighttime, with fluxes near zero at noontime. Diurnal cycles are also evident from the data obtained at the other sites, lower N_2O emissions (i.e., Guri forest site) or N_2O consumption (i.e. Calabozo) are observed during nighttime, with early afternoon maximum emissions. It is likely that higher daytime temperatures enhance the microbial activities that produce N_2O .

No significant spatial variations of the N_2O fluxes are observed among locations (separated by hundreds kilometers) during the rainy season (relatively wet soils), with averages values around 10×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$. On the other hand, during the dry season large differences are found between locations, with average values ranging from -2.6×10^9 to 2.6×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$. At present, we do not know the reasons for the differences observed under dry conditions; it is likely that the explanation is related to the competition between the microbial processes that produce and consume N_2O in the soils. It is worth mentioning that there are not significant differences among the fluxes obtained from different plots (separated by a few meters) at the same site.

In order to estimate the contribution of tropical savannah soils to the global atmospheric budget, it is important to take into consideration the spatial (specially during the dry season), seasonal and diurnal variability observed in the soil fluxes; however, not enough information is available to reduce the present uncertainties related with the estimated sources and sinks of nitrous oxide. A better characterization of the world savannah region, as well as the parameters that control the N_2O fluxes is needed. The mechanism by which dry savannah soils consume atmospheric N_2O should be elucidated.

O-7-3 PYRITE AND HYDROGEN FORMATION UNDER ANAEROBIC CONDITIONS. E. DROBNER, G. WACHTERSCHAUER, AND K. O. STETTER. Institute of Microbiology, University of Regensburg, Regensburg, FRG.

The production of molecular hydrogen had previously been attributed to biogenic origins, geothermal exhalations and tropospheric decompositions. The reaction $\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2$ postulated as energy source for an autotrophic origin of life, could be a further natural source of H_2 . Yet the theory clashed with the conventional assumption that elemental sulfur or a sulfur equivalent (polysulfide or thiosulfate) is the mandatory oxidation for pyrite formation. Here we report the formation of both pyrite and molecular hydrogen under fastidiously anaerobic conditions in the aqueous system of FeS and H_2S .

PA-4/5-5 EXTRAPOLATION OF ECOSYSTEM PROCESSES TO REGIONAL SCALES: DEVELOPMENT OF THE REGIONAL ECOSYSTEM SIMULATION SYSTEM. J.L. DUNGAN and D.L. PETERSON, TGS Technology, Inc. and, NASA Ames Research Center, Moffett Field, California, USA.

Two alternative approaches to estimate ecosystem production of carbon, water, or other compounds over large regions without direct measurement are: 1) develop simulation models representing the aggregate of processes occurring over the region, or 2) develop simulation models representing processes occurring over land surface units much smaller than that of the region and aggregating results. The second of these approaches has been used to estimate carbon production and evapotranspiration in coniferous forests over a 1700 km^2 area using a stand level ecosystem simulation model called FOREST-BGC (Running and Coughlan, 1988). Band et al. (in press) describe the basis for this approach and methods of parameterizing this model. The geographic distribution of required input data is obtained through a combination of point measurements, microclimatological modeling, and estimates derived from remote sensing data.

Data analysis and visualization software was used in an interactive computing environment to analyze and display model inputs; including leaf area index, initial soil water content, and elevation; and outputs, including CO_2 exchange from photosynthesis and respiration, and water vapor. This software can be used to examine results of sensitivity studies, compare spatial and frequency distributions, and compare results using different parameterizations. This computing environment will provide a component of a Regional Ecosystem Simulation System (RESYS). The poster will present this integrated system for analyzing and displaying model inputs and results in a flexible, interactive way.

O-7-2 INSIGHT INTO THE MECHANISM OF MnO_2 REDUCTION BY MARINE BACTERIAL STRAIN BIII 88. H.L. EHRLICH. Rensselaer Polytechnic Institute, Troy, NY 12180 USA.

Mn(IV) oxide can serve as terminal electron acceptor in the respiration of a number of different facultative and anaerobic bacteria. In some facultative bacteria, this type of respiration takes place only anaerobically; in others it can take place in air as well. In general, Mn(IV) oxides are very insoluble in water, and some, like reagent-grade MnO_2 , are not easily reduced at neutral pH. Thus, when bacteria use Mn(IV) oxide as electron acceptor at pH 7.0 in their respiratory process, they must somehow transfer electrons to the

extracellular insoluble oxide. Using 0.5 mM acetate as electron donor and 0.1 g of reagent-grade MnO_2 as electron acceptor in the presence and absence of carbonyl cyanide m-chlorophenyl hydrazone (CCCP), an uncoupler of oxidative phosphorylation, the present work provides direct evidence in support of a working model in which gram-negative marine bacterial strain BIII 88 with an active aerobic and anaerobic respiratory system transfers electrons from acetate to MnO_2 by a chemiosmotic mechanism. The CCCP in a concentration range of 35 to 340 μM stimulated MnO_2 reduction by resting cells of strain BIII 88 in both aerobic and anaerobic incubation at 15°C. Since the pH in these experiments remained at 7.0, and since the acetate is expected to be oxidized to CO_2 and H_2O , it does not seem likely that an electron carrier resulting from acetate oxidation and released by the cells would transfer electrons from the respiratory chain of the bacteria to the surface of MnO_2 particles. The cells using MnO_2 particles as electron acceptors in their respiration must be in intimate contact with them and somehow inject the electrons into the crystal lattice of the MnO_2 . This is a problem similar to one faced by *Thiobacillus ferrooxidans* when it attacks a metal sulfide directly, except that in that instance, it withdraws electrons from the crystal lattice of the metal sulfide and transfers them with its respiratory system to oxygen.

O-2-3 UNCERTAINTIES IN THE GLOBAL ATMOSPHERIC NITROUS OXIDE BUDGET. JAMES W. ELKINS, JAMES H. BUTLER, and THAYNE M. THOMPSON, Climate Monitoring and Diagnostics Laboratory (CMDL), National Oceanic and Atmospheric Administration (NOAA), Boulder, CO 80303 USA

Atmospheric nitrous oxide (N_2O) plays an important role in stratospheric ozone depletion and the greenhouse effect. Atmospheric N_2O is increasing at a rate of about 0.2% per year. The cause for the growth of atmospheric N_2O is uncertain. It was believed that the growth resulted primarily from the production of N_2O during combustion in coal-fired power plants. However, recent combustion work showed that an artifact in the sampling technique of previous work from coal-fired power plants gave substantially higher N_2O values than actual values. The N_2O concentration was found to grow with time in sampling flasks because of aqueous chemistry occurring from high levels of NO and SO_2 . In addition, biomass burning releases for N_2O also were overestimated as a result of the same sampling artifact. The uncertainties for the combustion source strengths has reopened the fertilizer issue, perhaps with significant contributions from polluted groundwater and acid deposition. While the dominant sources for N_2O are biological, we will examine other anthropogenic disturbances to the natural nitrogen cycle. We will present data of trends and distributions from NOAA/CMDL baseline stations, three ocean cruises, and field experiments.

O-6-4 METHANOGENESIS IN GASSY AFRICAN LAKES: AN IMPORTANT RELEASE TRIGGER? EVANS, W. C. and WHITE, L. D., USGS, Menlo Park, CA 94025. TUTTLE, M. L., USGS, Denver, CO 80225, KLING, G. W., Marine Biological Lab, Woods Hole, MA 02543

Three African lakes, Nyos, Monoun, and Kivu, are known to contain high concentrations of abiological CO_2 . The CO_2 steadily enters bottom-waters after degassing from magmas at depth beneath the lakes. The amount of biologically produced CO_2 is a small part of the total, but several recent samplings of Nyos and Monoun and a

limited 1989 collection at Kivu show the importance of bacterial methanogenesis. At Nyos, CH_4 concentrations have increased significantly after the 1986 gas release at all depths below the oxycline, while increases in CO_2 and inorganic constituents have been restricted to the deepest levels (near 200 m depth). The additional CH_4 produced at mid-depths must be bacterially-formed rather than thermogenic, even though $\delta^{13}\text{C}\text{-CH}_4$ values are heavy, (-44.4 to -53.5 ‰). At Monoun, CH_4 concentrations have not shown definitive increases since a 1984 gas release, but the larger range of $\delta^{13}\text{C}$ values (-44.4 to -62.0 ‰), rules out a single thermogenic source. The lighter values occur just below the oxycline and are similar to the -64.6 ‰ obtained for CH_4 in a separate basin of the lake, which presumably contains biogenic gas. The heaviest values occur in the deepest samples and may reflect a thermogenic component, but are similar to values for bacterially produced CH_4 at Nyos. In addition, isotopic changes have occurred in the bottom-water of Monoun; $\delta^{13}\text{C}$ values of -44.4 and -54.6 ‰ have been measured near 95 m depth on separate sampling dates. Such temporal fluctuations strongly suggest biological controls. The strong stratification of the water column maintains hypolimnetic O_2 , NO_3^- , and SO_4^{2-} concentrations near zero, but changes in CH_4 production/utilization may occur in response to variable supplies of fresh organic matter and oxidized iron particles settling through the hypolimnion. At Kivu, there has been disagreement in the literature over the correct $\delta^{13}\text{C}\text{-CH}_4$ value, -45 and -58 ‰ being reported. Our measured values, -57.2 and -57.9 ‰ at 300 and 200 m depth, respectively, support the latter value, but the results from Monoun and Nyos suggest that both previous values may have been correct for the date and location of sampling. Other apparent chemical changes in Kivu since 1971 may be consistent with changes in bacterial methanogenesis.

Models of the CO_2 releases from Monoun and Nyos (and of a potential release from Kivu) call for the slow, steady build-up of magnatic CO_2 in stratified water columns until concentrations reach levels where degassing can be triggered. However, bacterially produced CH_4 also adds to the total gas pressure, up to 1.23, 1.44, and 11.6 atm. in Nyos, Monoun, and Kivu respectively. Our data show that large-scale changes in CH_4 concentrations and possibly in CH_4 production pathways can be relatively rapid and hence, of possible importance in gas release triggering.

O-10-5 PLANT HYDROCARBON EMISSIONS TO THE ATMOSPHERE: WHAT IS THE LINKAGE BETWEEN PHOTOSYNTHESIS AND ISOPRENE EMISSION? R. FALL, A. GUENTHER, C. JAEGER, J. GRINSPOON AND R. MONSON University of Colorado, Boulder, Colorado, USA

Isoprene is the single major volatile hydrocarbon emitted by plants to the atmosphere, and it plays an important role in tropospheric chemistry. Surprisingly little is known about how or why plants synthesize isoprene, why some species expend energy to emit isoprene at rates between 1-8% of the photosynthetic CO_2 assimilation rate, and whether future changes in global atmospheric CO_2 and temperature will affect isoprene emission rates. To address some of these questions we have conducted laboratory studies of leaf isoprene emission rates in response to changes in light, temperature and CO_2 levels using a newly developed real-time isoprene analyzer combined with a gas exchange system and chlorophyll fluorometer. This system allows simultaneous measurements of photosynthetic CO_2

assimilation and electron transport, stomatal conductance, and isoprene emission rates. We have demonstrated that a) the internal pool of isoprene is small and that the instantaneous emission rate is tightly coupled to its light-dependent synthesis rate; b) isoprene emission occurs from the leaf surface(s) bearing stomates, but is independent of stomatal conductance; c) varying CO_2 level or leaf temperature reveals that the linkage of isoprene emission to chloroplastic processes is not dependent on the rate of CO_2 pentose phosphate pathway, but depends on other factors associated with the photosynthetic light reactions; and d) isoprene emission rates correlate with photosynthetic electron transport rates but not CO_2 assimilation rates. Recent investigations of the role of leaf development on isoprene emission rates have revealed that emissions increase significantly (in some cases >100-fold) in developing leaves and then decline in older leaves. In contrast, leaf photosynthetic competence and stomatal conductance develop well before isoprene emission occurs. This result may have some bearing on the question of why plants emit isoprene. The regulation of isoprene biosynthesis, effects of plant stress on isoprene emission rate, and role of isoprene emission in global carbon cycling will also be discussed.

PA-7-1 THE TRACE - ELEMENT BIOGEOCHEMICAL CHARACTERISTICS OF DEPOSITIONAL ORGANIC MATTER IN INLAND SEDIMENTS. BELFENG, WE ZHENG, and QIN TIANWO, Supported by National Science Foundation of China Chengdu College of Geology, Chengdu, Sichuan, 610059, P.R.China

This paper takes the depositional organic matter in the modern deposits in Queng Ming Plateau lake of Yun Nan Province, Tertiary in Bai-se basin of Guang Xi District, Jurassic-Cretaceous in Shong Liao and Hai-la-er basins as the main objects of study. The relationships between the accumulation of organic matters and micro-(trace-) elements are discussed in mud and peat in the modern deposits, in dark-colored mudstone and coal which are the main source rock, and in crude oil of continental facies, in order to probe into the biogeochemical environments and features.

PB-9/10-2 FORMATION OF METHYLMERCAPTAN AND DIMETHYLSULFIDE FROM METHOXYLATED AROMATIC COMPOUNDS IN ANOXIC MARINE AND FRESH WATER SEDIMENTS. K. FINSTER, F. BAK, AND G.M. KING. Department of Ecology and Genetics, University of Aarhus, Aarhus, Denmark.

During enrichment experiments, designed to obtain aromatic compound-degrading sulfate reducers, a new obligately anaerobic acetogenic bacterium was discovered which is capable of fermenting methoxylated aromatic compounds [e.g. syringate (4-hydroxy 3, 5, -dimethoxybenzoate) or 3, 4, 5, -trimethoxybenzoate] with concomitant production of dimethylsulfide (DMS) and methylmercaptan (MSH). The present study was initiated to investigate if anoxic sediments have a capacity to produce volatile methylated sulfur compounds from methoxylated aromatic monomers via the newly discovered bacterial mechanism. The sediment samples were from marine, brackish, and fresh water origin. Syringate was chosen as a model compound because it is a potential product of lignin degradation.

It was shown that the formation of DMS and MSH in anoxic sulfide-containing slurries from marine and fresh water sediments was stimulated by addition of syringate and 3,4,5,-trimethoxybenzoate. The release of DMS and MSH occurred during the consumption of the aromatic monomers and ceased after their depletion. DMS was the dominant methylated sulfur compound in fresh water sediments, in

contrast to marine sediments where MSH was predominant. No production of volatile organic sulfur compounds was observed in slurries containing gallate (3,4,5-trihydroxybenzoate) or in autoclaved controls. About 50-65% of the methoxy carbon could be accounted for by peak accumulation of DMS and MSH. In the saline sediments, large amounts of CH_4 were formed during the period when DMS and MSH disappeared. About 65-70% of the methylcarbon of the volatile methylated sulfur compounds (VMSC) could be accounted for in the produced CH_4 . This study demonstrates a previously unknown microbial process by which DMS and MSH are formed during anaerobic decomposition of methoxylated aromatic compounds in marine and fresh water sediments.

O-6-2 OXIDATION OF METHANE BY DEEP-SEA MUSSELS WITH METHANOTROPHIC SYMBIONTS. C.R. FISHER. Department of Biology, Pennsylvania State University, University Park, PA, USA.

Although methanotrophic symbioses have been suggested in a variety of marine hosts, they have only been demonstrated in three species of invertebrates. Two of these species are mussels related to the deep-sea hydrothermal vent mussel *Bathymodiolus thermophilus*, and the third is a species of small pogonophoran from a Norwegian fjord. The mussel found associated with shallow hydrocarbon seeps (600-900 m) in the Gulf of Mexico can be maintained in the laboratory at ambient pressure. Using this species, a variety of physiological investigations have demonstrated its dependence on methane and elucidated parameters of methanotrophy in-hospite, which allow predictions to be made concerning the habitat (methane and oxygen) requirements of this mussel and its *in situ* methane oxidation capacity.

During a series of ALVIN dives last April yet another species of "Bathymodiolus-like" mussel containing methanotrophic symbionts was discovered at a deep-seep site (2,200 m) near Alaminos Canyon in the Gulf of Mexico. The biomass observed at this site appears higher than has been reported for other seep sites and rivaled the apparent biomass found at flourishing hydrothermal-vent sites observed by the author. Enzyme analyses and ultrastructural investigations reveal the presence of two physiological and morphological types of bacteria in this one species of mussel (although the relative abundance of the two types varies considerably between individuals). High activities of RuBP carboxylase, ATP sulfurylase, and methanol dehydrogenase were demonstrated in pieces of gill from 10 different individuals. Elemental sulfur was also demonstrated in the gills of five of the individuals. This data as well as the ultrastructure of the bacteria suggests that there are both chemoautotrophic sulfur oxidizing and methanotrophic symbionts in the gill cells of these mussels. Furthermore both morphological types of bacteria are present in the same individual (n=4), often in the same bacteriocyte (gill cell), and sometimes even in the same vacuole.

The nutritional plasticity of the "Bathymodiolus like" mussels is apparent in the investigations of the group as a whole, as well as in the most recently discovered species. Their physiology, distribution, and biomass in some communities, suggest that these symbiotic associations may oxidize a significant amount of the methane at sites where it is released at appreciable concentrations.

O-7-9 ANTHROPOGENIC LEAD IN ANTARCTIC SURFACE WATERS. A.R. FLEGAL (Institute of Marine Sciences, University of California, Santa Cruz, CA 95064), S. NIEMEYER (Nuclear Chemistry Division, Lawrence Livermore National Laboratory, Livermore, CA 94550) and H. MARING (Center for Atmospheric Chemistry Studies, University of Rhode Island, Narragansett, RI 02882)

Preliminary measurements of lead concentrations and isotopic compositions in Antarctic Surface Waters attest to the pandemic dispersion of contaminant lead throughout the world ocean. These data were not available for a previous characterization of the oceanic lead cycle (Flegal and Patterson, 1983), which was based on the initial measurements of lead concentrations and isotopic compositions in the North Pacific (Schaule and Patterson, 1981; Flegal and Patterson, 1983), South Pacific (Flegal and Patterson, 1983) and North Atlantic (Schaule and Patterson, 1983). While those data have been substantiated and expanded upon by numerous investigators (Yeats, 1988), there have been no comparable reports on both lead concentrations and isotopic compositions in the Southern Ocean within the past decade. The following data are also unique in that they include the lowest lead concentrations ($\leq 10 \text{ pmol kg}^{-1}$) ever reported for any oceanic lead in Antarctic Surface Water is still predominantly (>80%) composed of lead from anthropogenic sources. While this is consistent with measurements of aeolian lead inputs in the Antarctic Polar cell, which indicate that industrial lead fluxes ($100 \text{ fmol cm}^{-2} \text{ y}^{-1}$) are ten-fold greater than natural lead fluxes ($10 \text{ fmol cm}^{-2} \text{ y}^{-1}$) within that cell (Zoller and Tenzel, 1985; Dick and Peel, 1986; Boutron and Patterson 1987; Patterson and Settle, 1987), most of the lead in Antarctic Surface Water appears to have been derived from atmospheric depositions in other water masses.

O-12-1 MODELS OF TERRESTRIAL AND OCEANIC SINKS FOR CARBON DIOXIDE. L. FUNG. NASA Goddard Institute for Space Studies, New York, New York, USA.

CO_2 in the atmosphere is increasing as a result of the releases from fossil fuel burning and land use modification. In the 1980's, the annual increase, $\sim 3.0 \text{ GtC/y}$ ($1 \text{ Gt} = 10^{12} \text{ kg}$), is equivalent to $\sim 57\%$ of the fossil fuel release. The oceans and the terrestrial biosphere together act as sinks for the anthropogenic CO_2 , with a total sink strength of $\sim 3.0 - 5.0 \text{ GtC/y}$ deduced from mass balance. The partitioning of the sink between the northern and southern hemispheres, and between land and ocean, is unclear and is the subject of considerable debate.

A review will be presented of existing models of the carbon cycle and the atmospheric CO_2 measurements used to infer the broad patterns and strengths of the anthropogenic CO_2 sink. Strategy for constructing global models for investigating changes in carbon cycling will be discussed.

PA-4/5-6 BIOELEMENT DYNAMIC IN THE LEAF AND NEEDLE DECOMPOSITION PROCESSES IN THREE EVERGREEN FOREST ECOSYSTEMS OF THE DUERO BASIN (SPAIN). J.F. GALLARDO, I. HERNANDEZ AND I. SANTA REGINA. Instituto de Ecología Terrestre, Salamanca, 37071 (Spain).

Experimental litter decomposition of *Quercus rotundifolia* leaves and *Pinus pinaster* and *P. Pinag* needles in three evergreen forests of the semiarid area of the Duero Basin has been carried out.

Different patterns of bioelement losses have been observed, increasing the relative content of N and Ca, and occurring strong losses of K and Mg, and also absolute losses of P and Na; there are exceptions that depend on the origin of the leaves or needles. Climatology roughly limits the productivity of these ecosystems.

PA-7-2 THE EFFECT OF DIFFERENT CO_2 CONCENTRATIONS UPON THE EMBRYONIC DEVELOPMENT OF SEA URCHIN *STRONGYLOCENTROTUS INTERMEDIUS*. R.V. GAREYEVA

and A.P. NEDASHKOVSKY, Pacific Oceanological Institute of the Far Eastern Branch, USSR Academy of Sciences, Vladivostok, USSR.

The embryos of sea urchin *Strongylocentrotus intermedius*, are very suitable objects for experimental embryology because it is easy to obtain and to grow them. We conducted the series of model experiments in which we investigated the influence of different CO_2 concentrations upon the embryonic development of sea urchin. Certainly, adding of CO_2 in sea water changes pH of this medium and therefore it's difficult to distinguish, whether it is effect of CO_2 or that of pH. Nevertheless, we observed morphological anomalies and conducted quantitative analysis. The two-blastomere state was initial for experiment. We registered normal development at pH range from 7.00 to 8.50. Adding of CO_2 in sea water (pH changed from 6.33 to 6.60) resulted in 100 % lethal effect at the stage of 16-32 blastomeres. In sea water without CO_2 (pH 8.47), at gastrula state, we revealed practically normal embryos. When increasing pH to 8.63 at the state corresponding to prism in control we found delay of development (early gastrula stage). The appearance of 50 % of abnormal larvae was observed in sea water totally deprived of CO_2 (pH 8.7) at pluteus I stage. In this medium we revealed the following anomalies: insufficient development of arms, sometimes, rarely, damaged archenteron. The investigation of the abnormalities of embryonic and larval development arising in extreme environment is the part of biological monitoring.

PA-1-2 VIABLE MICROORGANISMS IN PERMAFROST AS AN INDICATOR OF GLOBAL CLIMATE CHANGES IN PLEISTOCENE. D.A. GILICHINSKY, Institute of Soil Science and Photosynthesis, USSR Academy of Sciences, Pushchino, 142292. Moscow Region, USSR.

Paleoreconstructions of global climate change can be observed in the cryolithosphere because it is a native storehouse of geological and biological information. It is the most mobile Earth cover and its existence in time and space is obliged to climatic oscillations. In the Pleistocene they were clearly displayed as aggradations of frozen thickness into cryochrones and their degradation into thermochrones. In the last case, vertical sections of permafrost were evident with stratigraphic levels of thawing. The depth of deposition of these levels corresponded to the climate at that time, the same as the depth of today's summer thawing of tundra soils corresponds to the modern conditions. After the next cooling the thawed thickness was frozen again and "a young" permafrost was closed with "old" permafrost in one monolithic, frozen section.

The border between them can be established on the base of existing, different viable microorganisms in the permafrost. We have been working on this method on North-East Eurasia (Kolyma-Indigirka lowland) where the most maximum age of viable microorganisms was fixed at about 3 millions years.

Modern frozen soils were studied. They thawed at about 0.5 m during the summer. At this depth we fixed the horizon of microbial accumulation at 10^6 cells/g of microorganisms, which is comparable with the number in the A-horizon. We also studied the frozen thicknesses of the top part, which thawed during the Holocene (5-8 thousand years ago) and then refroze. The lower part did not thaw since it had been formed in late Pleistocene (15-40 thousand years ago). The border between them is on the depth of 2.5 - 3 m in places where the rocks containing only segregation ice were thawing and up to 15 m where there was thawing in the rocks with ice veins. This boundary line is marked in the following ways: First - at this place is the peak of number of viable cells, which are much more than in

upper and underlying deposits. Second - in the "young" permafrost, the number of viable cells is more than two orders of magnitude higher and they are obviously different in morphology and ecology compared with unfrozen "old" permafrost. In particular, in "old" permafrost eukaryotic cells and sulfate-reducing bacteria are not present and nonspore forming cell predominate. Third - the different temperature of cell growth: in the Holocene, microbial complex is psychrophilic-psychrotrophic, in the late Pleistocene-psychrotrophic with participation of mesophiles. In perspective we are going to learn more ancient levels of thawing.

O-6-7 MARINE SOURCES OF ATMOSPHERIC METHYL HALIDES. K.D. GOODWIN, S.L. MANLEY, AND W.J. NORTH, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, U.S.A.

Methyl halides (CH_3X where X is Cl, Br, I) are important atmospheric gases since they are involved in reactions that lead to stratospheric ozone depletion. In addition, they may play a tropospheric role in the greenhouse process. The ocean is apparently the principal source of natural CH_3X to the atmosphere, and marine algae and phytoplankton have been suggested as major CH_3X producers. Therefore, unintentional or intentional environmental changes in the ocean could significantly affect the atmospheric flux of these gases. It is essential to understand marine CH_3X production in order to predict the consequences of ocean changes brought about in an effort to ameliorate global warming. One aspect of our project addresses the role of nearshore kelp bed regions in global methyl halide production. Seawater samples taken in and around a kelp bed were extracted into nitrogen and the gas-phase was analyzed by electron-capture gas chromatography. Elevated levels of CH_3X were observed in kelp bed regions relative to controls taken ~200m outside the bed. Open water samples taken 5 miles offshore show further reduction in CH_3X levels. These data indicate that kelp beds produce methyl halides and are a potential source of these compounds to the atmosphere.

PA-7-3 THE INTEGRAL ESTIMATION OF EXTREME ENVIRONMENTAL CONDITIONS BEFORE AND AFTER CHERNOBYL CRASH. A.M. GRISHCHENKO, Institute of Nuclear Research, Kiev, USSR, I.G. GALAKTIONOV, Medicine biology Center "BIONT", Vladivostok, USSR, R.V. GAREYEVA, Pacific Oceanological Institute of the USSR Academy of Sciences, Vladivostok, USSR.

The embryos of sea urchins are good bioindicators because of their high sensibility to damage action of physical and chemical factors. We determined the total embryotoxic and teratogenic effect of 6677 specimens of soil and bottom sediments sampled at different times before and after Chernobyl crash and in several zones with different degrees of Chernobyl influence. The estimation of the results of determination of embryotoxicity and teratogenicity of soil samples is carried out according to previously developed 9-point scale of toxicity. It has established the correlation of specific weight (in %) between soil samples of insignificant toxicity (1 - 3 points), of middle toxicity (4 - 5 points) and of high toxicity (6 - 8 points). Soil was sampled in zones of Kiev, the Crimea and Donbass in 1986 - 1990 before and after Chernobyl crash. For part of samples the estimation of toxicity was carried out using LD - the solid weight in mg, resulted in the death of 50% of the embryos. The application of our method, except the objective appreciation of Chernobyl influence, allows us to realize the environmental monitoring at different extreme situations in any region of the Earth.

O-5-5 LARGE-AREA ESTIMATES OF DENITRIFICATION AND NITROUS OXIDE FLUX IN A TALLGRASS PRAIRIE LANDSCAPE. P.M. GROFFMAN. University of Rhode Island, Kingston, RI 02881.

We took two distinct approaches to produce large area estimates of microbial gas fluxes of N_2 and N_2O . First, we developed simple moisture driven models of gas flux and used soil moisture model output to produce large area estimates of flux. The idea behind this approach was that since denitrification and N_2O flux have been shown to be strongly controlled by soil moisture in many studies, aircraft-mounted remote sensors or models capable of depicting soil moisture over large areas should be useful as drivers for large area N gas flux models. The second approach was to establish relationships between annual site productivity and annual N gas fluxes. Our hypothesis was that there should be strong relationships between these parameters since they are both controlled by water and N availability. These relationships would be useful tools for landscape and regional scale analyses since satellite estimates of plant productivity could be used as drivers of large scale gas flux models.

The research reported here was done as part of the First ISLSCP Field Experiment (FIFE, ISLSCP=International Satellite Land Surface Climatology Program). FIFE took place on a 15 x 15 km site in and around the Konza Prairie Research Natural Area, near Manhattan, Kansas. Our experimental design stratified the landscape based on management and soil factors. We had three unburned prairie sites, three burned prairie sites, three burned and grazed sites and an agricultural site. For each of the native prairie management systems, there was one top-slope, one mid-slope and one toe-slope site. Denitrification and N_2O flux were measured five times during 1987 and early 1988 using soil core techniques.

We observed strong relationships between both denitrification and N_2O flux and soil moisture. However, there were a significant number of points which had high moisture contents but low N gas fluxes. The lack of activity at these points could not be explained statistically by soil nitrate levels. It is likely that soil carbon availability played an important role in influencing fluxes. Overall, moisture explained only 35-45% of the variance in gas fluxes, but among the sites/dates that were active, moisture explained nearly 80% of the variance in activity. We produced estimates of flux for one of the FIFE watersheds by combining soil moisture model outputs with our gas flux-moisture algorithms. There were strong relationships between maximum annual total biomass (defined as total site biomass in early September) and annual gas fluxes ($r^2 > 0.80$). We used a satellite-derived estimate of plant productivity, to produce site-wide estimates of fluxes. These simple models, when used along with more complex models, should be useful for refining our understanding of the factors controlling trace gas fluxes at landscape and regional scales.

O-11-1 METHANE EMISSIONS FROM NORTHERN HIGH LATITUDE WETLANDS: A REVIEW AND ASSESSMENT. R.C. HARRISS. University of New Hampshire, Durham, New Hampshire, USA.

Emissions from natural wetlands are estimated to be a major source of global atmospheric methane. Historical records of atmospheric methane concentrations obtained from air trapped in ice cores indicates that this source has been variable on geological time scales, with significant positive correlations between methane and air temperature. More recently, methane sources related to human activities have become the dominant control on increasing concentrations of atmospheric methane.

Existing data on the geographical distribution of natural wetlands, and on methane emission rates from these environments, indicate that northern high latitude and tropical wetlands are especially important. In this paper we focus on a review and assessment of factors which influence methane emission rates to the atmosphere from the high latitude wetlands of North America. The influence of soil temperature and moisture on emission rates is variable in ecosystems studied to date. Some boreal wetlands exhibit particularly high summer season methane emission rates. Emissions from Minnesota kettle bogs exhibit a strong response to changes in peat temperature, but lesser response to seasonal changes in water table. Emission rates from Alaskan tundra are very responsive to small changes in both water table and peat temperature.

Two major challenges for future research on methane emissions from northern wetlands are: (1) to increase the accuracy of emission estimates for the extensive peatlands of the Soviet Union and Canada, and (2) to develop improved modeling and measurement strategies for assessing potential feedback to climatic change.

O-7-5 IN VIVO CONSTRUCTED PCB DEGRADING STRAINS: DEGRADATION AND STABILITY IN SOIL. J. HAVEL AND W. REINEKE, Universität Wuppertal, Chemische Mikrobiologie, Gaubstr.20, 5600 Wuppertal 1, FRG.

Eight strains were enriched with biphenyl as sole source of carbon and energy. All strains grew readily with 4-chlorobiphenyl releasing quantitative amounts of 4-chlorobenzoate. With 3-chlorobiphenyl slower growth was observed. 2-Chlorobiphenyl allowed only minor growth of the strains, and dichlorinated biphenyls did not support growth. Two of the biphenyl degrading strains which were identified as *Pseudomonas putida* were able to transfer the genes of the biphenyl degradation sequence. As a recipient strain J11230 was chosen, a *Pseudomonas cepacia* strain able to degrade several mono- and dichlorinated benzoates. One hybrid strain of the matings, J11R2, was further characterized. Adaptation to growth with 2-chlorobiphenyl led to strain J11R22. This strain was able to eliminate chloride from all monochlorinated biphenyls as well as from 2,4- and 3,5-dichlorobiphenyl. Within 30 hours more than 60% of the chlorine content from Aroclor 1221 was released as chloride by cells of strain J11R22.

The frequency of transconjugation in soil was observed under different conditions. Survival of J11R22 and four more biphenyl- and chlorobenzoate degrading strains in soil of a mixed forest was investigated as well as stability of the hybrid strains under different conditions. The degradative capabilities of the strains in soil were proven by disappearance of chlorinated biphenyls, occurrence of metabolites (HPLC) and excretion of chloride (ionchromatography). In current investigations we try to expand the substrate spectrum of our strains to cover more of the possible products of anaerobic reductive dechlorination of PCBs.

O-2-2 ON THE INTERACTION BETWEEN THE BIOGEOCHEMICAL CARBON CYCLE AND THE PHYSICAL ASPECTS OF THE CLIMATE SYSTEM. K. HIGUCHI, D. CHAN, C. LIN*, N. SARGENT, AND Y.-H. CHAN.** Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ont. M3H 5T4, Canada*, Department of Meteorology, McGill University, Montreal, Que., H3A 2K6, Canada**, Western Ecological Services Ltd., 2-2563 Penryn St., Victoria, B.C., V8N 1G2, Canada.

Some of the major processes of partitioning and distribution of carbon among the reservoirs of the global carbon cycle are highly dependent

on physical climate parameters, such as temperature and fluid circulation. It is therefore essential that any attempt at prediction of how the global carbon cycle, in particular the rate of rise of the CO_2 content in the atmosphere, is going to evolve in the future must be framed and explored within the bounds of how the physical climate is going to change. Since there is a strong interactive feedback relationship between the carbon cycle and the physical aspect of the climate, one cannot claim adequate understanding of the dynamics of the global carbon cycle without understanding how it is tied to the dynamics of the physical climate system. We will present some preliminary results of an integration of a 2-dimensional (latitudinal and height) coupled climate-carbon cycle model. The atmospheric component is based on a model developed by Peng, Chou, and Arking (1987), and is connected to an idealized 2-D advective-diffusive ocean model with incorporated inorganic carbon cycle. The land biota carbon cycle model has latitudinal resolution, with carbon content of individual ecosystem modelled as a function of surface temperature, precipitation, and radiation.

PB-9/10-3 MICROBIAL RESPONSE TO HYDROCARBON MICROSEEPAGE IN THE ARKOMA BASIN, OKLAHOMA. D. HITZMAN, D. C. HITZMAN, J. D. TUCKER. Geo-Microbial Technologies, Inc., Okemah, Oklahoma, USA.

Prolific gas deposits are being located in the highly thrust faulted Arkoma Basin in southeastern Oklahoma. It is generally accepted that pressured hydrocarbon reservoirs leak gas to the surface through microseeps. Microorganisms respond to the presence of such hydrocarbon gases in the soil. A series of large scale reconnaissance microbial soil surveys covering approximately 84 square miles were conducted January - March, 1991, to determine the presence of hydrocarbon-indicating microorganisms. The location to these specific microbial populations were plotted in relation to faults, fractures, and the known production of the survey area. The microbial response pattern demonstrates a positive correlation with buried gas reservoirs producing from depths of approximately 12,000 - 14,000 feet. Geological parameters such as faults, fractures, and geophysical data are also compared. The results are examined and presented with ongoing exploration and drilling results.

O-9-8 SEASONAL VARIATIONS IN METHANE OXIDATION AND PRODUCTION IN AN ANOXYC MARINE SEDIMENT. T. M. HOEHLER, M. J. ALPERIN, D. B. ALBERT, AND C. S. MARTENS. Curriculum in Marine Sciences, University of North Carolina, Chapel Hill, NC, 21599-3300 USA.

Rates of methane oxidation (MO) and methane production from carbon dioxide (MPC) were measured in anoxic sediments from Cape Lookout Bight, North Carolina using carbon-14 tracer methods. MO and MPC rates were also measured in a laboratory "jar" experiment in which Cape Lookout Bight sediment was incubated at 23 °C in a headspace-free glass vessel, with weekly withdrawal and analysis of samples over a 120 day period. In both winter and summer, as well as in the jar experiment, methane production rates were very low in the presence of sulfate, then rose rapidly following sulfate depletion. During the summer and in the jar experiment, MO rates followed much the same trend. Rates remained very low until sulfate depletion, then displayed profiles similar to those of MPC rates. The MO/MPC ratio increased with depth in the field study and with time in the jar experiment, but did not exceed 0.25 or 0.10, respectively. The covariance of methane oxidation and production rates in field and laboratory studies suggests a close relationship between methane production (MPC) and methane oxidation in Cape Lookout Bight sediments. Winter methane oxidation rates exceeded methane

production rates from carbon dioxide and acetate by as much as 700% in the bottom 10 cm of the sulfate containing zone. Limitation of substrates (hydrogen, acetate, etc.) at this depth interval may cause sulfate reducing or other bacteria to utilize methane as an electron donating substrate.

PA-4/5-7 RESPIRATION OF CULTIVATED HISTOSOLS IN FIELD AND LABORATORY MEASUREMENTS AND THE RELATIONSHIPS BETWEEN RESPIRATION AND SOIL CHARACTERISTICS. T. L. HOKKANEN AND J. SILVOLA. University of Joensuu, Department of Biology, P.O. Box 111, SF-80101 Joensuu, Finland.

There are about 500,000 ha of cultivated histosols in Finland and much stored carbon will be lost as CO_2 from soil to atmosphere when peat mineralizes. Decomposition also liberates stored nutrients - especially nitrogen - and CO_2 evolution rates thus reflects soil fertility.

We measured CO_2 production in four field sites using three methods. A static method (Method 1) was used for *in situ* measurements: air samples were taken with syringes from closed chambers and CO_2 concentration was analyzed with IRGA. In laboratory CO_2 production was measured from large, intact soil cores at different temperatures using open IRGA (dynamic method, Method 2). Method 3, was to bulk and sieve large soil cores and to measure respiration from small samples at different temperatures. The chemical properties (pH, basic cations) of the sites were determined from sieved soil. To compare the respiration results from methods 2 and 3 we calculated them to correspond the temperatures prevailing in the surface soil during field measurements. Respiration of small samples was calculated to represent surface soil (20 cm layer).

Study sites 1 and 2 are influenced by mineral soil (Loss On Ignition is 10-70 %) and sites 3 and 4 are pure peat (LOI is about 90 %). Peat from Site 1 is highly humified Sphagnum-peat and the carbon content is about 58 %, which is higher than in the other peats. Peat from Site 2 is also highly humified, but it is obviously Carex-type. Peat from Site 3 is highly humified Sphagnum-peat, too, but the dissolved carbon content is higher than in the other sites. Peat from Site 4 is Sphagnum-peat, but it is the least humified and contains less N per OM than the others, and the average pH is highest.

Average site respiration in laboratory measurements (Method 3, +15 °C) varied from 1 to 9 $\text{mg CO}_2 \text{C}^{-1} \text{ (d. wt.)}$. Respiration at sites 3 and 4 was higher than in sites 1 and 2. Average site respiration calculated per organic matter (+15 °C) varied from 5 to 10 $\text{g CO}_2 \text{C}^{-1} \text{ (OM)}$. These results show Site 1 respiration was lower than at all the other sites. When *in situ* measurements (Method 1) were used, the average site respiration varied from c. 600 to 1100 $\text{mg CO}_2 \text{m}^{-2} \text{h}^{-1}$.

Bulk soil chemical characteristics do explain the variation in soil respiration (Method 3), but they account for the variation in field respiration (Method 1) and in dynamic method (Method 2) poorly.

The ratio of average results by methods 2 and 1 was nearly unity (Method 2/Method 1 = 1.04). The ratio depended, however, on the respiration rate and decreased from c. 1.5 to 0.5 with field respiration rate (Method 1) increasing from 300 to 1300 $\text{mg CO}_2 \text{m}^{-2} \text{h}^{-1}$. The relation between methods 1 and 3 was not as clear as between methods 1 and 2. The ratio varied from 0.6 to 0.2 at the respiration rates mentioned above. These results show that CO_2 production from different soil components (bulk soil, roots, litter) is not represented similarly by different methods. Both the field measurements (Method 1) and the intact core measurements (Method 2) emphasize the role of litter decomposition and root derived CO_2 on the total CO_2 evolution even from organic soils

PA-7-4 AN UP TO NOW UNKNOWN METABOLISM OF METAL-MOBILIZING *THIOBACILLUS*: AEROBIC HYDROGEN OXIDATION. H. HUBER, E. DROBNER, AND K.O. STETTER. Institute of Microbiology, University of Regensburg, Regensburg, FRG.

Three novel rod-shaped *Thiobacillus*-like isolates have been obtained from a uranium mine in Germany. They are obligate autotrophic organisms growing by the oxidation of galena (PbS) producing $PbSO_4$. Alternatively, they are able to oxidize molecular hydrogen, a physiological property, up to now unknown within the genus *Thiobacillus*. This metabolism was proved by using D_2 as energy source. After growth HDO could be determined in the medium by NMR spectroscopy. Further investigation demonstrated, that also *Thiobacillus ferrooxidans* is a facultative aerobic hydrogen oxidizer. This ability was not observed in 8 other species of the genus *Thiobacillus* and in *Leptospirillum ferrooxidans*.

PA-4/5-8 NITRIC AND NITROUS OXIDE EVOLUTION FROM MANAGED SUBTROPICAL GRASSLAND. G.L. HUTCHINSON, USDA-ARS, Fort Collins, CO, G. P. LIVINGSTON, NASA, Ames Research Center, Moffett Field, CA, and E. A. BRAMS, Cooperative Agrkultural Research Center, Prairie View A&M University, Prairie View, TX.

Biogenic NO and N_2O production in tropical forest and grassland soils is believed to contribute a disproportionately large share of the global fluxes of these gases to the atmosphere, but little is known about N oxide emissions from similiar ecosystems in subtropical climates. Subtropical grasslands may have particular importance because of their large geographical extent, and because they have typically been subject to intense anthropogenic disturbance. We used a soil cover technique to monitor NO and N_2O emissions from a Bermuda grass (*Cynodora dactylon*) pasture on sandy loam in humid, subtropical southern Texas. The two treatments imposed on the pasture were minimum cultural management (spring harvest followed by a single annual maintenance application of N and P fertilizers) and intensive cultural management (harvest and fertilization repeated on a 9-week cycle throughout the growing season). Emission of N_2O was monitored periodically for one year, but measurement of NO evolution was limited to one 9-week period in early summer.

During early summer, the emission of NO, but not N_2O , was stimulated by clipping and removing the grass, probably because eliminating the shading provided by the dense grass canopy changed these plots from cooler to warmer than unharvested plots, thereby stimulating the activity of soil microorganisms responsible for NO production. Neither gas flux was affected by application of 52 kg N ha^{-1} as $(NH_4)_2(SO_4)$ until subsequent rainfall dissolved and moved the surface-applied fertilizer into the soil. Immediately thereafter, emissions of NO and N_2O increased dramatically to peaks of 160 and 12 g N $ha^{-1} d^{-1}$, respectively, and then declined at a rate that closely paralleled the nitrification rate of added NH_4^+ , indicating that the gases resulted from the activity of nitrifying microorganisms, rather than denitrifiers.

The emission of N_2O during other 9-week periods followed patterns similar to that observed during early summer, but had smaller magnitude during cooler seasons. Total N_2O evolution during the year averaged 0.6 and 1.2 kg N ha^{-1} for plots under minimum and intensive cultural management, respectively, which more closely resemble the low fluxes characteristic of temperate-region grasslands than high

fluxes characteristic of the tropics. Ancillary data suggest that the lower fluxes reflect reduced occurrence of conditions supporting denitrification, because of lower rainfall, more rapid drainage, and lower available C than at a typical tropical site. Nitric oxide emissions during early summer averaged 1.2 times greater than N_2O emissions and accounted for 3.2% of the added N. Total NO evolution during the 9-week period was 0.7 and 2.4 kg N ha^{-1} from plots under minimum and intensive cultural management, respectively. If these amounts represent the same fraction of total annual emissions as was measured for N_2O (26 and 29% under minimum and intensive cultural management, respectively), then annual NO evolution from plots under the two management schemes would total about 3 and 8 kg N ha^{-1} . Emissions of this magnitude would place humid, subtropical grasslands among the largest biogenic NO sources, suggesting that they contribute significantly to the global atmospheric NO_x budget.

O-12-5 THE GLOBAL METHANE CYCLE IN THE OCEAN. M.Y. IVANOV, Institute of Microbiology, USSR Academy of Sciences, Moscow, A. YU. LEIN, Vernadsky Institute of Geochemistry, Moscow, USSR.

1. Three main methane sources play the most important role in the global methane cycle in the ocean.
 - 1.1 Biogenic methane formed by methanogenic bacteria in reduced sediments of shelf and continental slope. Its flux makes n. 100 Tg per year and $\delta^{13}C$ value varies from -64 to -94‰.
 - 1.2 Abiogenic methane coming from hydrothermal vents of rift zones in the middle oceanic ridges. Its flux is estimated at n. Tg per year, $\delta^{13}C$ value ranges from -15 to -17‰.
 - 1.3 Methane from low-temperature vents of subduction zones and other fluids seeps. Its flux makes up n. Tg per year, $\delta^{13}C$ value ranges from -40 to -70‰.
2. The main part of biogenic methane formed in bottom sediments is oxidized by methanotrophic bacteria in upper sediment layers whereas a considerable part of methane from hydrothermal and low temperature vents is oxidized in water bulk of the ocean.
3. Some part of methane is utilized by symbiotrophic microorganisms inhabiting special tissues (trofosomes) and gills of marine invertebrates.
4. Microbiological processes of methane formation and oxidation are very important for the carbon cycle in the ocean.
 - 4.1 During these processes the fractionation of stable carbon isotopes occurs that results in the enrichment of biogenic methane and products of its oxidation with isotope ^{12}C .
 - 4.2 Biomass of methanotrophic bacteria serves as an additional source of organic matter and is used for nutrition of sea animals.
 - 4.3 Isotopically light CO_2 and resulting isotopically light carbonates are produced as a result of methane oxidation.
 - 4.4 Finally, some part of biogenic methane formed in the shallow sediments can enter the atmosphere thus being involved in the formation of greenhouse gases.

O-10-7 METHYLOTROPHIC BACTERIA: BIOMARKER LIPIDS AND CONTROLS ON THEIR CARBON ISOTOPIC COMPOSITION. J. I. JAHNKE AND R. E. SUMMONS. NASA-Ames Research Center, Moffett Field,

California, USA and Bureau of Mineral Resources, Geology and Geophysics, Canberra, Australia.

Triterpenoid hydrocarbons with chemical structures suggesting derivation from methylotrophic bacteria are known to be preserved in sediments as old as 1,700 Ma. This study was designed to show whether or not carbon isotopic data from fossil hydrocarbons could support and enhance inferences gained from the chemical structure signatures and give information about the methane cycle of earlier times.

Studies of extant methylotrophs have shown the ^{12}C is oxidized more rapidly than ^{13}C leaving the residual methane isotopically "heavy". We have found that the direction and extent of this fractionation is also evident in the methane derived biomass and lipid constituents of *Methylococcus capsulatus*. Cells were grown in an open system with CH_4 (50%), CO_2 (0.2%) and O_2 (range of concentrations from 0.5 to 10 %). The presence of CO_2 , while essential for growth, contributed only about 1.5% (w/w) to cell carbon and this is likely to cause an insignificant isotopic shift in comparison to other factors which affect the fractionation. We found that the ^{13}C depletion in total biomass relative to starting CH_4 ($\delta^{13}\text{C} = -30.4\text{‰}$ PDB) was greatest in cells grown at low oxygen concentrations (0.5 % O_2 gave $\Delta 18.6\text{‰}$) compared to those grown at higher oxygen concentrations (10% O_2 gave $\Delta 14.1\text{‰}$). Additional fractionation was evident in the intracellular carbon pool with the total lipids for the low and high oxygen experiments being - 51.3 and 47.4 ‰ PDB respectively. Further depletions in the acetate-derived metabolites were evident with values of - 52.1 and - 49.7 ‰ PDB for the hopanol portion of the bacteriohopane polyols and - 52.8 and 50.8 ‰ PDB for the methylsterols synthesized under low and high oxygen concentrations respectively. Having identified oxygen concentration as a major factor affecting isotopic fractionation we are now examining influences due to the biochemistry of the carbon assimilation pathway and physical parameters such as growth temperature.

Large isotopic fractionations such as those observed in this study should enable us to identify bacterial triterpenoids from disparate sources and more confidently assign those arising from methanotrophic bacteria. In turn, this may provide a rigorous means of identifying methane cycling in ancient environments though unambiguous detection and quantification of methanotroph biomarkers.

PA-4/5-9 **USE OF THE AVIRIS IMAGING SPECTROMETER FOR REMOTE ESTIMATION OF FOLIAR BIOCHEMICAL CONTENT ALONG THE OREGON TRANSECT.** **L.E. JOHNSON**, TGS Technology Inc., NASA/Ames Research Center, Moffett Field CA 94035, USA.

Data from the Airborne Visible and Infrared Image Spectrometer (AVIRIS) have been acquired over several diverse forest sites in support of the NASA Oregon Transect Ecosystem Research project. Collections occurred at several key times during the growing season, to assess the temporal as well as spatial sensitivity of AVIRIS spectra to the presence of foliar biochemical concentration. Assay of several key biochemical components was performed on a small number of foliage samples harvested at each site, in support of each overflight. A comprehensive field effort was made to collect foliage from a fertilizer-amended plot and a neighboring control plot. These samples were scanned in both fresh and dehydrated form by a laboratory spectrophotometer (400-2500 nm) and then assayed for nitrogen concentration. Current research involves analysis of these lab spectra

for the influence of foliar nitrogen, and extrapolation of results to the AVIRIS spectra. In addition, stepwise multilinear regression and partial least squares techniques are being used to develop statistical prediction equations for nitrogen, lignin, and starch in the pooled AVIRIS dataset. The capability for remote estimation of biochemical concentrations will provide insight into regional nitrogen and carbon cycles. Toward this end, AVIRIS results will ultimately be interfaced with the nutrient cycling element of a forest ecosystem simulation model.

PB-6-6 COMPARATIVE FLUXES OF FIXED NITROGEN RESULTING FROM CONTEMPORANEOUS NITROGEN FIXATION AND DENITRIFICATION IN TOMALES BAY, CA. **S.B. JOYE** and **H.W. PAERL**, Institute of Marine Sciences, University of North Carolina at Chapel Hill, Morehead City, North Carolina, USA.

The availability of fixed nitrogen is commonly accepted as the factor limiting (primary) production in marine systems. The pool of bio-available inorganic nitrogen is controlled by rapid, microbially-mediated cycling of nitrogen between organic and inorganic forms. Coupling of individual processes, for example nitrification and denitrification, has received considerable attention. However, the contemporaneous interactions of nitrogen fixation and denitrification, which represent the autochthonous sources and sinks of fixed nitrogen, are thus far poorly characterized.

Fluxes of fixed nitrogen resulting from these two processes have been examined in three sedimentary and two intertidal microbial (cyanobacteria-dominated) mat systems in Tomales Bay, California. Denitrification rates were determined on both whole cores and slurries of sediment samples using the acetylene block technique. Nitrogen fixation was determined using the acetylene reduction technique on slurries of sediment and on (aerial) sections of microbial mats. Denitrification and nitrogen fixation were measured jointly on microalgal mat samples. At all three sedimentary sites, fluxes of fixed nitrogen associated with denitrification dominated the net balance of fixed-nitrogen cycling. At intertidal sites, nitrogen fixation far outweighed denitrification on almost every occasion. Preliminary results suggest that sedimentary sites in Tomales Bay represent a net sink for fixed nitrogen, but that the loss is offset to some extent by the nitrogen fixation. Intertidal sites represent a net source of fixed nitrogen for the system, while supporting a significant denitrification potential. Potential environmental controls on both processes, diel variations in rates, and ramifications on the fixed nitrogen cycle of Tomales Bay will be discussed.

O-7-6 ENVIRONMENTAL FORENSIC GEOCHEMISTRY: CHARACTERIZATION OF BIODEGRADED PETROLEUM CONTAMINANTS IN SOIL AND WATER TO DETERMINE SOURCE OF POLLUTANTS AND TIME OF SPILL. **IR. KAPLAN**, Global Geochemistry Corporation, 6919 Eton Avenue, Canoga Park, CA 91303, and Department of Earth and Space Sciences, University of California, Los Angeles, CA 90024-1567, USA.

When crude or refined oil products enter soil, groundwater or an aqueous environment (river, lakes or ocean) they begin to be degraded by numerous microbiological or physical processes. The result of such changes is to alter the molecular composition of the product so that its source is unrecognizable. Numerous methods have been devised in the petroleum exploration industry to characterize source rock bitumens and reservoir hydrocarbons. A modification of these methods has been successfully applied to identify the source of the fugitive hydrocarbons.

The methods use different chemical classes for identification. For mildly altered products a detailed statistical comparison is made of the paraffinic or n-alkane distribution between C_{12} - C_{35} for heavy products, C_4 - C_7 for the gasoline range and C_1 - C_3 for the gas range products. For highly altered products, a search is made for complex organic molecules which have undergone the least alteration. Among such groups are the long chain polynuclear aromatic hydrocarbons and the polycyclic paraffinic hydrocarbons, frequently referred to as biomarkers. The aromatic products often contain nitrogen or sulfur. The non-aromatic compounds have many isomeric forms which are characteristic of their sources. Elemental composition, especially sulfur, vanadium and nickel, for crude oil, and lead or manganese for refined gasoline products can help identify sources. Lead alkyls in leaded gasoline are especially useful in determining residence time of product in ground water. The isotopic ratios of $^{13}C/^{12}C$ and D/H have been shown to be very useful natural tracers for gasoline, diesel and heavy oil. The $^{34}S/^{32}S$ ratio may also be useful for heavy oils.

The methods employed by GGC may allow three important questions to be answered. These are: 1) identification of the product type which has occurred in the spill, 2) source of the pollutant and, 3) approximate time frame that the petroleum product(s) has been in the soil/groundwater.

O-1-7 LONG-TERM CONTROLS ON ATMOSPHERIC CO_2 : IMPLICATIONS FOR THE PAST AND FOR THE FUTURE. J.E. KASTING. Department of Geosciences, 211 Peike, Penn State University, University Park, PA 16802.

On long time scales the atmospheric CO_2 level is controlled by the balance between volcanic outgassing and the weathering of silicate minerals followed by deposition of carbonates. Silicate weathering is a poorly understood process. The rate at which it occurs is generally considered to be a monotonically increasing function of temperature, runoff, exposed land area, and the CO_2 partial pressure in soils; however, data bearing on this process are scant and do not always bear out the hypothesized relationships. It, nonetheless, seems likely that Earth's climate has been stabilized over the long term by a negative feedback between atmospheric CO_2 and climate: Low solar luminosity in the past should have led to slower silicate weathering rates and higher atmospheric CO_2 levels. This, in turn, would have increased the greenhouse effect and helped to keep the planet warm. Atmospheric CO_2 partial pressures of 100 to 1000 times the present value are likely during the first half of Earth's history if CO_2 and water vapor were the dominant greenhouse gases.

Silicate weathering is also the process that will ultimately remove the excess CO_2 that is currently being added to the atmosphere by the burning of fossil fuels. Calculations with simple geochemical cycle models indicate that the atmospheric CO_2 concentration will increase by a factor of six or more if we burn most of our fossil fuel reserves. While most of the excess CO_2 will be removed in 5 to 10 thousand years by weathering and/or dissolution of carbonate minerals, the atmospheric CO_2 level could remain significantly elevated for hundreds of thousands of years before silicate weathering brings it back down. Thus, anthropogenic perturbations to the Earth's climate could be effectively permanent. Additional calculations are being performed to determine how sensitive the CO_2 removal time scale is to the details of the carbonate and silicate weathering parameterizations.

O-5-7 A SEASONAL STUDY OF SOIL-ATMOSPHERE METHANE, CARBON DIOXIDE, AND ^{222}Rn FLUX IN

A TROPICAL MOIST FOREST. M. KELLER, National Center for Atmospheric Research, Boulder, Colorado, U.S.A. and R.F. STALLARD, U.S. Geological Survey, Water Resources Division, Denver, Colorado, U.S.A.

We studied the soil-atmosphere exchange of methane (CH_4), carbon dioxide (CO_2), and radon (^{222}Rn) over a period of 18 months in a mature semi-deciduous moist forest site on clay textured soil at Barro Colorado Island, Panama. We examined both undisturbed sites and sites which were irrigated during the dry season. The purpose of our study was to quantify the fluxes of two greenhouse gases (CH_4 and CO_2), and to understand the physical controls on gas fluxes using naturally produced radon as a tracer. Enclosures were used to assay soil surface gas exchange. Permanently emplaced stainless steel probes allowed us to sample the soil atmosphere. Carbon dioxide and methane concentrations were quantified using gas chromatography. Gas phase alpha scintillation counting was used to measure radon activity.

Methane flux was significantly seasonal at both irrigated and undisturbed sites. On an annual basis both undisturbed and irrigated sites had a net atmosphere to soil flux (consumption) of methane, $-0.5 \text{ mg m}^{-2} \text{ d}^{-1}$ and $-0.2 \text{ mg m}^{-2} \text{ d}^{-1}$ respectively. Under both treatments consumption was greatest in the dry season although irrigation muted the seasonal pattern. Soil carbon dioxide emission also displayed a distinctly seasonal pattern; emissions were greatest in the wet season. Irrigation significantly increased soil carbon dioxide flux over the undisturbed levels. Radon fluxes were highly variable. We measured fluxes from 0.01 to $1.65 \text{ atoms cm}^{-2} \text{ s}^{-1}$. Particularly high fluxes were not restricted to any given site or time of the year. Dry season fluxes significantly exceeded wet season fluxes.

Examination of gas concentrations in the soil atmosphere complemented the study of surface exchanges. Methane concentrations were frequently unmeasurable ($< 100 \text{ ppbv}$) at depths below 40 cm. Radon concentrations generally increased with depth to at least 80 cm. Methane consumption was focused in the surface soil while radon production occurred throughout the profile. Models of diffusive radon transport may be used to aid interpretation of soil-atmosphere exchange of biologically active gases such as methane and carbon dioxide. However, we must pay careful attention to the assumptions of these models.

O-2-4 THE GLOBAL METHANE CYCLE. M.A.K. KHALIL and R.A. RASMUSSEN, Global Change Research Center, Oregon Graduate Institute, Beaverton, Oregon 97006 U.S.A.

In this paper we will describe the present understanding of the global methane cycle. The global cycle of methane is driven by emissions of around 550 tg/yr from both natural and sources related to anthropogenic activities, particularly the production of food and energy. Major sources are rice agriculture, domestic ruminants, and wetlands. Methane is removed from the atmosphere mostly by reacting with OH radicals. Some methane is removed by the soils and other processes. Over the past decade methane concentrations have been increasing at about $1\%/yr$ or 16 ppbv/yr . A record of atmospheric methane extending back 150,000 years has been constructed from the analysis of polar ice cores. It shows that, during this time, methane concentrations have never been more than half of present levels. The recent increase of methane is probably caused by increasing emissions. Some of the increase may also be attributed to decreasing levels of OH.

PA-1-3 ATMOSPHERIC RECORDS OF METHANE & NITROUS OXIDE IN GLACIAL ICE. M.A.K. KHALIL

and R.A. RASMUSSEN, Global Change Research Center, Oregon Graduate Institute, Beaverton, Oregon 97006 U.S.A. M.J. SPENCER and P. MAYEWSKI, Institute for the Study of Earth, Oceans, and Space Science & Engineering Research Building, University of New Hampshire, Durham, New Hampshire 03824 U.S.A.

Deep polar ice cores have provided a remarkable record of atmospheric CO_2 , CH_4 , and N_2O that extends back to thousands of years before the present. Deep cores, however, are rare and expensive. Shallow ice cores of a few hundred meters depth can be drilled inexpensively and on demand for specific investigations. These cores provide an alternative to conduct detailed studies atmospheric composition and chemistry during recent times going back a few hundred years. We will report N_2O and CH_4 data from two such cores. Included is the first study of trace gases in an alpine glacier. The results are found to be consistent with measurements from deep cores.

O-11-5 TEMPERATURE AND MOISTURE CONTROLS OVER CARBON FLUX IN AN ARCTIC TUNDRA SOIL. K.KIELLAND AND J.P.SCHIMEL. Institute of Arctic Biology, University of Alaska, Fairbanks, Alaska, USA.

Arctic tundra contains a large proportion of the earth's soil carbon and has been identified as an area sensitive to climatic perturbation. It is unclear, however, to what extent this ecosystem will become a net producer or consumer of greenhouse gases under the projected scenarios of global climate change. In the laboratory we measured simultaneously the net flux of CO_2 and CH_4 in a tussock tundra soil from northern Alaska under a variety of temperature and moisture regimes to determine 1) the temperature sensitivity of these processes and 2) evaluate how changes in the water table might affect the trajectory of carbon flux from tundra environments. Under the conditions of temperature and moisture prevailing in the field, this soil is a net producer of CO_2 and net consumer of CH_4 , and the processes appear to be largely independent. Both processes are relatively insensitive to temperature in that 25-50% of the production/consumption rate at 15°C is retained at 2°C . Increased soil moisture had only a small depressing effect upon CO_2 production. The moisture effect on CH_4 dynamics was more complex. Methane consumption remained linear down to a stable concentration of 0.25 ppm for samples at or below field moisture content. At the highest temperature (15°C) and moisture content (200% moisture holding capacity), however, the soil changed from a net consumer to a net producer of CH_4 . Adjusting the headspace concentration of the incubation jars to 7ppm allowed us to better describe the kinetics of CH_4 production. After about a 20 hr delay, the production rate was steady at $5 \mu\text{g CH}_4 \text{ g}^{-1} \text{ d}^{-1}$. This rate translates into $\sim 90 \text{ mg m}^{-2} \text{ d}^{-1}$, which is within the range of net production rates for tundra soils observed in the field. Whereas the CH_4 -C flux under these conditions represents only $\sim 20\%$ of the CO_2 -C flux in the field, the greenhouse effect of CH_4 is over 50X greater than that of CO_2 , and consequently this rate of CH_4 evolution may amplify the effects of increased CO_2 concentration on the climate. Thus, we conclude that increased soil moisture could be of greater importance than increased temperature in affecting C-flux from this type of tundra soil, largely because of its effect on CH_4 dynamics.

O-6-8 FACTORS AFFECTING THE CONCENTRATION OF DIMETHYLSULFIDE IN SEAWATER. R.P.KIENE.

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The oceanic emissions of dimethylsulfide (DMS) contribute approximately 50% of the global biogenic sulfur input to the atmosphere. DMS is oxidized in the atmosphere to sulfate and methanesulfonate, both of which form aerosols in the troposphere. These non-sea-salt aerosols form the bulk of the cloud condensation nuclei (CCN) over the oceans. The number of CCN in the atmosphere is a critical factor governing the density of water droplets in clouds, which in turn, affects the reflectivity of clouds towards solar radiation. The reflectivity or albedo of cloud cover over the oceans influences global heat balance. Because DMS appears to be intimately involved in marine cloud formation, and DMS is a biogenic compound, the notion of climate regulation by the biota has been proposed (e.g. Charlson et al., 1987). Thus, considerable attention focuses on the factors which control the emissions of DMS from the oceans. The flux of DMS out of the oceans is highly dependent on the concentration of DMS in the surface waters. This study used experiments with freshly collected estuarine and oceanic seawater to examine biological factors involved in the production and consumption of DMS. DMS is formed from β -dimethylsulfoniopropionate (DMSP), an osmolyte produced by certain marine phytoplankton. Production of DMSP by phytoplankton in water samples from a turbid estuary was strongly light-dependent, with concentrations increasing as much as 2-4 fold during 12 h incubations. Other factors affecting net DMSP production included the presence of grazing organisms ($>63 \mu\text{m}$), and the presence of glycine betaine ($5 \mu\text{M}$), an alternative osmolyte. Dissolved DMSP was degraded rapidly by microbial populations to DMS in both estuarine and oceanic waters. The production rate of DMS from DMSP (DMSP-lyase activity) depended on the concentration of DMSP, with saturation of activity occurring at lower DMSP concentrations in oceanic water (20 nM) as compared with estuarine water ($> 100 \text{ nM}$). DMS metabolism occurs in both estuarine and oceanic waters at rates which suggest that biological removal of DMS is the major sink for DMS. DMS consumption activity was also a function of its concentration. Turnover of DMS in estuarine waters was much more rapid than in oceanic waters, despite similar DMS concentrations. The metabolism of DMS is inhibited by chloroform, whereas the production of DMS from dissolved DMSP is not affected. A quantitative examination of changes in total DMSP (total = dissolved + particulate) and the production of DMS during dark incubation experiments, indicated that $<30\%$ of the consumed DMSP could be accounted for as DMS. This was true even when CHCl_3 was used to prevent biological DMS consumption. These findings suggest that DMS is not the major sulfur product of DMSP metabolism in seawater. Therefore, in addition to the familiar DMSP-lyase pathway which yields DMS, a major alternative pathway, possibly involving demethylation is suggested. The results of this study indicate that the concentration of DMS in seawater is controlled by complex interactions between the phytoplankton, grazing organisms and bacteria which metabolize both DMSP and DMS.

O-6-3 DETERMINANTS OF AEROBIC METHANE OXIDATION IN WETLAND SEDIMENTS. G.M.KING and P. ROSLEV. University of Maine, Walpole, ME 04573.

Aerobic oxidation limits methane flux across the sediment-water interface of wetland sediments. Parameters that affect the distribution of molecular oxygen are of paramount importance as determinants of oxidation. In a variety of sediment types, ranging from silty clays to peats, benthic photosynthesis enhances oxidation; the effect is maximal at light intensities of about $4000 \text{ E m}^{-2} \text{ d}^{-1}$; oxidation under

dark conditions decreases by a factor of 2-3. The water status of peats and sediments also plays a key role. The extent of oxygen penetration is related to compressibility. Decreases in water table height insufficient to cause air entry result in decreases in oxygen penetration and methane oxidation and increases in methane flux. The depth range over which oxidation occurs can vary at a given site by a factor of 2-4 on a scale of hours. Such variations expose methane-oxidizing bacteria (MOB) to extended periods of anoxia. The rapid and reversible response of MOB to anoxia represents a key physiological adaptation that maintains a high potential for oxidation under conditions of changing oxygen availability.

O-11-3 PARTIAL PRESSURES OF METHANE AND N_2O IN SURFACE AND SOIL WATERS IN ARCTIC ALASKA: MOVEMENT OF DISSOLVED TRACE GASES FROM TUNDRA TO SURFACE WATERS TO THE ATMOSPHERE.

KLING, G. W. (The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543), KIPPHUT, G. W. (Center for Great Lakes Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53204), MILLER, M. C. (Department of Biological Sciences, University of Cincinnati, Cincinnati, OH 45221)

Estimates of the CO_2 balance for tundra environments have been revised recently to include the transport of particulate and dissolved carbon from terrestrial environments to lakes and streams and then to the atmosphere. We determined whether this mechanism of transport was also involved in the cycling of dissolved methane and N_2O by measuring partial pressures of these gases in surface waters and soil waters on the North Slope of Alaska. The mean surface water P_{CH_4} for the 9 sites examined was 272 ± 50 ppmv (± 1 SE, $N=10$), or more than 150 times the pressure at atmospheric saturation. The calculated CH_4 flux to the atmosphere ranged from 0.08 to $1.02 \text{ mmol m}^{-2} \text{ d}^{-1}$, and was uncorrelated with latitude or lake morphology. We also measured directly a CH_4 flux of $0.13 \text{ mmol m}^{-2} \text{ d}^{-1}$ from a lake using a floating plexiglass chamber. Methane pressures in two soil waters were also supersaturated (36, 500 and 12,500 ppmv). These values are much higher than the values measured in lakes and rivers, suggesting that terrestrially produced CH_4 in groundwater moves into surface waters where it is released to the atmosphere. In contrast, the mean N_2O pressure in 4 lakes was 304 ± 14.6 ppbv (± 1 SE, $N=9$), which is in equilibrium with the atmosphere. Similar values were measured in two soil water samples (323 and 326 ppbv). Thus the transport of dissolved N_2O from terrestrial to aquatic environments and finally to the atmosphere is probably very small.

Measured $\delta^{13}C$ values of terrestrial plant material (-28‰) and DIC in surface waters (-8‰) were used to identify the sources and cycling of carbon as it moves from land to water. The large difference in isotopic composition between initial terrestrial carbon and DIC in lakes and rivers is due to (1) equilibration of soil and surface water CO_2 with bicarbonate during degassing, (2) input of isotopically heavy CO_2 produced as a result of methanogenesis in soils, and (3) gas exchange between surface waters and the atmospheric pool of CO_2 at -7‰ . Thus the isotopic measurements are consistent with the hypothesis that large fluxes of carbon from land to water are important in the cycling of CO_2 between tundra and the atmosphere.

O-11-7 METHANE EMISSIONS IN RELATION TO ECOLOGICAL PATTERNS IN THE HUDSON BAY LOWLANDS. L.E. KLINGER, P.R. ZIMMERMAN, J.P. GREENBERG, AND L.E. HEIDT, National Center for Atmospheric Research, Boulder, Colorado, USA.

In conjunction with the Canadian Northern Wetland Study sponsored by CIRAC, measurements of methane flux were taken during July of 1990 at 50 chambers arranged along a transect extending 80-km inland from the shore of James Bay, near Moosonee, Ontario. Twenty of these chambers were also sampled once for non-methane hydrocarbon emissions. Paleocological studies indicate that this transect represents vegetation communities spanning approximately 5,000 years of succession. These communities include (in order of increasing successional age): coastal marsh, tamarack fen, spruce island/sedge fen, string bog, and raised bog.

Although areally averaged estimates are not yet available, average July emissions of methane based on all our chamber measurements ranged from -10 to over $200 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Methane emissions tended to decrease from early- to mid-successional communities, but were relatively high in some of the late successional sites. The mesoscale ($10\text{-}100 \text{ m}^2$) spatial variability of methane emissions tended to increase in the later successional stages, perhaps due to the development of mesoscale topographic features in the older peatland communities. Differences in water table relations and soil temperatures among the different successional stages appear to explain much of the variation in methane emissions between successional stages.

PB-11-3 PERMAFROST AND GAS HYDRATES AS SOURCES OF METHANE AT HIGH LATITUDES. K.A. KVENVOLDEN¹ AND T.S. COLLETT². U.S. Geological Survey, Menlo Park, CA 94025¹, USA; Denver, CO 80225², USA.

The United Nations Intergovernmental Panel on Climate Change has identified permafrost and gas hydrates as important high-latitude methane sources on the basis of minimal quantitative information. Permafrost and gas hydrates are associated in two distinct high-latitude settings: (1) on shore, where the permafrost is continuous and the zone of gas-hydrate stability ranges in subsurface depth from about 200 to 1,200 m; and (2) on the nearshore Continental Shelf, where relict permafrost has persisted since times of lower sea level when the present inundated shelf was exposed to very cold subaerial temperatures. Three studies that consider methane occurrence in examples of these settings are reported here. (1) The current release of methane from gas hydrates on the Continental Shelf was estimated at about $3\text{-}5 \times 10^{12} \text{ g/yr}$, on the basis of the inferred distribution of methane in permafrost-associated gas hydrates and the transgression history of the Arctic Ocean during the Holocene. (2) Hydrocarbon-gas compositions were measured in 17 surface-sediment samples collected through the ice cover of Harrison Bay. This bay is off shore from an area of known gas-hydrate occurrence on the North Slope of Alaska. Geophysical surveys indicate the presence of offshore permafrost and of gas anomalies in the sediment. No major methane anomalies were detected in these surface sedimentary deposits, and deeper sampling is required to test more completely this nearshore region. (3) The gas composition of ground ice in permafrost was measured at two sites near Fairbanks, Alaska. In the air of a tunnel, where permafrost is subliming, methane concentrations were about 13 ppmv, whereas outside the tunnel, methane concentrations were only 1.7 ppmv. An ice sample from the tunnel contained 0.036 mL methane per liter of melted ice. At the second site, near the University of Alaska campus, samples from a short core of permafrost contained as much as 6 mL of microbially derived methane ($\delta^{13}C = -74\text{‰}$) per liter of melted ice. These preliminary results indicate that (1) gas hydrates may currently contribute methane to the atmosphere and (2) shallow ground ice can contain varying amounts of methane at low concentrations and thus be a high-latitude source of methane.

O-10-4 CH₄ PRODUCTION VIA CO₂ REDUCTION IN A TEMPERATE BOG: A SOURCE OF ¹³C DEPLETED CH₄. J.M. LANSDOWN, P.D. QUAY, AND S.L. KING. School of Oceanography, University of Washington, Seattle, WA, USA.

The flux and $\delta^{13}\text{C}$ of CH₄ released from an acidic peat bog (pH = 3.5), located in the foothills of the Cascade Range, were measured using static chambers. The CH₄ flux ranged from 2 to 585 mg CH₄-C m⁻² d⁻¹, with an annual average of 61 mg CH₄-C m⁻² d⁻¹. The average $\delta^{13}\text{C}$ of the CH₄ flux was $-74 \pm 5\text{‰}$.

Measurements of the rate of acetoclastic methanogenesis versus CO₂ reduction in peat soil, determined using ¹⁴C-labeled acetate and sodium bicarbonate, show that acetate is not an important CH₄ precursor at this site, and that CO₂ reduction accounts for >80% of CH₄ production, as determined by soil incubations. Measurements of the $\delta^{13}\text{C}$ of coexisting CH₄ and CO₂ in soil water and bubbles also indicate that CO₂ reduction is the primary CH₄ production pathway (Whiticar et al., 1986).

The kinetic isotope effect for CO₂ reduction, calculated using the $\delta^{13}\text{C}$ of soil water CO₂ and the CH₄ flux, is 0.93 ± 0.01 . This value shows a larger isotopic discrimination than isotope fractionation effects reported for CO₂ reduction by laboratory cultures (range 0.94 to 0.98), and is within the range (0.90 to 0.95) reported for marine sediments.

O-12-2 BIOGEOCHEMICAL FEEDBACKS FROM GLOBAL WARMING. D.A. LASHOE, Natural Resources Defense Council, 1350 New York Ave., NW, Washington, DC 20005.

Global warming during the next century is likely to be more rapid than at any time during the last 10,000 years, and is likely to yield global average temperatures higher than any time for at least 150,000 years, if current emission trends continue, according to the recent assessment conducted by the Intergovernmental Panel on Climate Change. As indicated by the ice core record, climate change of this magnitude will have profound effects on all major global biogeochemical cycles, including those that influence the concentrations of the greenhouse gases giving rise to the projected warming.

Changes to the carbon cycle may influence concentrations of CO₂, CH₄, CO and hydrocarbons through changes in ocean circulation and chemistry, destabilization of methane hydrates, changes in wetland area and temperature, and changes in ecosystem distribution and function, including fire frequency. Changes in the nitrogen cycle may influence concentrations of N₂O and NO_x through changes in soil processes and fire frequency. Finally, changes in the sulfur cycle may also influence climate through changes in DMS and sulfate concentrations.

While there is great uncertainty about the magnitude, and even the sign, of many of these effects, an attempt is made to estimate their overall impact on climate change during the next century. While no single biogeochemical feedback appears to be large in comparison to geophysical feedbacks, the number and complexity of biogeochemical feedbacks significantly increases the risk of unpleasant surprises in a greenhouse world.

PB-6-7 THE ELEMENT DISTRIBUTION IN SEDIMENTS AND ENVIRONMENT EVOLUTION OF QINGHAI

LAKE. M.B. LIN, Lanzhou Institute of Geology, Academia Sinica.

The Qinghai Lake is the largest enclosed brackish water lake in western plateau of China. At present, the lake surface is gradually shrinking, therefore causing great concern about its future influence on its surroundings.

On the basis of the analyses date of some elements in the bottom sediments, the distributions of Si, Ti, Mn, Fe, V, Co, Ni, P, Na, K and Cl are worked out which illustrate the characteristics of oxidation-reduction environment of Qinghai Lake. These are summarized as follows:

1. Features of differentiation & accumulation of elements are not only dependent on their own geochemical properties, but, are also influenced by the hydrodynamics of lake water.
2. That the formation, concentration and decomposition of organic matter is extremely an important factor to the dispersion and accumulation of elements mentioned above.
3. It's deduced, that Qinghai Lake will shrink and, after an evolution of 5000 years it will become a salt-lake.

O-2-9 A NEW INSTRUMENT FOR PRECISE MEASUREMENT OF ATMOSPHERIC N₂O AND CH₄. M. LOEWENSTEIN, Earth System Science Division, NASA Ames Research Center, Moffett Field, CA 94035, USA.

Over the past several years measurements of chemical tracers in the atmosphere, e.g. N₂O, CH₄, and CFC-12, have made an important contribution to our understanding of conditions in the winter, polar atmosphere and the genesis of the Antarctic ozone "hole". Currently there is a need to extend our tracer measurement capability to higher altitudes and also to increase the accuracy and precision of these measurements.

We will describe a newly designed lightweight, dual-channel instrument for the measurement of N₂O and CH₄. The instrument will be capable of attaining 1% precision and 3% accuracy for these two molecules over an altitude range from the mid-troposphere (5 km) to the lower stratosphere (25 km). The measurement rate will be 0.1 Hz and for typical airborne platform speeds the spatial resolution of the measurements will be 1 to 2 km. This new instrument is specifically designed to be carried on small autonomous aircraft (Mach number about 0.3) or on light payload balloons. While its primary application is to be an integral part of a stratospheric chemical/dynamical research payload, the precision measurement of these important biogeochemical gases will certainly be valuable to the broader global climate change research community. In addition to describing this new instrument, we will discuss the types of data sets we anticipate gathering and their application to atmospheric chemical and dynamical research in the coming years.

PB-6-8 METHANE AND OTHER HYDROCARBON GASES IN THE FLOATS OF THE GIANT KELP *MACROCYSTIS PYRIFERA*. T.A. LORENSON, K. A. KVENVOLDEN, and R. S. OREMLAND U.S. Geological Survey, Menlo Park, CA 94025 USA.

In a preliminary study we have observed that floats of the living giant kelp *Macrocystis pyrifera* contain trace quantities of methane (3-14 ppmv) and no detectable amounts of the higher molecular weight hydrocarbon gases. In addition the floats have about 350 ppmv CO₂, and the balance gas was measured as air. After the kelp was removed from the ocean, the gases in the floats underwent a dramatic change in composition. We measured this change over a period of 14 days.

Methane concentrations rapidly increased to a maximum of 2,300 ppmv in 3 days, returned to about 100 ppmv in 5 days and then declined slowly to nearly 10 ppmv by day 12. In parallel, CO₂ concentrations reached a maximum of 43,000 ppmv and then declined to the initial level of about 350 ppmv. Higher molecular weight hydrocarbons were observed after 1 day. Ethane concentrations increased to a maximum of 6 ppmv after 3 days, then declined to fluctuating levels of 2 to 5 ppmv. Ethene concentrations reached a maximum of 7 ppmv after 13 days. The amount of propane steadily increased to 26 ppmv within 11 days and remained near this value. Propene concentrations also increased over 13 days to 22 ppmv. Butane concentrations remained below 0.25 ppmv at all times. An unresolved mixture of pentanes and hexanes also increased in concentration during the 14 days. The observed increase in hydrocarbon gas concentrations is believed to arise from microbially mediated decomposition of the kelp. Experiments are in progress to evaluate the geomicrobiological processes that account for our observations.

O-9-5 INFLUENCE OF MICROBIAL Fe(III) REDUCTION ON METHANE PRODUCTION IN FRESHWATER ENVIRONMENTS. D. R. LOVLEY AND E. J. P. PHILLIPS, Water Resources Division, U. S. Geological Survey, Reston, VA 22092

Shallow freshwater environments such as rice paddies, marshes, and swamps are an important source of atmospheric methane. A characteristic feature of these environments is that the soils often undergo alternating cycles of flooded (anaerobic) and drained (oxic) conditions. Iron is generally abundant in such soils. Our previous studies have indicated that when Fe(III) oxides are available, Fe(III)-reducing microorganisms inhibit methane production by maintaining the concentration of important substrates for methane production (hydrogen, acetate) at concentrations too low for methanogenic bacteria to metabolize. Therefore, factors controlling competition between Fe(III)-reducing and methanogenic bacteria in freshwater sediments were investigated.

After extended anaerobic periods, most of the reactive iron in freshwater aquatic sediments was recovered in the Fe(II) state. In contrast to the general perception that Fe(II) is highly soluble, most of the Fe(II) was found to be retained in solid forms. Under oxidizing conditions, the Fe(II) was recycled to Fe(III) oxides. Thus, when the sediments were placed back under anaerobic conditions, Fe(III) oxides were the most abundant potential electron acceptor for organic matter decomposition. The extent to which microbial Fe(II) reduction diminished methane production varied considerably, depending on such factors as the concentration of Fe(III) oxides, the mineral forms of Fe(III) that were available, and the rate of organic matter decomposition in the sediments. In some sediments as much as 75% of the Fe(III) oxides were unavailable for microbial reduction and thus, methane production proceeded despite high Fe(III) oxide concentrations.

These studies suggest that the activity of Fe(III)-reducing microorganisms can greatly diminish the extent of methane production in shallow freshwater environments that undergo alternating flooded and drained cycles. Since the relative influence of Fe(III) reduction on methane production may vary widely between different environments, attempts to model methane emissions from shallow freshwater environments need to consider the iron biogeochemistry of the environment.

O-10-2 CONSUMPTION OF FREONS F-11 AND F-12 IN METHANE-PRODUCING AQUATIC SEDIMENTS. D. R. LOVLEY AND J. C. WOODWARD, Water Resources Division, U. S. Geological Survey, Reston, Virginia 22092

Freons F-11 and F-12 are generally considered to be biochemically inert. In concurrence with previous studies, F-12 and F-11 were not consumed in aerobic soils. However, when anaerobic sediments from a variety of environments were incubated in the presence of approximately atmospheric concentrations of F-11 and F-12, both freons were consumed over time. There was no F-12 uptake if the microorganisms in the sediment were killed with heat prior to the addition of F-12. However, if heat-killed sediments were reinoculated with microorganisms, then F-12 uptake resumed as microbial metabolism was reestablished. The temperature optimum for F-12 uptake was consistent with an enzymatically catalyzed reaction. Cell suspensions of the anaerobic microorganism *Clostridium pasteurianum* also consumed F-12.

F-11 was consumed in heat-killed sediments, but at a slower rate than in live sediments. Reinoculation of heat-killed sediments stimulated F-11 uptake. This suggests that there was an enzymatic as well as nonenzymatic mechanism for F-11 uptake. F-11 was not consumed in heat-sterilized aerobic sediments. This suggests that F-11 consumption in anaerobic sediments results from a reaction with reduced components in the anaerobic sediments. A potential model for this nonenzymatic uptake was the finding that a suspension of a reduced iron porphyrin consumed F-11.

The rates of F-12 and F-11 uptake in anaerobic sediments was minor in comparison to the current anthropogenic release of these compounds. However, because of the long tropospheric lifetimes of F-12 and F-11, this sink could have a significant long-term impact on the amounts of F-12 and F-11 which reach the stratosphere.

PA-7-5 HEAVY METAL EFFECT UPON THE EMBRYONIC DEVELOPMENT OF MARINE INVERTEBRATES. V. V. MALAKHOV, Moscow State University, Moscow, USSR, L. A. MEDVEDEVA and R. V. GAREYEVA, Pacific Oceanological Institute of the Far East Branch, USSR Academy of Sciences, Vladivostok, USSR.

Embryos and larvae of marine invertebrates are significantly more susceptible to the effect of different pollutants than adults. In the experiments conducted we investigated the influence of heavy metals (Cu⁺⁺, Zn⁺⁺ and Cd⁺⁺) on the embryonic development of widely spread commercial species of bivalve molluscs (*Patinopecten yessoensis*, *Mytilus edulis*, *Macrura chinensis*, *Spisula sachalinensis*, *Callista brevisiphonata* and *Crassostrea gigas*), sea urchins (*Strongylocentrotus intermedius* and *S. nudus*) and sea star *Aphelasterias japonica*. We revealed, that the appearance of 50 % abnormal larvae should be expected at copper ions concentration of 4 ppb, 100 ppb of zinc ions and 500 ppb of cadmium ions. In the development of sea urchins we found the appearance of 50% abnormal larvae under the effect of the following concentrations 20 ppb of copper ions, 55 ppb of zinc ions and 2.33 ppb of cadmium ions. This exceed, by two orders of magnitude, the susceptibility of adult forms of the same species. Specific anomalies arising by the action of heavy metals were found. The effect of copper ions damages morphogenetic processes, for example the evagination of the shell field, but does not prevent the deposition of calcium carbonate. In this case, calcium carbonate forms large-scale globules inside of the larva. Zinc blocks the deposition of calcium carbonate, and cadmium causes the development of an abnormal wrinkled shell. Echinodermata affected by copper have abnormal arms and ciliary bands of deformed structures. Zinc blocks the formation of the calcium skeleton and causes exogastrulation and animalization of embryos. Cadmium does not influence the formation of calcium skeleton but causes the vegetalization of the embryo. The high susceptibility and specificity of anomalies in embryos and larval

stages of marine invertebrates allows for their use as biological monitors of heavy metals in the marine environment.

PB-6-9 BIOGEOCHEMICAL BASIS OF ECOLOGICAL INVESTIGATION OF NEAR SAKHALIN OFFSHORE.
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The ecological situation in water objects of near Sakhalin offshore is determined by influence of natural and anthropogenic factor water ecosystems. Petroleum and hydrocarbon pollution prevails as a result of exploration and developing of discovered oil and gas deposits and of natural hydrocarbon shows and seepages as well. These factors cause the great changes in the natural balance of water ecosystems. Measuring of biochemical active substances concentrations by biochemical methods are used for quantitative characteristics of these changes, and assessment of water system biochemical conditions is made on this base. The association of microorganisms (size 0, 4-200 mkm) is applied as a test object due to high sensitivity to environmental variations. Modern techniques to realize field investigations are developed. Five stages for testing water objects with a consistent task complication and increasing amount of samples and investigation parameters are proposed: 1) determination of biochemical condition at the research moment; 2) assessment of variance from the norm; 3) study of water environment factors effecting organisms metabolism, defining the pollution substances; 4) search for source of pollution; 5) area survey and the object mapping.

On the initial stage (marking water basin) grid sampling is carried out at 3-5 points equally spaced in the water area. The integral and bottom water samples, bottom sediment samples are taken at each point-station. Then to solve research problems the optimum quantity of stations is determined. The system of bottom samplers including three devices for marine investigations and three modifications for shallow water basins and the system for accumulation and captation of fluid streams as well is applied here. The most possible evaluation of samples is realized in field, but the final assessment is made in the laboratory conditions. Concentrations of ATP, alkaline phosphomonoesterase activities and some environmental parameters, such as concentrations of hydrocarbon gases, helium, hydrogen, the sediments components are measured. On the basis of measurement results the assessment of these water objects ecological state is given. Biologically active and passive media are defined, normal state, eutrophication or depression by impact of pollution are determined. The classification by biochemical feature is introduced into practice for the latter.

O-6-1 LIGHT HYDROCARBONS, ORGANIC ACIDS, AND MICROBIAL PROCESSES IN HYDROTHERMALLY-ALTERED SEDIMENTS OF THE GUAYMAS BASIN, GULF OF CALIFORNIA. **C.S. MARTENS, D.B. ALBERT, G.G. PAULY, E.A. CANUEL,** Marine Sciences, CB-3300, University of North Carolina, Chapel Hill, N.C. 27599, U.S.A.; **AND J.P. CHANTON,** Department of Oceanography, Florida State University, Tallahassee, FL 32306, U.S.A.

Light hydrocarbons and short chain organic acids were measured in sediment pore waters and hot brines exiting hydrothermally-altered sediments of the Guaymas Basin, Gulf of California. *In situ* gas samples were collected near microbial mats by DSV ALVIN using a pore water probe and flow-through flux chamber. ALVIN push cores were squeezed to obtain additional samples. Temperature data were collected utilizing a thermistor probe.

Pore water methane concentrations ranged from 0.05 to 10 mM; ethane, 0.5 to 180 μ M; propane, 0.02 to 15 μ M; isobutane, up to 1.2

μ M; butane, up to 1.3 μ M. Methane $\delta^{13}\text{C}$ values ranged from -38 to -44‰; C_1/C_2 ratios ranged from 30 to 150. Pore water organic acid concentrations were generally proportional to *in situ* sediment temperature up to 200°C. Maximum acetate concentration observed was 1966 μ M; propionate, 318 μ M; isobutyrate, 78 μ M; butyrate, 18 μ M; lactate, 20 μ M. Organic acid concentrations generally increased with depth.

Facultative chemolithotrophs living in microbial mats overlying sulfidic Guaymas Basin sediments and surrounding brine fluid vents may utilize organic acids and light hydrocarbons as carbon and energy sources. Sedimentary sulfate reduction producing over 6 mM pore water sulfide concentrations may, in part, be supported by oxidation of organic acids generated from organic detritus by hydrothermal alteration.

O-11-4 ISOTOPIC CHARACTERIZATION OF METHANE FROM YUKON-KUSKOKWIM DELTA TUNDRA AND MINEROTROPHIC FENS IN NORTHERN QUEBEC. **C.S. MARTENS, C.A. KELLEY, W. USSLER III, R.J. MACAFFREY,** Marine Sciences, CB-3300, University of North Carolina, Chapel Hill, NC, 27599, U.S.A.; **J.P. CHANTON, J. HAPPELL,** Department of Oceanography, Florida State University, Tallahassee, FL, 32306, U.S.A.; **S. TRUMBORE,** Center for AMS, Lawrence Livermore Laboratory, Livermore, CA 94550, U.S.A.

The methane flux from the Yukon-Kuskokwim Delta, western-Alaska, is controlled by warm season emissions from wet meadows (marshes and bogs) and ebullition from organic-rich lakes. The mean $\delta^{13}\text{C}$ value of wet meadow emissions is -65.82‰ (2.21, one sigma; n=18). The sediments of small lakes loaded with organic detritus contain abundant methane-rich gas bubbles. The calculated ebullitive methane $\delta^{13}\text{C}$ value is -62.9‰ (1.9). Heavier $\delta^{13}\text{C}$ and lighter δD values for bubbles methane near detritus-rich lake bank edges suggest control of spatial isotopic variations through changes in methane production mechanisms and substrate isotopic values. AMS ^{14}C measurements reveal bomb carbon content (107-121% modern age) in six of eight samples suggesting recently produced plant detritus as a principal methane source.

Methane emissions from two subarctic fens near Schefferville, northern Quebec ranged from 5.11 to 511 mg/m² day during 4 June 90 through 4 Aug. 90. The mean $\delta^{13}\text{C}$ value for methane emissions was -75.87‰ (4.54; n=63), significantly lighter than the value for Alaskan tundra. Pore water methane concentrations were high throughout the warm season at water covered sites, producing gas bubble saturation in the peaty sediments of open water pools. Gas bubbles were collected for C and H isotopic analyses.

PA-4/5-10 METHANE AND CARBON DIOXIDE FLUXES, AND NITROUS OXIDE PRODUCTION AT SOME VIRGIN AND DRAINED PEAT SITES IN FINLAND. **P.L. MARTIKAINEN¹, H. NYKANEN¹, J. SILVOLA², AND P. CRILL³.** ¹National Public Health Institute, Department of Environmental Hygiene and Toxicology, P.O.B. 95, SF-70701 Kuopio, Finland. ²Department of Biology, University of Joensuu, P.O.B. 111, SF-80101 Joensuu, Finland. ³Institute for the Study of Earth, Oceans and Space, University of New Hampshire, New Hampshire 03824, USA.

In Finland there are about 10 million ha of peatlands, 6.5 million ha of which have been drained, mainly for forestry. This drainage disturbance of the peatlands may be considered directly analogous to long term changes in water supply to northern wetlands as a result of changing precipitation patterns due to "greenhouse" warming. In 1990

we began a study of carbon dioxide, methane and nitrous oxide exchange in virgin and managed peatlands.

Methane and carbon dioxide fluxes were measured *in situ* by using a closed chamber technique. Air was sampled with plastic or glass syringes and analyzed in laboratory with a gas chromatograph (FID). Samples for methane and carbon dioxide were taken from soil profiles by probes connected to the syringes. Carbon dioxide was analyzed with an IR analyzer or a gas chromatograph (TCD). Carbon dioxide fluxes were measured also with a dynamic flow method using portable IR gas analyzer. Nitrification and denitrification were studied in laboratory experiments. Nitrous oxide was determined with a gas chromatograph (ECD). At virgin sites in autumn 1990, methane emissions ranged from 12 to 90 mg CH₄ m⁻² d⁻¹ and carbon dioxide fluxes from 2,400 to 7,200 mg CO₂ m⁻² d⁻¹ depending on the site type. Some drained sites consumed methane *in situ* (0.1 to 0.8 mg CH₄ m⁻² d⁻¹). Oxidation of methane was also indicated by methane concentrations below ambient air levels at depth in the drained soils. Carbon dioxide evolution from the drained sites had increased up to 7 200-19 200 mg CO₂ m⁻² d⁻¹.

In laboratory experiments, methane oxidation and nitrous oxide production was found to occur simultaneously in samples taken from drained peat soil. The preliminary results indicated that draining will stimulate nitrification and nitrous oxide production especially at fertile (minerotrophic) sites.

O-12-9 AN ECOSYSTEM APPROACH TO A NITROUS OXIDE BUDGET FOR TROPICAL ECOSYSTEMS. P. A. MATSON, AND P. M. VITOUSEK. NASA-Ames Research Center, Moffett Field, California, USA and Stanford University, Stanford, California, USA.

We measured fluxes of nitrous oxide in a range of tropical ecosystems arrayed along gradients of soil fertility, climate, and disturbance. Average fluxes from intact forests on different soil types ranged from 0.38 to 3.0 ng cm⁻² h⁻¹. Pastures that had been converted from tropical moist forest had three-fold greater annual fluxes than did intact forest. We used this information on fluxes to calculate the tropical contribution to the global nitrous oxide source; we estimate that moist and wet lowland tropical forests account for 2.4 Tg/yr, tropical dry forest contributes around 1 Tg/y, and forest conversion to pasture add 0.7 Tg/y of N₂O-N.

O-10-1 BIOLOGICAL AND CHEMICAL TRANSFORMATION OF HALOGENATED ALIPHATIC COMPOUNDS IN AQUATIC AND TERRESTRIAL ENVIRONMENTS. P. L. MCCARTY AND M. REINHARD, Western Region Hazardous Substance Research Center, Stanford University, Stanford, CA 94305-4020.

Halogenated Cl- and C2-compounds are among the most important compounds affecting stratospheric ozone levels and are among the most frequently found chemicals at hazardous waste sites. While once believed to be resistant to transformation by aquatic and terrestrial processes, these compounds are now known to be transformed at rates that may affect global distribution. Aerobic and anaerobic microbial cometabolic processes have been shown to transform a wide range of halogenated carbon compounds including Freon 11, Freon 113, 1,1,1-trichloroethane, carbon tetrachloride, tetrachloroethylene, trichloroethylene and vinyl chloride. Environmental transformation of some chemicals can include both chemical and biological transformations, either in parallel or sequentially. The rates of such transformations depends on substrate structure and geochemical conditions.

Under anaerobic conditions halogenated substrates are susceptible to hydrogenolysis, especially those which are highly chlorinated. For example, perchloroethylene may sequentially be reduced to trichloroethylene, dichloroethylenes or vinylchloride. If conditions are sufficiently reducing, the transformation may proceed to ethylene. C2-halogenated aliphatics with vicinal halogens, such as ethylene dibromide or hexachloroethane, may undergo dihalo-elimination leading to ethene or perchloroethylene, respectively.

Biological oxidation of chlorinated ethenes can also occur, although the prevalence in natural systems is not presently known. One group known to be effective in such oxidations are methanotrophic bacteria that oxidize methane under aerobic conditions to obtain energy. These organisms contain a non-specific monooxygenase used in the first step of methane oxidation, that can oxidize a wide range of chlorinated and nonchlorinated hydrocarbons by cometabolism. An example of this process is the oxidation of trichloroethene, the first step of which is expected to be epoxidation of the double bond.

Some reductive transformations which have been observed in biological systems have also been observed in the presence of geochemical reductants under abiotic conditions. For example, hexachloroethane and carbon tetrachloride have been shown to be transformed by electron donors such as Fe(II) and S(II) compounds. Humic acid and mineral surfaces have been shown to catalyze the reaction. Transformation via nucleophilic substitution and elimination are significant for some substrates. Hydrolysis rates tend to decrease rapidly as the degree of halogenation increases. Hydrogen sulfide may act either as a nucleophile or a reducing agent, depending on substrate structure and catalysts present. The influence of redox conditions on environmental transformation pathways and rates is subject of current research.

O-10-9 CALCIFICATION, PHOTOSYNTHESIS, AND GLOBAL CO₂ CONCENTRATIONS. T. A. MCCONNAUGHEY. U.S. Geological Survey, Box 25046, MS 413, Federal Center, Denver, Colorado 80225-0046, USA.

Calcium carbonate is the most abundant form of carbon on earth, hence calcification plays a significant role in the global CO₂ cycle. Most calcification is mediated by photosynthetic organisms, chiefly algae and algae-invertebrate symbioses. Experiments using the fresh water calcareous alga *Chara* explore calcification physiology and illustrate its connection to photosynthesis. Extracellular calcification appears to be initiated by active H⁺ uptake in electroneutral exchange for Ca²⁺. CO₂ leaks from the cell and precipitates with Ca²⁺, generating protons for the alga (Ca²⁺ + CO₂ + H₂O = CaCO₃ + 2H⁺). The alga translocates the 2H⁺ to separate "acidic bands" along the cell surface, where, ideally, they protonate 2HCO₃⁻ to produce 2CO₂. Calcification uses one CO₂, leaving one for photosynthesis. In mildly alkaline waters such as the oceans, it is therefore common to observe approximately 1:1 ratios of calcification to photosynthesis.

The association of calcification with aquatic photosynthesis has many geochemical consequences. Calcification helps prevent CO₂ depletion and pH elevation in aquatic systems, and thus reduces the potential of natural waters to absorb atmospheric CO₂. This effect is most striking in freshwater. An approximate balance between fossilization of limestone and organic carbon may have prevailed over much of the earth's history, contributing to the stability of atmospheric CO₂ and temperatures.

O-6-5 METHANE EMISSIONS FROM THE AMAZON FLOODPLAIN: ENHANCED RELEASE DURING

EPISODIC MIXING OF LAKES AND A HABITAT-BASED REGIONAL ASSESSMENT. J.M. MELACK, AND D. ENGLE, Department of Biological Sciences, University of California, Santa Barbara, California, USA.

Tropical wetlands such as riverine floodplains are an important source of atmospheric methane. The floodplain of the central Amazon basin covers 110,000 km² and includes large areas of lakes, floating macrophytes and flooded forest. Methane emission from these habitats varies considerably. To extrapolate the available measurements from the few sites to regional estimates requires knowing the areas covered by the major aquatic habitats. We have used synthetic aperture radar and Landsat imagery to assess the areas covered by these habitats in a reach of the Amazon River between the Purus and Negro Rivers, and have calculated methane emissions for high water periods for the region.

During the annual 10 m rise and fall of the Amazon River, vertical mixing within the floodplain lakes ranges from diel mixing to stratification persistent for several months with the exception of rare episodes of deep mixing. We illustrate the large efflux possible during intermittent deep mixing.

O-7-7 DOES ORGANIC MATTER ACT AS A REDUCTANT IN THE DEPOSITION OF METAL ORES? P.A. MEYERS¹, R.M. KETTER², AND E.S. HO¹.

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Organic matter has been implicated as a possible reductant in causing precipitation of metalliferous ores from their soluble forms in migrating fluids. The results of the consequent oxidation range from alterations of organic matter, such as incorporation of oxygen and sulfur into organic molecules, to oxidative destruction of total organic matter. We have investigated the possible role of organic matter in the formation of metal ores in three different types of Ancient ore deposits. Organic matter from mineralized and non-mineralized strata at each deposit was characterized by combinations of elemental, isotopic, molecular, and spectrophotometric procedures tailored to each setting. Samples from the White Pine copper district, hosted in the Middle Proterozoic Nonesuch Formation, show loss of organic matter as a result of precipitation of native copper and silver and copper sulfide from hydrothermal fluids. Sphalerite-bearing Mississippi Valley-type ores in the Ordovician Knox Group of east Tennessee exhibit similar hydrothermal degradation of organic matter relative to non-mineralized rocks. Oxidation of organic matter appears to have contributed to the emplacement of minerals in these two ore formations. In contrast, organic matter in the Devonian Pilot Shale at Alligator Ridge, Nevada, was apparently not directly involved in the formation of local sediment-hosted gold deposits, even though sulfidized and oxidized by migrating fluids. Oxidation of organic matter is evidently a factor in forming some, but not necessarily all, metal-containing ore deposits.

PA-7-6 SOURCES AND MIGRATION OF METHANE-RICH GAS IN SEDIMENTARY ROCKS ON THE EXMOUTH PLATEAU, NORTHWEST AUSTRALIAN CONTINENTAL MARGIN. P.A. MEYERS¹ AND L.R. SNOWDON². ¹Department of Geological Sciences, the University of Michigan, Ann Arbor, Michigan, USA; ²Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, Calgary, Canada.

Samples of rock obtained by drilling during Ocean Drilling Program Leg 122 on the northwest Australian margin record the accumulation

of sediments from Early Cretaceous to modern times. Neocomian siltstones from the Exmouth Plateau are lithologically equivalent to portions of the more deeply buried, onshore Barrow Formation, which hosts production of oil and gas. Organic matter in the siltstones is predominantly derived from land plants, and it is thermally immature. Gaseous hydrocarbons are nonetheless abundant, and their composition is dominated by methane in most of the samples. This composition mimics biogenic gas. Deeper samples (~1000m) contain significant amounts of thermogenic C₂ to C₆ gaseous hydrocarbons but no change in organic matter character. The change in gas compositions suggests that the primary margin of methane throughout this sedimentary column is from thermal decomposition of continental organic matter and that the source is from stratigraphic units more deeply buried on the Exmouth Plateau. Preferential enrichment of methane has occurred during upward migration of gas through these fine-grained sediments.

O-4-9 THE METHANE CYCLE IN DECOMPOSING AGRICULTURAL PEAT SOILS OF THE SACRAMENTO-SAN JOAQUIN DELTA, CALIFORNIA. L.G. MILLER, C.W. CULBERTSON, R.S. OREMLAND (USGS, Menlo Park, CA, USA), and M. SARGENT (UC Irvine, CA, USA)

Flux of methane from peat ecosystems to the atmosphere is of interest because of questions concerning the quantity of radiocarbon-depleted CH₄ annually transferred. Despite this uncertainty, relatively little information is available from peat ecosystems with regard to the nature of the methane cycle operative therein. Additionally, little work has been done in the case of buried peats underlying agricultural soils. A buried peat deposit located on Sherman Island, a subsiding region in the Sacramento-San Joaquin River Delta (Neil and Deverel, 1991), was chosen for investigation. Local concentrations of methane in the ambient air at this site were 2.26 ppm, suggesting enrichment above the 1.7 ppm value for the northern hemisphere. This enrichment could have resulted from local inputs. Flux of methane from the soils to the atmosphere was measured with static chambers and yielded values of 760 ± 360 mmol m⁻² d⁻¹ CH₄ (n = 5). Profiles of methane in the soils and the underlying peats were determined by augering to a depth of 2.4 m and extracting CH₄ from the recovered samples using a headspace technique. Methane in surface soils (above 0.5 m) was 1.3 ± 0.7 μmol kg⁻¹, and increased to 582 ± 72 μmol kg⁻¹ below 0.75 m. The presence of peat and the water table occurred at depths below 0.75 m. Experiments with anaerobically incubated slurries of soil/peat material recovered from various depths indicated the presence of methanogenesis at depths below 0.75 m. This activity could be stimulated by hydrogen. Incubation of subcores with ¹⁴HCO₃⁻ resulted in the formation of ¹⁴CH₄ in samples from this zone. In contrast, the presence of methane oxidation was detected in aerobically incubated slurries in only a narrow zone (0.59 - 0.66 m). Addition of ¹⁴CH₄ to aerobic subcores resulted in the formation of ¹⁴CO₂ at this depth, and also at 1.4 m. These results suggest that an active methanogenesis occurs within the buried peats and that some of this methane escapes through the surface soils to the atmosphere. Methane oxidation in the upper part of the soil column limits the quantity of methane released to the atmosphere.

O-4-4 EMISSION OF BIOGENIC SULFUR GASES FROM A RICE PADDY IN JAPAN. K. MINAMI, K. KANDA and H. TSURUTA. National Institute of Agro-Environmental Sciences, Tsukuba, Japan.

During recent years, SO_2 emission from anthropogenic sources into the atmosphere has steadily increased at a rate of approximately 2.4% per year. To determine the disturbances caused by the impact of human activity, we need to know the amount of sulfur emission from natural sources. Although recent estimations have shown that the total natural sulfur emissions are equivalent to the current anthropogenic emissions of 80 Tg S per year, there still remain large uncertainties about the chemical speciation and the magnitude of natural emissions.

One of the major natural sulfur sources is the emission from soils. Although we have some information about emission rates of sulfur gases from upland soils, very little is known about the occurrence of the sulfur gases in rice paddy fields. In this study, we present the results of rice paddy field measurements of DMS, COS and CS_2 emission, and of the sources of these gases released from paddy soils. The closed chamber method was used for the measurements of fluxes. Emission rates of these gases from rice paddies measured in our study ranged between 3.2 and 4.3 $\text{mgS m}^{-2} \text{yr}^{-1}$. It was concluded that cystine, cysteine and thio-cyanate represented main sources of the COS released from the soils, thiosulfate, cystine and cysteine were sources of the CS_2 , and methionine, methionine sulfoxide, methionine sulfone and S-methyl cysteine were sources of DMS.

PB-6-10 METHANOGENIC ACTIVITY IN THE MANGROVE SEDIMENT OF INDIA. R. MOHANRAJU, T. RAMAMURTHY AND R. NATARAJAN. Center of Advanced Study in Marine Biology, Portonovo 608502, India.

The presence of methanogenic bacteria in tropical mangrove sediments (Pichavaram 11°26'N; 79°48'E) is being reported. The methanogenic bacterial population was studied employing the most probable number for a period of one year from September 1986 to August 1987. Trimethylamine with $\text{N}_2:\text{CO}_2$ (80:20%) as gas phase was the substrate. Maximum methanogenic bacterial number of 1.1×10^5 cells/g of wet sediment was observed during the summer and premonsoonal months, while the monsoon season showed the minimal bacterial population of 2.3×10^3 cell/g of wet sediment.

The post-monsoon months showed an upward trend in the bacterial numbers. Results showed that the methanogenic bacteria are a good component of this highly organic rich anoxic mangrove sediments and the salinity was found to influence the methanogenic population to a greater extent.

O-1-3 THE PALEOCLIMATE OF PANGAEA DURING ITS FORMATION (LATE PERMIAN) AND DISINTEGRATION (LATE JURASSIC). G. T. MOORE¹, D. N. HAYASHIDA¹, C. A. ROSS², AND S. R. JACOBSON¹. ¹Chevron Oil Field Research Company, La Habra, California, ²Chevron, USA, Houston, Texas, U.S.A.

General circulation models (GCM) that run on today's supercomputers can be valuable tools in recreating the paleoclimate of brief and important geologic time intervals. Using a version of the National Center for Atmospheric Research's Community Climate Model, we report the results from multiple seasonal simulations in the Late Permian and Late Jurassic. Certain time frames exist where the arrangement of tectonic plates relative to one another has changed slowly enough that we can model the temporal evolution of paleoclimate using several simulations at critical thresholds. This rationale and approximation are more reasonable considering the fragmentary nature of the geologic record, the imprecision of plate location, the poorly constrained paleoatmospheric greenhouse gas concentrations, and the large grid cell size of current GCMs. The

formation, existence, and disintegration of Pangea lends itself to such a study.

Pangea's early Late Permian (255-252 Ma Kazanian) formation created a chain reaction of events that produced an inhospitable paleoclimate by disrupting zonal atmospheric circulation, an elevated greenhouse effect which warmed the planet, and falling sea level which severely restricted the shallow water marine environments. Collectively they produced an extinction event that progressed over 10-15 my and was the most severe of the Phanerozoic Eon. Disintegration of Pangea occurred approximately 100 my later. The Late Jurassic Kimmeridgian and Tithonian stages (154.7-145.6 Ma) represent time when seaway connections became established between eastern and western Gondwana, North America, and EurAsia. Rising eustatic sea level throughout the Jurassic flooded large parts of the continents. These conditions contributed significantly to climate amelioration by the mid Mesozoic.

The simulation of a Late Permian warmer Earth with an elevated greenhouse effect fits geologic observations and isotope signals. The entire planet warms with the greatest temperature increases north of 50° latitude and the least in the tropics. Warming causes the poleward retreat of sea ice in both hemispheres. Precipitation and evaporation increase and runoff is confined only to areas of heavy rainfall. Monsoons are limited to the southern hemisphere. Southern Pangea receives year-round rainfall. Precipitation occurs on the western coasts of Pangea where storm tracks make land fall. The restricted Zechstein, Perm (USSR), and Permian (USA) basins, times of evaporite deposition, are characterized by negative precipitation-evaporation (P-E) rates. Interior Pangea at mid to high latitudes endures torrid summers (60°C) and frigid winters (-40°C).

Two Late Jurassic simulations examine different paleoatmospheric greenhouse conditions. The geologic record favors an elevated greenhouse effect. Sea ice is restricted to high latitudes, making landfall only in restricted areas. The trade winds bring heavy seasonal rainfall to eastern Gondwana and to the Tethys Sea margins. A strong JJA monsoon occurs over southeast Asia. The distribution of coal-forming environments correlates with precipitation sufficient to maintain gymnosperm forests. Evaporites are localized to areas of negative P-E. Runoff is restricted to regions of intense precipitation. A strong positive correlation occurs between model generated wind-driven coastal upwelling and the distribution of oil prone marine kerogens.

These experiments on Pangean formation and disintegration show that GCMs can generate paleoclimatic simulations for different plate tectonic settings. These simulations predict the distribution of large scale zonal phenomena (e.g. evaporites, carbonates, coals) and more complex, environmentally sensitive deposits (e.g. corals and oil-prone kerogens). The GCM results are impressive considering the model's simplistic nature, coarse grid, and many parameterizations.

O-11-6 METHANE EMISSIONS FROM NORTHERN WETLANDS, CANADA. T.R. MOORE, A. HEYES (Geography, McGill University, 805 Sherbrooke St. W., Montreal, Quebec H3A 2K6, Canada), R. KNOWLES (Microbiology, Macdonald Campus of McGill University, Ste. Anne de Bellevue, Quebec H9X 1C0, Canada) and N.T. ROULET (Geography, York University, North York, Ontario M3J 1P3, Canada)

Seasonal variations in methane flux from wetlands were measured by a static chamber technique in areas near Schefferville (Quebec), Moosonee (Ontario) and Churchill (Manitoba) in subarctic Canada, where wetlands generally cover >25% of the land surface.

In the Schefferville area, characterized by fens, methane fluxes were strongly related to ecological type, with the lowest fluxes occurring in the forest margins (summer average fluxes 1 - 50 mg

CH_4 $\text{m}^{-2} \text{d}^{-1}$) and the highest fluxes from the inundated and floating fens (25 - 125 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$). Development of surface topography of strings and pools in patterned fens resulted in low fluxes (5 - 10 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$) from the strings, raised 10 - 20 cm above the water table, and high fluxes (30 - 70 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$) in the pools, where the peat base is covered by 20 - 30 cm of water. Significant fluxes of methane were recorded from flat fen sites as the frozen peat thawed, as well as also episodic releases of methane during the mid- to late-summer, apparently triggered by small declines in water table.

In the Moosonee and Churchill areas near the coasts of James and Hudson Bays, coastal marshes and pools produced high summer fluxes when inundated or saturated (<300 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$). Low fluxes (<15 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$) were recorded in coastal fen and tamarack fen areas, and also in the interior fen and hummock-hollow, forested and bog sections away from the coast (0 - 20 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$). Significant fluxes, however, were recorded from degrading pools and peat sections (40 - 130 $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$). Estimated annual emissions of methane from the subarctic wetlands range from 0.1 to 25 $\text{g CH}_4 \text{ m}^{-2} \text{y}^{-1}$.

The seasonal evolution of methane can be related to thermal and hydrologic regimes, and combinations of the two. Multi-year measurements of flux at Moosonee and Schefferville revealed that differences in seasonal precipitation could produce substantial differences in seasonal flux. Methane flux at Churchill in dry and average precipitation summers revealed ratios from 0.1 to 1.4, whereas wet: average precipitation ratios for methane flux at Schefferville ranged from 1.7 to 3.5. Within sites, however, the relationship between temperature/water table and methane flux is frequently poor, illustrating the complex mechanisms and controls on flux.

The role of the edaphic factor in determining methane emissions has been evaluated through the laboratory incubation of surface peat samples under anaerobic and aerobic conditions, and the determination of methane production and consumption rates and carbon dioxide production rates. Methane rates show 1000-fold differences between samples, generally in accordance with field fluxes. Further work has also been done to identify the microbiological and substrate controls on methane production and consumption in these wetlands.

PB-11-4 TEMPORAL AND SPATIAL ENVIRONMENTAL CONTROLS ON CH_4 EMISSIONS FROM ARCTIC TUNDRA. L.A. MORRISSEY, G. P. LIVINGSTON, and D. J. DES MARAIS, NASA Ames Research Center, Moffett Field, CA.

Quantification of regional and annual CH_4 emissions from northern high-latitude ecosystems under present and predicted climates requires an understanding of the environmental controls on the production, consumption, and emissions processes. The results summarized here represent *in situ* enclosed chamber observations of CH_4 emission rates between 1987 and 1989 from the Alaska North Slope on local-to-regional and hourly-to-seasonal scales of variability.

Methane emissions proved highly variable in both spatial and temporal domains, mirroring the heterogeneity of the Arctic environment. Mid-summer emission rates ranged from 0 to 286.5 $\text{mg CH}_4 \text{ m}^{-2} \text{hr}^{-1}$ on local spatial scales of 0.5 m, equal to or exceeding variability on regional scales of 10^2 km . The location of the local water table relative to the surface, substrate temperature, and the pathway (diffusive vs. plant mediated transport) by which methane

was released into the atmosphere accounted for most of the spatial variability in emissions although the effects of soil pH and differences between physiographic provinces were also noted. Emissions from inundated sites averaged 5 fold greater than from sites where the water table was 4 cm or more below the surface. The temperature response of emission rates at anaerobic sites represented a 15 fold linear increase over the 3 - 13 $^{\circ}\text{C}$ substrate temperature range observed. Plant mediated transport increased rates of emissions 7-25 times over that by diffusive processes alone. Temporal variability in emissions was significant although the magnitude of the range was much less than observed spatially. Diel variability in emissions on anaerobic vegetated sites was not evident near the summer solstice, but increased through the season, averaging 36% by early August. Seasonally repeated measures of emissions from selected sites varied over a factor of 15 and were multi-modally distributed, reflecting environmental changes associated with storm events. Interannual differences in emissions provided insight into the local and regional scale response of Arctic tundra to climatic warming. Observed increases in soil temperatures of nearly 5°C between 1987 and 1989 resulted in a regional scale 34-fold increase in CH_4 emissions.

The variability of methane emissions reported for *in situ* studies has highlighted current uncertainties in the global estimates of the source strengths of high-latitude ecosystems. Quantitative understanding of the key environmental controls on *in situ* emissions opens the way not only for improved sample allocation and regional-annual estimation strategies but also substantiates concerns regarding potential biological feedback to climatic warming.

O-4-5 IMPACT OF CHANGING LAND USE ON METHANE AND NITROUS OXIDE FLUX IN THE SHORTGRASS PRAIRIE. A.R. MOSIER, K.F. BRONSON, D.W. VALENTINE AND D.S. SCHIMEL. USDA-ARS and NREL, Colo. St. Univ., Fort Collins, CO, USA.

Methane (CH_4) and nitrous oxide (N_2O) are long lived, radiatively active trace gases that account for about 20% of the total anticipated atmospheric warming. Atmospheric concentrations of both gases have increased dramatically during the past century. Increased biospheric production is generally suggested as the reason for the increases, but altered source/sink relationships due to changes in land use may also be important. To test this hypothesis we established gas flux measurement sites in a native grassland, a N-fertilized grassland, an unfertilized, nonirrigated wheat field and a N-fertilized, irrigated wheat field in the northeastern Colorado shortgrass steppe. Both CH_4 and N_2O fluxes in these sites have been measured weekly since spring 1990, using a closed chamber method. Nitrogen fertilization, increasing cultivation intensity and irrigation generally increased N_2O emissions and decreased CH_4 uptake. The large extent of grassland conversion to other uses during the past century and the impact of these changes on gas fluxes may be contributing to increasing atmospheric CH_4 and N_2O concentrations.

PB-12-2 DEUTEROMETHANES AS POTENTIAL FINGERPRINTS OF THE SOURCES OF ATMOSPHERIC METHANE. E. LMROZ. Los Alamos National Laboratory, Los Alamos, New Mexico, USA.

Uncertainty in three-dimensional models of atmospheric methane could be reduced if the fluxes from the source categories were better constrained. The isotopic composition of methane can provide this constraint. The isotopic composition of methane from any source reflects both the isotopic composition of the starting materials and the effects of isotope fractionations occurring during the biochemical

methanogenesis. This initial isotopic signature can be subsequently modified by methanotrophs or chemical oxidation processes before the methane enters the atmosphere. Traditional methods of determining the isotopic composition of methane require the combustion of the molecule to CO_2 for $\delta^{13}\text{C}$ analysis and reduction of the concomitant water to H_2 and D analysis. If isotopic analysis could be accomplished without the combustion step, then there are 10 isotopomers (a conjunction of "isotope" and "isomer") of methane available for fingerprinting the sources of methane to the atmosphere. We presently have evidence that methane-20 ($^{13}\text{CHD}_3$ and/or $^{12}\text{CD}_4$) is anomalously enriched in the atmosphere. We have shown that mass spectral resolution of about 15,000 is sufficient to separate and detect the two methane species at mass 17 ($^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$) and also at mass 18 ($^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$) and also at mass 18 ($^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$). The limit of the precision of the isotopic ratio measurement is about $\pm 10\%$ using Daly-type detectors. This precision will have to be reduced to about $\pm 1\%$ to detect natural isotopic fractionations.

PA-7-7 PHYSIOLOGICAL AND BIOCHEMICAL ASPECTS OF A HEAVY METAL (Pb^{2+}) IN AGRICULTURAL PLANTS IN A SEMI-ARID ENVIRONMENT. K. MUTHUCHELIAN, School of Energy, Environment and Natural Resources, Madurai Kamaraj University, Madurai 625 021 INDIA.

Heavy metals are distributed throughout the biosphere, mainly in the vicinity of industrial plants such as smelting works. Among the metals, lead (Pb^{2+}) is widely distributed in the atmosphere, earthcrust, ocean and ground water; it is absorbed, gets accumulated and can be identified in most plant and animal tissues (Vallee and Ulmer, 1972). The amount of Pb^{2+} available in the soil to plants is dependent on the cation-exchange capacity, the content of mineral and organic matter, pH, oxidation-reduction conditions on soil moisture, and on the granular composition of the soil (Kacabova and Nitr, 1986). In spite of increased knowledge about the interaction of Pb^{2+} with environment there is, however, less information available on physiological and biochemical changes induced by Pb^{2+} . This led to the current investigation to elucidate the influence of heavy metal, Pb^{2+} on physiological and biochemical aspects of *Phaseolus mungo* L., an important food legume in the Indian agriculture. *P. mungo* L. grown at different concentration of Pb^{2+} (0, 10, 100, 1000 ppm) exhibited retardation in shoot and root growth. Pb^{2+} taken up by the roots is transported to the shoots. The accumulation of metal ions was as follows: Root > stem > leaves. Biomass productivity decreased with increasing Pb^{2+} . Disruption of chlorophyll synthesis was greater in Pb^{2+} stressed leaves. The chlorophyll a/b ratio decreased indicating that Pb^{2+} affected chlorophyll b more than chlorophyll a. The leaf soluble protein decreased very slightly with an increasing Pb^{2+} . RuBP carboxylase (EC 4.1.1.39) and Nitrate reductase (EC 1.6.6.1) activities were drastically inhibited by Pb^{2+} . Inhibition of net photosynthesis (measured by Infrared gas analyser, LICOR, USA) was accompanied by increased stomatal diffusive resistance (monitored by steady state porometer, LICOR, USA). The results thus evident that the metal, Pb^{2+} affects the growth and metabolism of *P. mungo* and its implications due to its increase in the environment are also discussed.

PB-6-11 METHANE-CYCLING IN EUTROPHIC LAKES AND THE CORRESPONDING POSSIBLE GLOBAL TROPOSPHERIC EMISSION. M.

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Methanogenesis and methanotrophy are the major compartments of methane cycling in aquatic ecosystems. Quantification of the different positions in the carbon cycle makes it possible to formulate a balance between the carbon in- and output. This carbon balance was established in the temperate Plusssee Lake in Northern Germany after fulfilling annual analytical requirements. Part of the methane cycle is the methane ebullition to the atmosphere. This, together with the methane emission from different sources has a direct influence on our climate (Enquete-Kommission 1990), especially on the chemistry of ozone as a main greenhouse gas. The small eutrophic lake Plusssee, with a surface area of 142905 m^2 , releases a total average ebullition of 1000 kg C/a (about 7g $\text{CH}_4 \text{ m}^{-2} \text{ a}^{-1}$). The global magnitude of the methane emission from rivers and lakes, as given in the literature, is uncertain and is indicated in an extremely broad range between 1 and 25 Tg/a. However, it is very likely that this magnitude would follow their relative real distribution. If we should provide a tentative global estimate for methane emission from lakes according to the scarce data available we calculate a value of 24 Tg/a. Together with a vague estimate of emissions from rivers of 16 Tg/a, we get a total emission from freshwater ecosystems (excluding wetlands and rice paddies) approximating 10 Tg/a. This indicates that the previously published range from 1 to 25 Tg/a is underestimated and would possibly lie in a higher range between 15-50 Tg/a. This represents approximately 6 % of the total tropospheric methane budget of ca. 500 Tg. The major signs for methane are photochemical oxidation in the biosphere. The logical strategies to combat the increasing methane emission in the atmosphere are decreasing the sources and increasing the sink mechanisms. Decreasing the number of ruminants; increasing the efficiencies of sludge and wastewater treatment plants, as well as collecting and making use of methane from landfills, though primarily based on economical motives, these practices will still contribute to the reduction of the emission of methane into the atmosphere.

O-4-8 ATMOSPHERIC CARBON INPUT FROM DECOMPOSING PEAT SOILS OF THE SACRAMENTO-SAN JOAQUIN DELTA, CALIFORNIA. J.M. NEIL and S. J. DEVEREL, U.S. Geological Survey, Sacramento, California, USA.

Estimating the amount of carbon being released from peat soils in drained wetlands is difficult because of spatial variability within each region and temporal variability of the peat oxidation. For example, the annual mass of carbon being released from the islands of the Sacramento-San Joaquin Delta, California, has been estimated as approximately 7.6×10^{12} g by Stephens et al. (1984). This estimate was based on an average subsidence rate of 7.6 cm a^{-1} , a drained area of 100,000 ha, and a peat soil with characteristics similar to the Everglades Agriculture Area soil of Florida. Data from a study of near-surface subsidence and peat decomposition in the western part of the delta suggest that this estimate is high owing to an erroneous assumption for the organic-matter content of the soil and using too large a value for the subsidence rate.

Subsidence rates vary both geographically and temporally. Subsidence rates estimated from land-elevation decreases along transects of Sherman Island in the western delta indicated a time-averaged rate of about 2.3 cm a^{-1} from 1910 to 1988. From 1952 to 1988, the estimated rate was about 1.5 cm a^{-1} . In the central delta, the time-averaged subsidence rates ranged from 5.1 to 7.6 cm a^{-1} from 1926 to 1980.

The organic-matter content of the near-surface delta soils seems to have decreased with time and is spatially variable. Soil samples taken from depths of 15 and 30 cm at each of the sites of the Sherman Island transects ranged from about 10 percent organic material near the levees to about 30 percent at the center of the island. This explains greater amounts of subsidence in the center of the island. Soil samples from depths greater than 1 m are almost entirely fibrous plant material, so the low organic-matter content at the surface probably is due to the accumulation of the mineral phases left after the decomposition of 3 to 7 m of peat.

Carbon is released not only as carbon dioxide but also as aqueous organic carbon compounds in the ground water removed to lower the water table, and as methane. The aqueous carbon output is approximately 1 percent of the gaseous carbon dioxide output, and the methane flux is very small relative to the carbon dioxide flux. The spatial and temporal variability in carbon dioxide fluxes is related primarily to soil-moisture content, temperature, and root respiration. Carbon dioxide fluxes ranged from $9.5 \times 10^{-5} \text{ g cm}^{-2} \text{ d}^{-1}$ in the winter months to $6.5 \times 10^{-4} \text{ g cm}^{-2} \text{ d}^{-1}$ in the summer months for the Sherman Island site. Similar seasonal variability and carbon partitioning among the three phases were seen at the other sites on Jersey Island and Owwood Tract.

On all three islands, subsidence calculated from the gaseous carbon flux is in close agreement with continuously measured subsidence using extensometers. Because subsidence is due almost entirely to gaseous carbon dioxide loss, the annual flux of carbon dioxide can be estimated from subsidence rates. Using historical and contemporary subsidence rates, estimates of annual carbon dioxide flux into the atmosphere range from about 1.25 to 703 mg cm^{-2} . This is smaller than Stephen's estimate of 2.8 g cm^{-2} for the annual carbon dioxide flux and demonstrates the factors affecting the estimate of carbon dioxide fluxes from drained peat soils.

O-5-3 SULFUR GAS EMISSIONS FROM AFRICAN SAVANNAH BURNING. B.C. NGUYEN, N. MIHALOPOULOS, B. BONSANG, J.P. PUTAUD, C. BOISSARD, Centre des Faibles Radioactivités, Avenue de la Terrasse, 91198 Gif-sur-Yvette, France, E. J.P. LACAUX, Laboratoire d'Aérologie, C. R. A., 65300 Lannemezan, France.

Sulfur dioxide (SO_2) and carbonyl sulfide (OCS) are the predominant precursors of sulfate aerosol respectively in the troposphere and the stratosphere during volcanic quiescent periods. These compounds could therefore have a negative radiative effect on global and/or regional climate.

In order to study fluxes and factors controlling the emission of sulfur gases from the African Savannah burning, both laboratory and field experiments have been conducted. The laboratory experiment has been performed in a combustion chamber (Laboratoire d'Aérologie, Lannemezan). The field experiments occurred during the dry season in African Savannah (January 1989 and January 1991).

During these experiments, OCS, SO_2 , CO_2 , CO, CH_4 and C_2H_2 have been simultaneously monitored. SO_2 and OCS ranged from 0.2 and 0.5 ppb out of the fires to 100 and 80 ppb in the plume, respectively. Simultaneously, CH_4 and CO_2 reach values as high as 59 and 5000 ppm in the fires, respectively. Fluxes of sulfur compounds and their relations with tracers of combustion processes (CO, CO_2 , C_2H_2) will be discussed.

PB-9/10-4 CATABOLISM OF DIMETHYLSULFIDE AND METHANETHIOL BY METHYLOTROPHIC METHANOGENS. S. NI AND D. R. BOONE, Oregon Graduate

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We demonstrated the ability of several methylotrophic methanogens to degrade dimethylsulfide and methanethiol to hydrogen sulfide, methane, and carbon dioxide. *Methanobolus siciliac* HI350, a methylotrophic methanogen isolated from an oil well, was grown routinely on trimethylamine. When this culture was inoculated into medium with 5 mM dimethylsulfide it began producing methane and hydrogen sulfide after a lag of about 3 weeks. Methane production was slow, with an apparent microbial growth rate of 0.00334 h^{-1} (about 3% as fast as growth on trimethylamine or methanol). When such a culture of *M. siciliac* HI350 growing on dimethylsulfide was subcultured several times in this medium, the lag time decreased and growth rate increased (ultimately to $0.0354 \pm 0.002 \text{ h}^{-1}$). Dimethylsulfide-grown cultures also had no lag when transferred to media with methanethiol. Stoichiometric quantities of methane and hydrogen sulfide were formed from either dimethylsulfide or methanethiol. Most surprisingly, this strain could be adapted to grow with high concentrations of dimethylsulfide or methanethiol, as high as 30 mM. Other methanogens which have been reported to catabolize dimethylsulfide are *Methanohalophilus zhilinae* (strain WeN5), *Methanohalophilus oregonensis* (strain WALI), and strain GS-16. In addition to these and *Methanobolus siciliac* HI350, we found that the type strain of *M. siciliac* (strain T4/M) also could catabolize dimethylsulfide. The *M. siciliac* strains and strain GS-16 were able to use methanethiol as their catabolic substrate (other strains were not tested). We tested other methylotrophic methanogens for their ability to use dimethylsulfide by inoculating trimethylamine-grown cultures into medium with 10 mM dimethylsulfide, as well as into three control media with the following catabolic substrates: (1) none; (2) 5 mM trimethylamine; and (3) 5 mM trimethylamine plus 10 mM dimethylsulfide. The cultures unable to catabolize dimethylsulfide produced methane only from control media containing trimethylamine; the presence of dimethylsulfide resulted in neither excess methane formation nor decreased methane from trimethylamine (trimethylamine catabolism was not blocked by the presence of dimethylsulfide). Cultures unable to catabolize dimethylsulfide included *Methanococcoides methylutens* (strain TMA-10), *Methanobolus tindarius* (strain Tindari 3), *Methanobolus vulcani* (strain PL-12/M), *Methanohalophilus mahii* (strain SIB), "*Methanococcus halophilus*" (strain Z-7982), *Methanosarcina mazei* (strain LYC), and *Methanosarcina frisia* (strain C 16).

PA-4/5-11 THE EFFECT OF PEAT SUBSTRATE AND DEPTH ON METHANE AND CARBON DIOXIDE CONCENTRATIONS IN SWEDISH MIRES. M. NILSSON and E. BOHLIN, Dept. of Forest Site Research, Swedish University of Agricultural Sciences, S-901 83 Umea, Sweden.

Concentrations of methane and carbon dioxide in interstitial peat water were measured. Profiles from both bogs and fens with different peat composition were sampled. To cover even more of the variation in peat composition, a further 24 different peat types were collected from twelve mires.

Methane concentrations ranged between 0.05-1.2 mM and carbon dioxide between 1.0-6.5 mM. The profiles with pure sedge peat contained significantly less of both gases compared to the profiles composed of high degree of sphagnum and wood remains. In most mire profiles the gas content either remained constant from one or two meters depth or decreased down to the bottom.

The relation between gas concentrations and botanical, chemical and physical variables were analysed with Partial Least Square

Regression (PLS). Totally 67% of the variation ($r^2=0.67$) for CO_2 was explained. Carbohydrates and Sphagnum masses were highly positively correlated to CO_2 concentrations, while different decomposition related variables were negatively correlated. No correlation occurred between depth and carbon dioxide. The variance in methane values was explained to 75% ($r^2=0.75$), depth, nickel and sulphur were the single most important variables positively correlated. The decrease in gas content close to the bottom indicates either oxidation, as methane is concerned, or transportation to the underlying ground water.

For carbon dioxide a close relation to the substrate also is obvious from the data analysis, while most of the variation in methane concentrations probably can be predicted just by depth.

PA-1-4 SODOM, GOMORRAH AND THE LOST CITY OF THE PLAIN - A CLIMATIC PERSPECTIVE. A. NISSENBAUM. Weizmann Institute of Science, Rehovot 76100, ISRAEL.

Several aspects of the Biblical story of Sodom and Gomorrah have become in recent years almost axiomatic, among them: the placing of those cities in the southern basin of the Dead Sea, the assumptions that those cities are now covered by the Dead Sea and that their destruction was due to geological causes such as an earthquake or volcanic activity. Textual analysis of the Book of Genesis, coupled with descriptions of the area by ancient pilgrims and travellers, enables a case to be made for the placement of those cities in the area north of the Dead Sea. Indeed, for 1500 years, from the 3rd century to the 16th century A.D. it was traditional to place those cities somewhere in the area near Jericho. The Bible, in its description of the Cities of the Plain prior to their catastrophic destruction and the transformation of the area into a wasteland, emphasizes the region's agricultural richness. Thus, if we strip the Biblical story of its moral and ethical overtones, the scenario is that of rapid climatic change which converted a densely inhabited and richly watered area into an infertile saline playa. The region northeast and southeast of Jericho, north of the Dead Sea, is today quite barren as a result of upward movement of saline groundwater, however, it holds some of the earliest known agricultural settlements dated to the Pre-ceramic Neolithic Period, about 9000 years B.C. Similar argument can be made even if the Cities of the Plain are placed in the traditional location near the southern basin of the Dead Sea. It is known that the well developed Early Bronze settlement in Bab-e-Draa, close to the area separating the northern and southern basins of the Dead Sea, was ruined prior to the Middle Bronze Period. Timing of the Sodom event to approximately the 23rd-21st centuries B.C. places it in one of the most tumultuous periods in the history of the Middle East. During this period, between the Early and Middle Bronze Ages, the Ancient Kingdom of Egypt and the Kingdom of Accad in Mesopotamia were destroyed, and the Fertile Crescent was invaded by the Amoritic nomads, of Semitic origin, bursting out of the deserts of Arabia. In Palestine, this period is characterized by the collapse of the budding urban society of the Early Bronze Age and its replacement by the semi-nomad society of the intermediate Bronze Age. If indeed, those momentous events were caused by climate change, then this also explains the roots of the story of Sodom and Gomorrah. Although the scientific data for climate change during this period is not very extensive, a desiccation event is indicated by palynological evidence pointing to the decimation of forests in northern Israel, the deposition at salt layers in the Dead Sea, the diminution in width of karstic salt caves in Mt. Sodom, the abandonment of almost all settlements in the Negev Desert of southern Israel, an increase in the 0-18 content of mollusc shells from the Mediterranean coastal plain and further away, the drastic lowering of the water level of Lake Moeris in Lower Egypt.

This scenario does not exclude a large earthquake which might have occurred during this period, delivering a coup de grace to an already collapsing society, and which became through the veils of time and legend, the sole agent of destruction,

PA-4/5-12 METHANE IN FLOODED SOIL WATER AND THE EMISSION THROUGH RICE PLANTS TO THE ATMOSPHERE. J. NOUCHI¹, S. MARIKO², Y. HARAZONO¹ AND N. OWA¹. ¹ National Institute of Agro-Environmental Sciences, Tsukuba, Ibaraki 305, Japan and ² National Institute for Environmental Studies, Tsukuba, Ibaraki 305, Japan.

Methane formation in flooded soil and emission from rice plants were examined by pot culture (soil and hydroponic cultures) experiments. Methane emission rates from rice plants grown in soil or hydroponic cultures were measured by using chamber methods. Soil water was collected through a long Teflon tube (1 mm in internal diameter) connected to a highly permeable sintered polyethylene filter cup (8 mm in diameter, 100 mm in length) buried horizontally at a depth of 5 cm in the pot soil. Soil water was exuded with siphonage, and was collected with a microsyringe. Methane concentration in the surface water above the soil was extremely low as compared to that in the soil water. In the high temperature (31 °C) treatments, methane concentration in vegetated soil was about one-third of that in unvegetated pots; methane emission rate was 20 times higher in vegetated than in unvegetated pots. These results indicate that rice plants have a large capacity to transport methane from rhizosphere to the atmosphere. There was a linear, positive relationship between methane emission rate from rice plants and methane concentration in the culture solution with a high methane concentration. These results indicate that rice plants have a large capacity for methane transport, and that rice plants play a primary role in terms of methane flux from paddy fields.

O-9-9 EMISSIONS OF AMMONIA, NITROUS OXIDE AND METHANE FROM CATTLE SLURRY. O. OENEMA, G.L. VELTHOF AND D.W. BUSSINK. Netherlands Fertilizer Institute NMI, P.O. Box 30003, 9750 RA Haren, The Netherlands.

In the Netherlands, emissions of ammonia (NH_3) from animal husbandry contribute as much as 90 % to the total NH_3 emission of about 230 Tg yr^{-1} . One of the various measures to reduce NH_3 emissions is the acidification of animal slurries with nitric acid (HNO_3) to about pH 4.5. Addition of HNO_3 decreases NH_3 emissions from slurries during storage and surface application effectively due to the shift in the equilibrium of $\text{NH}_3:\text{NH}_4^+$. It also increases the fertilizer value of the slurries. However, under anoxic conditions the added NO_3^- may be rapidly denitrified to N_2 and N_2O . Denitrification also increases the pH of the slurry and then NH_3 may still escape.

Batch experiments were conducted so as to examine the relationships between pH, Eh, denitrifying activity in, and fluxes of N_2O and CH_4 from non-acidified and acidified cattle slurry during storage for up to 5 months. The cattle slurry was acidified with HNO_3 to pH levels of 6, 5, 4.5, 4, 3.5 and 3, respectively. In addition, fluxes of NH_3 and N_2O from acidified and non-acidified slurries applied to grassland were measured for 7 days. The micro meteorological mass balance method was used for the determination of NH_3 emissions. Transparent covers were used for the accumulation and subsequent determination of N_2O and CH_4 emissions from surface applied cattle slurries.

There was an inverse relationship between pH and Eh. Acidification of the cattle slurry, with a native pH of about 8.4, to pH 3 increased Eh from about -400 to 200 mV. Denitrifying activity strongly decreased as pH was decreased and Eh increased. Emissions of N_2O were as high as 270 mmol kg⁻¹ day⁻¹ at pH 6.0 and about 1 mmol kg⁻¹ day⁻¹ at pH 5.0 or less. Emissions of CH_4 ranged from about 500 mmol kg⁻¹ day⁻¹ from non-acidified slurry to less than 1 mmol kg⁻¹ day⁻¹ from acidified slurries. Apparently, little methanogenesis occurred in acidified slurries.

Emissions of NH_3 were more than 10 times less from acidified than from non-acidified slurry, after surface application to grassland. Emissions of N_2O from acidified cattle slurry were about twice as high as those from non-acidified slurry, after surface application to grassland. N_2O emissions from 10 Mg acidified slurry ha⁻¹ ranged from 0.1 to 2.0 Mol ha⁻¹ day⁻¹. Emissions of CH_4 from the surface applied cattle slurries were negligible.

PB-6-12 REDUCTIVE BIOGEOCHEMISTRY OF THREE ALKALINE, SALINE LAKES. R.S. OREMLAND, L.G. MILLER, and C.W. CULBERTSON (USGS, Menlo Park, CA, USA).

Sulfate reduction rates and methane production rates were determined using radiotracer techniques in the sediments and anoxic water columns of three lakes: Big Soda Lake, Nevada; Mono Lake, California; and Soap Lake, Washington. These lakes are chemically similar ($Na-CO_3-Cl-SO_4$ type) but represent different stages of brine evolution. Bottom water (BW) salinities ranged from 90 g/L in Big Soda and Mono Lakes to 150 g/L in Soap Lake. Bottom water dissolved sulfate concentrations were 69 mM (BSL), 128 mM (ML), and 265 mM (SL). Dissolved sulfide and methane were present in the bottom water of all lakes during periods of stratification, but the concentration of these reduced compounds was not related to the duration of stratification. A small amount of dissolved methane ($\leq 1 \mu M$) was present in the surface water of all lakes and contributed to a diffusive flux to the atmosphere. Pelagic and littoral sediments contained varying amounts of dissolved sulfide and methane, with steep concentration gradients across the sediment-water interface in the littoral zones of all three lakes and in the pelagic zone of Mono Lake. Methane concentrations in the pelagic sediments ranged from 78 to 130 $\mu mole/kg$ in Big Soda Lake (BW = 60 μM), to 1200 $\mu mole/kg$ in Soap Lake (BW = 1200 μM) and 3500 $\mu mole/kg$ in Mono Lake (BW = 8 μM). Dissolved sulfide concentrations in the pelagic sediments ranged from 10 mM in Big Soda Lake and Mono Lake (BW = 8 and 0 mM, respectively) to 130 mM in Soap Lake (BW = 128 mM). In Big Soda and Mono Lake sulfate reduction and methane production rates were significantly lower in the pelagic sediments than in the littoral sediments (by factors of 2 and 10 respectively). Pelagic sulfate reduction rates were highest in Soap Lake, while methane production rates were highest in Mono Lake.

PA-7-8 PHYSICO-CHEMICAL MECHANISMS OF SOIL BUFFER ABILITY TOWARDS HEAVY METAL POLLUTION. T.Y. PAMPURA AND D.L. PINSKY. Institute of Soil Science, and Photosynthesis, USSR Academy of Sciences, Pushchino 142292, USSR.

The mobility of heavy metals (HM) in soils, their toxicity, and ability to be involved in biogeochemical cycles are mainly determined by the soils ability to bind these elements into immobile forms nonavailable for living organisms. This soil property can be considered as a buffer ability towards HM pollution. An attempt has

been made to study physico-chemical mechanisms of soil buffer ability. The experiments were carried out on the Chernosem of the Kursk region, USSR. The absorption of Ca, Zn and Cu from solutions with a constant ion strength 0.01 M/l, and the Cu:Zn concentration ratio 1:2 (M/l:M/l) was studied. The ratios (Cu+Zn) : (Cu+Zn+Ca) were: 0.08, 0.18, 0.28, 0.55, 0.85, 1.0 (M/l:M/l). Concentration of HM in soil samples, resulted from adsorption experiments ranged from 20 to 700 mg/kg of soil for Cu and from 60 to 1200 mg/kg for Zn. For all samples sequential chemical extraction procedure (Tessier, et al., 1979) was used for the partitioning of Cu and Zn into five fractions: exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter, and residual. HM concentrations were determined by flame atomic absorption spectrophotometry using the standard addition technique. The adsorption isotherms of Zn and Cu differ considerably, demonstrating in both cases the presence of heterogeneous binding sites. The coefficients of Zn distribution between soil and solution decrease gradually, whereas those of Cu increase while total concentration of elements in soil grows. At low Zn content in soil, its greater part is bound with Fe and Mn hydroxides (50%) and with residual fraction (30%). With the increasing of amount of Zn adsorbed, it accumulates due to its exchangeable form. At high Zn concentration this form contains more than 50% of cations. A percentage of Zn bound to Fe and Mn oxides decreases to 30%, whereas an absolute content of the element in the residual fraction is changed insignificantly. The largest percentage of Cu at the low total concentration of the element is in the residual form (60 - 90%). During accumulation of Cu in soil this form is saturated first, and the further enrichment of soil with Cu is determined by organic bound and then bound to Fe-Mn oxide fractions. The results obtained correspond to the properties of the elements considered, to their ability of complex formation and adsorption. In particular, Cu cations form complexes and associations under native conditions more readily than Zn. Thus, the rate of different soil components and physico-chemical mechanism responsible for the soil buffer ability is changed with the increasing of heavy metals pollution.

PA-4/5-13 METHANE PRODUCTION AND UPTAKE IN SOME TERRESTRIAL ECOSYSTEMS OF THE U.S.S.R. N.S. PANIKOV. Institute of Microbiology, USSR Academy of Sciences, USSR, 117811 Moscow.

The present investigation was devoted to the quantitative studies of methane production, emission and uptake in different terrestrial ecosystems of the European plain of the U.S.S.R. [hypersaline marshes of the Crimea, the arable soils of the Moscow region, the wetlands and dry forests soils of the Tver (Kalinin) and Syktyvkar regions, and tundra soils of the Polar Ural]. Three main approaches have been used: i) the dynamic studies of CH_4 -exchange rates between the soil and atmosphere by chamber and gradient methods, ii) the determination of the profile CH_4 distribution in the soil air, and iii) the estimation of CH_4 production and uptake in soil cores inside of the glass bottles which were incubated *in situ* under aerobic as well as anaerobic conditions. The highest rates of both CH_4 production and utilization have been observed in the acid ombrotrophic mires of the boreal forests. The wetlands were shown to be not only sources, but also the sinks for CH_4 . The methane cycle in most studied soils was found to be a closed one: the processes of methanogenesis in the lower horizons were completely balanced by methane oxidation in the upper horizons. The only exceptions were hypersaline marshes and the waterlogged depressions of the ombrotrophic mires where the activity of methanotrophs was absent or poorly expressed. In this case significant CH_4 emission from soils to the atmosphere (up to 50 - 120

mg CH₄ Ch⁻¹ m⁻²) was observed. Kinetic approach has been used for biomass estimation of both methanogenic and ethanotrophic bacteria. The close relationship was found between the activity and biomass of this bacteria in all studied ecosystems.

O-4-6 EMISSION OF N-OXIDES FROM ACID IRRIGATED AND LIMED SOILS OF A CONIFEROUS FOREST IN BAVARIA. H.PAPEN, B.HELLMANN, H.PAPKE, AND H.RENNENBERG. Fraunhofer-Institute for Atmospheric Environmental Research, Department of Soil Microbiology, D-8100 Garmisch-Partenkirchen, F.R.G.

The emission rates of N₂O and NO from acid irrigated, acid irrigated plus limed, limed, and untreated control soils of an 80 years old spruce stand ("Höglwald") in Southern Bavaria were measured in 1990 during field campaigns in spring, summer, autumn, and winter. N₂O-emissions were measured by the closed chamber method (GC with ⁶³Ni-ECD), and NO-fluxes were measured using dynamic chamber techniques (NO_x-analyzer). The fully automatic measuring system consisted of 4 static and 4 dynamic chambers per plot.

The limed and the acid irrigated plus limed plots showed about 50% lower N₂O emissions compared to the control and the acid irrigated plot. Similar results were obtained for emission of NO. The reduction in N-oxide emissions on limed plots may reflect the enhanced soil pH caused by liming, thereby allowing part of the denitrification population to further reduce N₂O to N₂. Independent from the treatments of the soils significant diurnal variations in N₂O and NO emissions could not be observed. This may be explained by the lack of significant diurnal variation of the temperature in the upper layer of the soil (1-5 cm). Even at highest solar radiation the closed forest could not be passed by light energy sufficient to increase soil temperature. On the other hand, seasonal changes in N-trace gas emissions were observed. Highest N₂O emission rates were measured at the end of winter (late February, early March), when the snow had just melted and the frozen top soil began to thaw, but dormancy of the stand was lasting. From late spring to summer and late autumn the emission rates gradually decreased. The high N₂O-emission rates in February/March may be interpreted as (1) release of gas entrapped during winter in the frozen soil with the onset of thawing, (2) the beginning of microbial activity like N-mineralization and nitrification producing nitrate; nitrate produced during this time of the year would be available as electron acceptor to denitrifiers in higher concentrations, since the main sink for nitrate, i.e. the spruce-trees was in the status of dormancy. From inhibitor studies with intact soil cores it is concluded, that only 10% to 55% of the N₂O emitted could be accounted for by denitrification. Since chemolithotrophic nitrifiers were not present in the control and acid irrigated plots, hitherto unidentified microbiological processes different from denitrification/chemolithotrophic nitrification must be responsible for the N-oxide emissions observed from these plots.

PA-4/5-20 BIOMASS BURNING IN TROPICAL DEFORESTATION SITES: YEAR-TO-YEAR PRACTICES. M.C. PEREIRA, AND A.W. SETZER. Brazilian National Space Instituto (INPE), Sao Jose dos Campos, SP, Brazil.

Concern about biomass burning associated with recent deforestation or with common agricultural practices has become a critical issue in biogeochemistry. Estimates about the numbers and frequencies of fires have been obtained in areas of tropical deforestation in Brazil from orbital remote sensing (NOAA-AVHRR-BANK 3 thermal technique). However, very little is known about the

actual practices of fire use, e.g., the number of years the same area is burned until all the wood is consumed, or how often pasture-converted forest is burned.

This paper describes preliminary results of a temporal analysis of fire and deforestation regimes based on analysis of information taken from high resolution Landsat images digitized in a Geographical Information System (GIS) for about 15,000km² in the region of Alta Floresta, MT, Brazil (56°W & 10°S), located in the tropical Amazon forest.

The images analyzed were those of 1978 (Landsat-MSS), and of 1984, 1987, 1988 and 1989 (Landsat-TM), on the scale of 1:250,000, and covered the period when development in the region began and also when intense deforestation with biomass burning took place.

Preliminary conclusions show that 1) biomass burning is not frequent before August, in agreement with the occurrence of rains in the region; 2) more than 50% of the deforested area is burned every year; 3) deforestation rates were not constant, and had a peak in 1987-88.

On-going work should also include results of the TM images of 1985 and 1986, and the GIS will provide estimates of re-occurrence of fires in the same areas. Fire detection and vegetation index products from NOAA-AVHRR in the same area will also be matched in the GIS to provide calibration for the use AVHRR in real time biomass monitoring and emission inventories. The information from this work should add a significant contribution to the already operational Brazilian systems of AVHRR detection of fires, and of fire density in grid units.

PA-7-9 A BIOGEOCHEMICAL STUDY OF EGGS OF BACKYARD HEN FROM PANCAMPETA BARYTE MINING AREA, ANDHRA PRADESH, INDIA. E.A.Y. PRASAD AND D.N. PRASAD; Department of Geology; Sri Venkateswara University; Tirupati-517 502, (A.P.), India.

A biogeochemical investigation of the eggs of the backyard hen from the Mangampeta baryte mining area (M) (Lat: 14°00'30" - 14°01'30" N; Long: 79°19'00" - 79°19'30" E) was undertaken to study the effect of mineralization. For purpose of comparison, the eggs were also collected from a rural part of the Tirupati area (Lat: 13°38'00" N; Long: 79°24'00" E) representing a non-mineralized zone (NM). The samples of each area were divided into three parts, viz., whole egg (WH), shell (SH), and edible part (EP) of raw eggs (RE). Such a division of the samples was also made from boiled eggs (BE). All the samples were collected during the same period to eliminate seasonal variations. The samples were digested in aquaregia and analysed on ash weight (A) and dry weight (D) bases for 18 elements (Al, B, Ba, Be, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, and Zn) by atomic absorption spectrometry. From this data, the loss of elements due to volatilization and solubility or insolubility under the influence of organic matter were computed for various elements.

This biogeochemical study shows that the eggs of the backyard hen serve as an important tool: a) in geochemical and agricultural reconnaissance surveys; b) to throw light on the nutritional status of the area in general and of the eggs in particular relation to human health; c) in biological monitoring of the levels of environmental pollution; and d) in understanding the adaptational mechanism of the birds in maintaining the homeostatic equilibrium with respect to mineral nutrients.

PA-7-10 COCONUT TREE IN BIOGEOCHEMICAL EXPLORATION. E.A.Y. PRASAD AND D. N. PRASAD, Department of Geology, Sri Venkateswara University, Tirupati-517 502, (A.P.) India.

In order to study the biogeochemical significance of the coconut tree (*Cocos Nucifera*), which is commonly developed in and around the Mangampeta baryte mining area (Lat: 14°00'30" - 14°01'30" N; Long: 79°19'00" - 79°19'30" E) in Cuddapah district, Andhra Pradesh, southern India, composite samples of its different parts consisting of 1) roots, 2) bark, 3) midrib of the leaf, 4) leaflets, and different parts of the fruit, viz... 5) fibrous part (pericarp and mesocarp), 6) shell (endocarp), 7) kernel (endosperm), and 8) coconut water, were collected. For purpose of comparison, the samples were also collected from the trees occurring in a rural part of Tirupati area (Lat: 13°38'00" N; Long: 70°24'00" E) representing a non-mineralized zone. All the samples were collected during the same period to eliminate seasonal variations.

These samples, ashed at 450°C, were digested in aquaregia and analysed for eighteen elements (Al, B, Ba, Be, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, and Zn) by atomic absorption spectrometry.

From the data the following observations are made:

1. In the mineralized zone, when compared to the non-mineralized area, all components of the tree; a) show a consistently higher concentration of Ba with a maximum of 19,000 ppm recorded in leaflets; b) show Ba concentration consistently higher than Sr.
2. Coconut water in the mining area shows 500 ppm of Ba but Cr is not detected; in contrast to this, in the coconut water of non-mineralized area Ba is not detected while Cr concentration is 8 ppm.
3. In both the areas, the distribution of Sr and Al is Acropetal with a general decrease in their concentration from root to fruit; and in the non-mineralized area there is a progressive decrease in the concentration of Ba, Sr, and B in the four parts of the fruit from fibre to water.
4. In both the areas, due to exclusion mechanism, Mo is confined to the root, but not detected in any part of the shoot; and Al is not detected in the coconut waters.
5. In the mineralized area, the concentration of base metals, viz... Pb, Zn, and Cu is lower in the root than in any part of the shoot.

This study reveals the significance of coconut tree as an important tool in biogeochemical orientation surveys and of coconut water in balneology.

O-7-10 A BIOGEOCHEMICAL STUDY OF QINGHAI LAKE SEDIMENTS. E. PU AND L. JINGGUI. Lanzhou Branch Academia Sinica, 234, Tianshui Road Lanzhou, 730000, People's Republic of China.

Qinghai Lake in Qinghai province is the biggest inland plateau brackish lake in China. Because there is no industrial pollution in the lake, it is an ideal lake for studying the organic geochemical characteristics of recent sediments and organisms in the lake. Analyses and comparisons were made between the recent sediments in six cores and some organisms (aquatic plants and animals) in Qinghai Lake. The biological samples and 100 mesh core samples were extracted with chloroform for 72hrs. The extracts were

fractionated on an Al_2O_3/SiO_2 column after precipitation of asphaltene with n-hexane. Three fractions were collected during the chromatographic separation: saturated hydrocarbons eluted with n-hexane, aromatic hydrocarbons eluted with benzene, and polar compounds eluted with ethanol. The polar compounds were further separated into fatty acids, fatty ketones, alcohols and esters. All the fractions were analysed by GC-MS using HP 5988 A capillary GC quadrupole MS- computer data system. In the sediments, a series of biomarkers were found. They are as follows: 1) bicyclic sesquiterpane, 2) diterpenoids, 3) extended tricyclic terpanes, 4) tetracyclic terpane, 5) pentacyclic triterpenoids (hopanes and hopenes), 6) steroids (C_{27} - C_{29} steranes and C_{27} - C_{29} sterenes). The fatty acids and other compounds (fatty ketones, fatty alcohols and sterols) were also found in the sediments and biological samples. From the above studied lipid distributions in the sediments and organisms, it is concluded that such compounds in the sediments are mainly from the organisms in the lake or the transformational products of lower state biogeochemical action of the organisms in the lake. Through relative content changes of the acidic, basic, neutral and total amino acid as well as the organic matter, the paleoclimate and water body environment over the past 10,000 years of Qinghai Lake were studied. It is indicated that the paleoclimate of Qinghai Lake has undergone five developmental stages, that is, dry-cold-->warm-damp-->dry-cold-->warm-damp-->dry-cold. The lake water medium has also undergone correspondingly five developmental stages, i.e., salinization-->desalinization-->salinization-->desalinization-->salinization.

PA-4/5-14 THE CHARACTERISTICS AND THE REGION DISTRIBUTION LAW OF THE SOIL ENVIRONMENTS BACKGROUND VALUE IN GANSU PROVINCE. W. S. PU, AND LIAN BING. Central Station of Environmental Monitoring in Gansu Province, China.

By investigating the soil environment background value (SEBV) in Gansu province, 230 soil samples from 76 sections in 15 statistics units in Gansu were collected. By using some advanced analyzing and measuring methods such as AAS, GFAA, HG-AFS, C-AAS, C-AFS, ICP-AES, XRF, INAA, 64 factors such as constants, trace elements, rare and scarce elements rare-earth elements, and radioelements were analyzed, and about 5500 data measurements were obtained. Based on the investigation, a series of procedures from location of samples, sampling, analyzing to data processing and mapping are made in high quality. So, the accuracy, the completeness and the comparisons were kept in high quality. Finally, the SEBVs of 64 elements and the maps of the SEBVs of 12 elements are obtained, the data and the sample libraries of the SEBVs in Gansu province are set up. On the basis of above mentioned studies, the characteristics and the region distribution law of the SEBVs in Gansu province are listed as follows:

- 1) Basically, the SEBVs in Gansu province are within the regions of the SEBVs inside and outside the China. Among them, over 8% SEBVs are similar to the China's SEBVs. Orderly, the values of Hg, Se, Mo, Br, I, F, Sn, Te are lower than those in the national SEBVs; the value of Hg is only a quarter of the national SEBVs. The values of Ca, Al, Fe, Mg, and PH value are higher, and the value of Ca is four times as much as the value of national SEBV.
- 2) By studying the relationships of the SEBVs, it is believed that the content of the SEBV is closed related with the mechanical assemblage of the SEBVs, and it increases with the amount of the organic matter. The relation of the SEBVs of the main elements is clearer.
- 3) By studying the vertical distribution in sections of the SEBVs, it is believed that the changes of the vertical

distribution in sections of the SEBVs of most of the elements are not clear. This means that the components of soils mainly result from the weathering of the original materials.

4). By studying the main SEBVs, it is believed that the clear tendency is that the SEBVs of black-brown soil, chemozem, loessial-soil are higher, and the SEBVs of gray-brown desersoil, brown desersoil are lower, the others are intermediate.

5). By studying the SEBVs of some main original materials of clays, it is believed that the SEBVs are inclined to increase in order of slope wash-- residual deposit, original material of loess and diluvial--alluvial deposits. The variation tendency of these pedogenic materials basically coincides with that of soils developing from those pedogenic materials, and this suggests the SEBVs depend on the pedogenic materials as well.

6). By studying the horizontal distribution of the SEBVs, it is believed that the general tendency of the region distribution of the SEBVs in Gansu province is: Firstly, the values in the southeastern part are bigger than those in the northwestern part; Secondly, the values in southern part are bigger than those in northern part.

PB-6-13 ENVIRONMENTAL BIOGEOCHEMICAL STUDIES IN THE CAUVERY RIVER BASIN, TROPICAL RIVER OF PENINSULAR INDIA. A.

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Cauvery river basin has a wide range of geology and diverse environmental conditions with intensive population all along its course offers an ideal opportunity for biogeochemical studies. Samples of water, bed, suspended and core were collected during the period 1985 to 1989. The major dissolved ions, chemical analysis, isotopic analysis and inorganic fractionation of heavy metals, in the sediments were done following the standard procedures [Ramanathan et. al., 1990, Tan & Strain (1983) and Vaithyanathan et. al., 1990]. Dissolved silica, sulfate, calcium and phosphate show considerable increase towards the downstream region indicating organic matter supply from the agricultural activities and the mixing of sea with riverwater. Further, the increase of organic carbon, TSM, and Mean size (in sediments) were also observed. Size fractionation of bulk sediments also indicate the dominance of clays downstream. Clay minerals are sensitive to environments and any change in the environment is reflected in their types. In the upstream region considerable amount of illite is present, followed by kaolinite in estuarine regions indicating the variation and changes in the environmental conditions. Stable carbon isotopes ($\delta^{13}\text{C}$) has been used to study the sources and transport of carbon and the degree of mixing in the estuarine regions. Study of inorganic fractionation of heavy metals also indicate the degree of pollution in the entire river basin. Rate of sedimentation in the core samples were done using Ra ²²⁶ and Pb ²¹⁰ isotopes. Accumulation of sediments along with its heavy metals and nutrients increases downstream. Calcium shows an increasing trend towards the depth whereas the phosphorous and heavy metals shows decreasing trend. Rate of accumulation of nutrient and heavy metals, diagenetic changes, paleoenvironment and degree of paleoenvironment pollution were also discussed in detail.

O-1-4 ICE CORE RECORDS AS A KEY TO UNDERSTANDING THE HISTORY OF ATMOSPHERIC TRACE GASES. D. RAYNAUD, Laboratoire

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Ice cores have been revealed as a powerful indicator of global environmental conditions of the pre-industrial time and the glacial-interglacial cycle (the last 150,000 years). Of special interest is the most direct evidence of past changes in radiatively active trace gases found in the ice record. We present here a review of the results concerning three of the main radiatively active gases: CO_2 , CH_4 and N_2O .

The record indicates that the three gases had significantly lower concentrations during the pre-industrial time and that we cannot disregard possible global fluctuations of the pre-industrial background over the last millennium. The large increase (by up to a factor two in the case of CH_4) between pre-industrial time and today is largely attributed to anthropogenic activities.

The glacial-interglacial cycle has been documented for CO_2 and CH_4 . Their variations are generally well correlated with global climatic changes showing strongly depleted concentrations (by up to about a factor two in the case of CH_4) during the full glacial conditions relative to interglacial periods. The gas records obtained from ice cores can be interpreted, at least qualitatively, in terms of flux changes between ocean, continental biosphere and atmosphere and, in the case of CH_4 , of changes in tropospheric destruction rate. These changes are assumed to be induced by direct or indirect climatic forcings. In turn the changes in CO_2 and CH_4 are participating on the paleoclimatic variability and information can be obtained from the record on the climate sensitivity of greenhouse gases.

PB-12-3 AN ESTIMATE OF GROSS GLOBAL METHANE PRODUCTION. W.S.

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Microbially-mediated aerobic and anaerobic CH_4 oxidation intercept CH_4 before it reaches the atmosphere. Both processes have been shown to modulate or limit CH_4 fluxes to the atmosphere. We adjusted the Cicerone and Oremland (1988) net global atmospheric methane budget with measurements and estimates of methane oxidation rates to estimate gross global methane production. We conclude that gross methane production is several-fold the amount entering the atmosphere annually. Systems where microbially-mediated methane oxidation might reduce atmospheric methane increases are considered. The ocean cycles methane very efficiently, but it does so on internally-produced methane and is probably incapable of consuming atmospheric methane. Soils and agricultural systems are poorly understood presently, but appear capable of intercepting internally-produced CH_4 and consuming atmospheric CH_4 .

PB-12-4 AN EXAMINATION OF THE ROLE OF ALASKA'S YUKON-KUSKOKWIM DELTA REGION IN THE GLOBAL BUDGETS OF METHANE, OZONE, AND CARBON MONOXIDE. LA. RITTER, C.E. WATSON, J.D.W. BARRICK, M.C. SHIPHAM, B.E. ANDERSON, AND M.A. WOERNER. Atmospheric Sciences Division, NASA-Langley Research Center, Hampton, Virginia, USA. G.W. SACHSE, AND J.E. COLLINS, JR. Flight

Electronics Division NASA-Langley Research Center, Hampton, Virginia, USA.

During the summer of 1988, NASA conducted an extensive field program in the Yukon-Kuskokwim Delta (YKD) region of Alaska. The program, entitled the Arctic Boundary Layer Expedition (ABLE-3A), is a component of the NASA Global Tropospheric Experiment (GTE) and is sponsored by the NASA Tropospheric Chemistry Program. During the study, both ground-level and airborne measurements were made to characterize the biosphere-atmosphere interactions of important trace species. In this study, airborne eddy correlation flux measurements were made for ozone, carbon monoxide, and methane. The spatial variation of the ground-level source and sink distribution for these species was determined over the YKD, and is juxtaposed on Multispectral Scanner imagery. In qualitative terms, the source and sink distributions thus determined correspond to changing land type. From this study, we found an average for the methane source strength over the YKD to be 66 mg/sq-m/day. If we assume that the distribution of tundra types over the YKD is representative of other tundra regions in the Arctic, we estimate a contribution of 42 Tg/a to the global methane budget stemming from northern wetlands. We also find that one-half of the loss of ozone in the Arctic, due to surface deposition, is attributable to tundra land types. Although we found a striking variation in the source/sink distribution for carbon monoxide over the YKD (deposition of carbon monoxide near the coast and emission inland), the total contribution to the global budget from this region is minimal for this species. The exchange rate between the boundary layer and the free atmosphere is also examined in terms of boundary layer growth and its subsequent collapse, as well as in regard to the venting of the boundary layer by convective cloud activity.

PB-11-5 METHANE IN PERMAFROST ROCKS AND ITS ECOLOGICAL IMPORTANCE. E.M. RIVKINA, V.A. SAMARKIN. Institute of Soil Science and Photosynthesis, USSR Academy of Sciences, Pushchino, Moscow Region, USSR, 142292.

Methane was determined in the permafrost rock samples obtained by drilling of Pleistocene sediments in the middle course of the river Bolshaya Chukochya on the territory of Kolyma-Indigirka lowland. Methane was sampled from these sediments each 1-2 m. The frozen samples were degassed at thawing in hermetically sealed vessels by the "headspace" technique. A gas chromatograph with a flame-ionization detector was used for methane determination. Two permafrost rock suits, lying one under the other, have been studied. The upper (edomic) suit (Q_{III}) consist of alewives with polygonal-vein ice. The deposits were formed under extreme geocryological conditions when cryoarid tundra land-scapes prevailed. The origin of edomic suit deposits is still unclear. However, it is known that permafrost was formed simultaneously with the deposit formation. At the Holocene optimum, the upper several meters of sediments thawed and then were frozen again 5 - 7 thousand years ago. The lower (olerskaya) suit ($N_2^3 - Q_1$ la) is composed of alluvial-lake fine grain sand and alewives. Buried soils and peat intercalations can be met in the suit cross section. During the period of accumulation of the olerskaya suit deposits, the territory was covered with thin deciduous forest and presented widely developed grass landscapes. The permafrost is of polygenetic character. Probably during the period of sediment formation there were several climatic changes in the course of which the permafrost thicknesses were formed and degraded on territory studied.

The experiments carried out showed that in the edomic suit sediment methane is present in the upper 2.3 meters, more-over, its

content is decreased from 20.6 ml/dm³ at the boundary of the layer of seasonal thawing (0.7 - 0.8 m) to 0.9 ml/dm³ of the depth of 2.3 m. In the samples taken from the lower horizons of edomic suit no methane was found (less than 0.001 ml/dm³). In the deposits of the olerskaya suit, methane was observed from all the samples and its concentration varied from 3.2 to 63.7 ml/dm³. The majority of values were within the interval of 15 - 35 ml/dm³, this which very close to the methane content (10-30 ml/dm³) in holocene flood plain deposits and modern over-moistened tundra soils.

It has been shown that the olerskaya suit sediments outcropped in the river valleys together with the modern tundra landscapes are an additional source of atmospheric methane. Besides, possible warming of the climate can lead to thawing of the olerskaya suit rocks and releasing of methane contained in them. This will increase the flow of radiative gases, which has been already enhanced, from the earth surface into the atmosphere on this territory.

O-2-7 OXIDATION OF METHANE IN THE TROPOSPHERE: ASSESSMENT OF UNCERTAINTIES AND IMPACT ON CALCULATED GLOBAL BUDGETS. J.M. RODRIGUEZ, S.FAN, M. K. W. Ko and N. Dak Sze. Atmospheric and Environmental Research, Inc. Cambridge MA. USA

Oxidation by reaction with OH constitutes the main loss mechanism for methane in the troposphere. Global sources of methane must balance this loss and account for the observed increase of about 1%/year. These constraints have been incorporated in one- and multi-dimensional models to derive budgets for methane consistent with observations. Several developments can alter the conclusions of such budget studies. Preliminary measurements of the reaction of methane with OH indicate rates slower than previous values. Furthermore, since no direct measurements of tropospheric OH exist, the average global concentration of the hydroxyl radical is tuned to agree with the lifetime of CH_3CCl_3 derived from measurements by the ALE/GAGE network. This analysis, however, must account for the stratospheric loss and additional removal mechanisms due to hydrolysis of CH_3CCl_3 in the oceans. Inclusion of these loss processes could reduce the derived average tropospheric concentrations by 30-40%. The global rate of methane oxidation could thus be decreased by up to a factor of two if the above data and processes are included. A complete assessment of the impact of the above changes should also include the non-linear coupling between CH_4 , CO, OH, and NO_x . We present results of a two-dimensional simulation of the methane budget incorporating the new kinetic data, and allowing for removal of CH_3CCl_3 in the stratosphere and oceans. The model is constrained by existing observations of CH_4 , CO, O_3 and NO_x . Uncertainties in the tropospheric OH are further constrained by requiring that the net atmospheric lifetime for CH_3CCl_3 be in agreement with that derived from the ALE/GAGE data (6.3 years). The model-calculated budget will be used to discuss implications of the existing uncertainties in tropospheric methane oxidation to our present understanding the global sources of CH_4 .

O-12-4 BIOSPHERIC -CLIMATIC FEEDBACKS IN METHANE EMISSIONS FROM NORTHERN PEATLANDS. N.T. ROULET (Dept. of Geography, York University, 4700 Keele St., North York, Ontario M3J 1P3 Canada), T. R. MOORE, AND J. BUBIER (Dept. of Geography, McGill University, Montreal H3A 2K6 Canada)

It is estimated that northern peatlands emit between 30 and 80 Tg $\text{CH}_4 \text{ yr}^{-1}$ (Mathews and Fung 1987; Aselmann and Crutzen 1989), which represents 7 to 15% of the annual atmospheric burden. These estimates are based on very sparse data, extrapolated over 1,000 km^2 . There are only a few flux measurements from the northern boreal, subarctic and arctic region (area of wetlands is $2.3 \times 10^{12} \text{ m}^2$) to improve these estimates (e.g. Sebacher et al. 1986; Whalen and Reeburgh 1988; Moore, Roulet and Knowles 1990). In 1990 the first CH_4 flux measurements were made in the largest continuous peatland of North America, the Hudson Bay Lowland ($2.7 \times 10^{11} \text{ m}^2$). A wide variety of peatland types were sampled over a 100 km transect that represents 5,000 years of peatland evolution. The median flux for the thawed season was between 5 and 30 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, depending on peatland type, yielding an total annual emission of $\approx 1 \pm 1 \text{ Tg CH}_4 \text{ yr}^{-1}$. These results, combined with those from other studies, suggest that the present contribution of CH_4 to the atmosphere from northern peatlands is probably at the lower end of the 30 to 80 Tg yr^{-1} interval.

To estimate the possible impact of predicted climate change on CH_4 emissions from northern peatlands, the physical, chemical, and ecological factors that relate to the CH_4 flux need to be determined. GCMs predict in a $2 \times \text{CO}_2$ scenario, summer temperatures and precipitation will increase in the region of North America that contains most of the peatlands, by 3°C and 1 mm d^{-1} (Mitchell 1989). Several studies have estimated that CH_4 emissions from wetlands would increase with a warmer climate, but these models implicitly assume that the wetland moisture regime will remain unchanged (Hameed and Cess 1983; Lashof 1989). While many factors appear related to the flux, maintenance of high moisture contents is a necessary prerequisite for large CH_4 fluxes. For raised bogs and swamps there is a clear, though scattered, relationship between CH_4 flux and location of the water table (e.g. Sebacher et al. 1986; Moore and Knowles 1989), but for fens and flat bogs the relationship is less clear (e.g. Moore, Roulet, and Knowles 1990). There is a discontinuous relationship between flux and water table for peatlands of the Hudson Bay Lowland. Fluxes are consistently highest, or lowest, for a given peatland in areas where the water table is, respectively, at, or near the surface, and greater than 0.1 m below the surface. Only in peatlands where the water table periodically varied between +0.05 and -0.1 m was there a continuous relationship. For peatland that remained saturated, the CH_4 flux was related to

temperature. To compare the possible change in flux induced by changes in moisture and temperature we developed a simple, one dimensional, seasonal hydrological model to predict the change in location of the summer water table and 10 cm peat temperature between the present and a $2 \times \text{CO}_2$ climate for a typical northern peatland. The model predicts peat temperatures would increase between 0.8 and 2.0°C and the summer moisture deficit would increase by 80 to 160 mm, lowering the water table an additional 10 to 15 cm, depending on the properties of the peat. Based on regression models of CH_4 flux and peat temperature and water table, we found the temperature induced change ($\approx +10\%$) was overwhelmed by the water table induced change (-60 to -100%). In this model we assume the ecology and structure of the peatland does not change. While we put little confidence in the absolute magnitude of our predictions, we believe the trend demonstrates that the CH_4 emission from northern peatlands is very sensitive to changes in the moisture regime within the range of change expected based on the predictions of general climate models. To be able to better delineate the sensitivity of the CH_4 flux to the moisture and thermal regime experiments are being

conducted on several northern peatlands that are being drained for forestry and horticultural purposes.

PB-11-6 METHANE IN TUNDRA SOILS OF THE KOLYMA-INDIGIRKA LOWLAND AND ITS FLUX TO THE ATMOSPHERE. V. A. SAMARKIN, E. M. RIVKINA, M. S. VECHERSKAYA. Institute of Soil Science and Photosynthesis, 142292, Pushchino, Moscow Region, USSR.

The northern wetland soils are an important source of the atmospheric methane. The work described was aimed at studying the methane contents, processes of methane generation and oxidation in the tundra bog and half bog gley soils and at measuring its flux to the atmosphere. Observation sites were located on the valleys of the river Bolshaya Chukochya and Lake Akhvelo and were representative of most tundra wetland ecosystems. The depth of the summer thawing of soils was 45-50 cm. Soil cores were taken with a stainless steel sampler 7 cm in diameter. Immediately after sampling the cores were cut into 100 cm^3 specimens which were then placed into the sealed glass vessels and degassed in the saturated NaOH solution. The gas phase was analyzed on a gas chromatograph supplied with a flame ionization detector. Methane generation and oxidation rates were examined with ^{14}C -labelled carbonate, acetate, and methane. Methane fluxes were determined by measuring the changes in gas concentrations in the atmosphere enclosed within a thin stainless steel chamber 40x40x25 cm in size. Gas samples from chambers were taken at time intervals 15 or 30 min. Deployment times ranged from 30 min. to 2 hours. Temperature, moisture, pH and Eh of soils, atmospheric pressure, and wind speed were also determined.

Methane concentration in soils varied from 0.007 to 28 mg dm^{-3} . Methane contents in the thawed soil layer under 1 square meter of surface were calculated. It varied from 0.13 to 3.7 $\text{g CH}_4 \text{ m}^{-2}$ and was usually higher in the bog soils lacking a mineral horizon, than in the bog soils with gley mineral horizon in the bottom. Methane flux from the soils varied within a wide range of values (from 0 to 78.6 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) and did not depend directly on CH_4 contents in soils.

Methane flux can change two or three times at the same site during the day. It was generally higher from soils covered by *Carex* than by *Sphagnum*. The rise of temperature in the soils during the summer activated methane release to the atmosphere. In the winter (February), methane flux was not revealed. Radioisotopic experiments showed the presence of modern methane generation and methane oxidation processes in soils at temperature 4-7 $^\circ\text{C}$. Therefore, the tundra bog and half bog soils accumulate considerable quantities of methane due to methanogenic bacterial activity, and maintain the active flux of CH_4 to atmosphere during the summer period. It is supposed, that the role of arctic wetlands in the global methane cycle will increase due to climate warming, prolongation of season with positive temperatures and increase of the seasonal soil thawing depth.

O-5-4 SPATIAL AND TEMPORAL VARIATIONS OF NO EMISSIONS FROM VENEZUELAN SAVANNAH SOILS. E. SANHUEZA¹, C. JOHANSSON², A. RONDON², L. CARDENAS¹, and J. ROMERO¹. ¹I.V.I.C., Apartado 21827, Caracas 1020 A, Venezuela. ²Stockholm University, S-106 91 Stockholm, Sweden.

NO_x are key compounds in tropospheric chemistry, especially in the regulation of O_3 . Ozone is an important greenhouse gas that also participates in the control of the OH concentration, which in turn controls the levels of several other greenhouse gases (i.e. methane). The global sources of atmospheric NO_x are about equally distributed

The global sources of atmospheric NO_x are about equally distributed between anthropogenic ($26 - 28 \text{ Tg N yr}^{-1}$) and natural ($22-28 \text{ Tg N yr}^{-1}$). Rough estimates indicate that microbial processes in soil could contribute with $\sim 20 \text{ Tg N yr}^{-1}$; results show that the dominant emission is NO with little emission of NO_2 .

Biogenic emissions of NO from soils have been measured at various locations in the Venezuelan savannah climatic region: a woodland savannah (Chaguarama), a semideciduous forest (Guri), a scrub-grassland savannah (Guri), and a trachipogon savannah (Calaboza) and a "natural" pasture (Calaboza). Emissions were measured using the enclosed chamber technique; NO was detected continuously with chemiluminescence analyzers: liquid phase NO_2 / luminol in Guri and NO/O_3 gas phase in the other locations.

Very large differences ($\sim$ a factor of 100) in emissions are observed between locations; also important variations ($\sim$ a factor of 10) are recorded at different sites inside a same location, variations up to 5 times were measured between plots at a specific site. In part, these differences are related to the nitrate, ammonium and water content in the soils. It is worth mentioning that the largest emission of NO observed until now has been recorded in Chaguarama (280×10^9 molecules $\text{cm}^{-2} \text{ s}^{-1}$); however, 100 times lower emission were found at the Guri site.

Significant seasonal variations are observed, with lower emissions during the dry season (changes in soil humidity); diurnal cycles are also recorded, with larger emissions during daytime (changes in temperature). In the rainy season large day to day fluctuation occur, which mainly depend on the rain pattern of the region; after a rainfall, emission abruptly increases and then decreases as the soil dries out over the subsequent days. Sporadic rains during the dry season produce very large increases (up to a factor of 10) of the emissions; biomass burning leads to increased NO emissions both from dry and wet soils.

The large spatial, temporal and diurnal variability observed makes it very difficult to estimate the regional contribution of tropical savannah soils to the global atmospheric budget of NO_x . The tropical savannah region is experiencing a rapid change in land use, therefore, to assess how these changes affect the NO emissions from soils, research programs addressing the variability problem should be undertaken.

PB-6-14 CARBON DIOXIDE AND METHANE FLUXES FROM CORAL REEFS AND OTHER LITHIFIED MARINE CARBONATES. E.L. SANSONE, G. W. TRIBBLE, AND P. R. HABERSTROH. *Oceanography Department, University of Hawaii, 1000 Pope Road, Honolulu, Hawaii 96822, USA.*

Our research group has recently reported on the widespread existence of suboxic and anoxic conditions within a variety of coral reefs and other shallow-water lithified marine carbonates. These conditions result from the importation of organic matter by the advection of seawater through the frameworks, with subsequent retention and decomposition of these materials within the frameworks. This organic matter degradation is reflected by stoichiometrically consistent increases in endproducts such as ECO_2 , inorganic nutrients, total alkalinity, and CH_4 in the framework porewaters.

The elevated endproduct concentrations in the porewaters result in the transport of these chemical species to the overlying and adjacent seawater by the processes of advection, diffusion, and turbulent mixing. Porewater-to-seawater transport rates in Checker Reef, Oahu, Hawaii were determined by means of hydrological modeling of data from 1) residence time estimates from rain-induced salinity perturbations, 2) *in situ* pressure sensor and manometer arrays, and 3)

direct measurements of porewater transport out of the reef. These data yielded average fluxes of CO_2 and CH_4 to the overlying seawater of 70 and 0.03 moles $\text{m}^{-2} \text{ yr}^{-1}$, respectively. (Experiments are currently in progress to directly measure the composition of the porewater advecting out of the surface of the reef.) Assuming a global coral reef surface area of 600,000 km^2 , these flux rates can be extrapolated to global CO_2 and CH_4 fluxes of 1800 and 0.3 Tg yr^{-1} , respectively. For comparison, world oceanic uptake of atmospheric CO_2 is $\sim 2000 \text{ Tg yr}^{-1}$, and the global input of CH_4 to the atmosphere is $\sim 540 \text{ Tg yr}^{-1}$.

Gas fluxes from large scale ($> 100 \text{ km}^2$) shallow marine carbonate platforms are much more difficult to estimate because of the lack of data on the rate of exchange of porewater with the overlying seawater. However, the global areal extent of carbonate platforms ($\sim 800,000 \text{ km}^2$) is similar to that of reefs, and their internal porewater composition is also similar to that of reefs; it is thus likely that their global CH_4 and CO_2 fluxes are similar to those of reefs.

These results suggest that lithified marine carbonates may play a significant role in global CO_2 budgets, but are likely to be relatively unimportant in the global CH_4 cycle.

PA-4/5-15 INCREASING CO_2 FIXATION RATE OBSERVED IN *ARAUCARIA ANGUSTIFOLIA* FROM UNPOLLUTED AREAS IN BRAZIL: PRELIMINARY RESULTS. R.L. SANTELLI*, A.DE LUCA REBELLO AND K.WAGENER. *Institute of Chemistry, University Federal Fluminense, Rio de Janeiro, and Dept. of Chemistry, Pontifícia Universidade Católica, Rio de Janeiro, Brazil.

Araucaria are the principal ring-forming trees in the southern tropics and the subtropics of South America. We used them for an investigation about possible variations in the CO_2 fixation rate over the last 400 years.

For each tree, the average growth rate was determined from the measured ring series over the whole cross section by using the best fit of a two parameter function. In this way, a characteristic value for any selected ring, e.g. the 30th ring, can be found based on the information content of the whole tree. Comparing then the characteristic width of these rings from trees with ages ranging between 330 and 28 years shows (as preliminary results) that the growth rate was essentially constant until the middle of this century, but then increased significantly.

In an earlier investigation on European oak trees we found a steep increase in the growth rate for the beginning of this century. In that case the most probable explanation led to the unintended fertilization resulting from industrial NO_x emissions. This reason can be excluded for the sampling areas of our araucarias. There is no record of significant climatic changes. We therefore believe it may be the effect of the increased atmospheric CO_2 level.

PA-4/5-16 SOIL EXCHANGE OF TRACE GASES IN LABORATORY INCUBATIONS. D.A. SCHAEFFER, and C. T. DRISCOLL, Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244-1190.

Soil organic matter is the largest pool of C and N in many ecosystems, and may show substantial fluxes of radiatively important CO_2 , N_2O and CH_4 . Each of these fluxes is suspected to change markedly under conditions of N saturation, but N saturation cannot be readily identified from commonly-observed state variables such as forest

pools available to soil microbial populations do not appear to correspond well to total soil C and N, or even the various chemically extractable C and N fractions. In an attempt to overcome this, we propose the incubation of soil organic matter in the absence of plant root uptake under laboratory conditions. This would permit microbial mineralization and subsequent competition among heterotrophic microbes (but not plant roots) for potentially limiting nutrients. We hypothesize that in such incubations, gases and dissolved chemicals will be released in proportions indicative of the C and N "status" of the organic matter. As an illustration, consider two soil column incubations with differing actual N availability, both subjected to periodic water extractions. The "headspace gas" is sampled periodically for C- and N-containing gases, and the extraction water is chemically analyzed for inorganic ions and organic C and N. In an N-limited soil environment, CO₂ (as gas and as dissolved bicarbonate) would be released by heterotrophic respiration, but N would be relatively tightly conserved. In contrast, in an N-saturated soil environment we would expect both respiration of C and the net mineralization and release of N. The ratio of C to N released in both the gaseous and aqueous phases may prove to be a sensitive test of the chemical environment of the microbes, obtained by relatively non-invasive means. This type of incubation could be used to screen a wide variety of soils to determine their potential roles in the retention and release of radiatively important trace gases. Preliminary results from incubations of Adirondack, NY soils of differing N status will be presented. This approach can readily be extended to incubations under different temperature and moisture availability regimes. Those more complex experiments would further increase our understanding of the role of climatic changes on trace gas exchange.

PB-6-15 EXPERIMENTAL HYPERSALINE PONDS: CARBON ISOTOPE GRADIENTS IN THE BENTHIC MICROBIAL COMMUNITY. M. SCHIDLowski. Max-Planck-Institut für Chemie (Otto-Hahn-Institut), D-6500 Mainz, Germany.

The biogeochemical characteristics of a newly established microbial mat have been traced along the slope of an artificially stratified, eutrophicated hypersaline pond as a function of the principal environmental parameters, notably temperature, salinity, and light intensity. The sharp decline in both visual mat development and productivity-related parameters such as cell numbers and chlorophyll-a content at the combined thermo- and haloclines shows productivity in the habitat to be primarily temperature- and salinity-dependent. Recordings of $\delta^{13}\text{C}_{\text{org}}$ over the pond profile give testimony that the generation of isotopically heavy microbial biomass goes along with high concentrations of organic carbon in the benthic mat - as well as with high cell numbers and chlorophyll-a concentrations. As a consequence, ^{13}C -enriched organic matter is confined to the pond littoral (depth < 35 cm) characterized by high rates of primary productivity. The sizeable variations of $^{13}\text{C}_{\text{org}}$ along the pond slope appear to be smoothed out in the corresponding $\delta^{13}\text{C}_{\text{org}}$ function with the sympathetic relationship between the two parameters disclosed only at a considerable magnification of the δ -scale for the carbonate curve. As a whole, the $\delta^{13}\text{C}_{\text{org}}$ functions recorded over the depth profile identify high rates of primary productivity as the agent mainly responsible for the generation of isotopically heavy biomass, negating the previously assumed role of salinity as principal steering variable. Heavy demands placed on the local carbon dioxide pool by high productivity rates sustained by the mat-forming microbenthos obviously give rise to severe CO₂-

limitation and, consequently, to a largely indiscriminate metabolization of available CO₂ supplies.

PA-1-5 ON RECENT STUDY OF ANCIENT ICE AIR CONTENT: THE VOSTOK ICE CORE. L.P. SEMILETOV. Pacific Oceanological Institute, Vladivostok, Russia.

As is known a deep ice core extracted at polar stations, Greenland and Antarctica, provides a record of atmospheric climate and CO₂ that is representative of global changes over the last glacial-inter-glacial cycle. It's assumed that ice core gas content reflects the ancient air composition directly. Usually the influence of the effect of primary air (PA) trapping during the formation of snowflakes is not considered due to a smallness. Although gas bubbles in snowflakes were obtained (Blanchard et al., 1957).

Consider the link of processes of air capture/release during the snowflakes formation-precipitation-methamorphism. In general, the gas content in the system water drop - snowflake is determined by the altitude of "air trapping" and temperature-humidity regime, aerosols concentration. Also it's known that particles of clay mineral are more effective nucleus of a crystallization than sea salt. Therefore, the air trapping altitude above Greenland might be less than in Antarctic. In consequence the value of PA in northern hemisphere might be more than it's in Antarctic. The deposited snow is changed under methamorphism when process of the sublimation-recrystallization is occurred. It's connected with snow accumulation rate and temperature-humidity regime. It might be possible that in most cold and dry condition with a little accumulation snowflakes are transformed completely. Note that foregoing effect might provide for 10 - 15% of the mean total gas content if the PA trapped on 600mb level is preserved during a methamorphism. In this "ideal" case the variability of total "air" content along Vostok ice core is provided by the PA trapping.

The PA content in snowflakes pockets should be different from air composition due to the specific of the solubility value. It seems that oxygen/nitrogen relation in these pockets are about 1:2. However, the recent study of ice core total N₂ - O₂ content shows the little difference with ambient air. Nevertheless, the polar gases as CO₂ and H₂S should be fixed as the ionic trace in the crystalline structure. It's support by close agreement between calculated and experimental value of bicarbonate content in rain drop. The discrepancy between DIC value which is obtained by "wet" technique and "dry" CO₂ air content might be determined by the foregoing effect.

Also, the possible mechanism of the Young Dryas sight imitation is considered.

The current study result by the Vostok ice core gas content measurement to about 2,540m are presented.

O-1-5 THE ROLE OF THE TERRESTRIAL BIOSPHERE IN CONTROLLING ATMOSPHERIC METHANE AND CARBON DIOXIDE DURING THE LAST GLACIAL MAXIMUM AT 18 KYR. J. SERVANT, Laboratoire d'Aerologie, 118 Route de Narbonne, 31062 Toulouse CEDEX, France.

The large change in the Earth's climate at 18kyr BP has altered the vegetation, extent of ice sheets and land areas as a result of lowered Sea level. Atmospheric methane (CH₄) and carbon dioxide (CO₂) have dropped from 650 to 350 ppmv and 280 to 200 ppmv, respectively. To explain the variation of the CH₄ level, the area and net productivity variations of the wetlands at different latitudes and longitudes are studied. In the northern hemisphere the CH₄ flux was

reduced by about 57 Tg $\text{CH}_4 \text{ yr}^{-1}$ (1 Tg = 10^{12} g), mostly between 80° and 54°N because of ice sheet advance reducing the boreal vegetation; the contribution of the intertropical zone (30° to 0°N) was only a few percent and due to wetland ecosystems in Africa. In the southern hemisphere the reduction of the CH_4 flux was significant, about 23 Tg $\text{CH}_4 \text{ yr}^{-1}$ between 0° to 30°S in the wetland ecosystems in South America. The total flux reduction, about 80 Tg $\text{CH}_4 \text{ yr}^{-1}$ was equal to half the value of the preindustrial global CH_4 flux.

The atmospheric CO_2 concentration drop is analyzed by considering terrestrial carbon storage. It is shown that, besides the carbon stored under the newly formed land ice sheets, the net productivity at the global scale must have dropped by 20% to 30%. The reduction of carbon load in the atmosphere is estimated to be 170 Gt C whereas for the terrestrial ecosystems we derived a value of 252 to 470 Gt C (1 Gt = 10^{15} g). Detailed explanations of the decrease of atmospheric CO_2 concentration must await further study of the role of oceans as a sink. We propose that accumulation of H_2CO_3 in the oceans is due to a reduction of the net exchange of CO_2 between the atmosphere and the ocean surface, then river input is no more balanced by sea output. The transfer of carbon from the atmosphere and continental biosphere to the ocean is done by transport of carbon in rivers.

O-5-8 METHANE CONCENTRATIONS AND GROUNDWATER FLOW IN PEAT, GLACIAL LAKE AGASSIZ PEATLANDS, NORTHERN MINNESOTA. D.L. SIEGEL, Dept. Geology, Syracuse University, Syracuse, New York 13244. P.H. GLASER, Limnological Research Center, Univ. Minnesota, Minneapolis, MN 55455. E.A. ROMANOWICZ, Dept. Geology, Syracuse University, Syracuse, New York 13244.

Large boreal peatlands are a sink for carbon dioxide and a significant source of methane in the global carbon budget. As part of an integrated project to evaluate methane and solute transport from peatland soils to the land surface, we obtained 31 profiles of hydraulic head, dissolved methane and solutes in peat pore-water from raised bogs and fens in the vast Glacial Lake Agassiz peatlands. Sampling was done in August, 1990, during the most extreme drought historically recorded in northern Minnesota.

The methane transported from peat to the atmosphere is generally thought to be produced in the first 50 cm of the peat profile. Our results suggest otherwise. Nearly 40% of the peat pore-water samples were supersaturated with respect to methane; the remaining samples were close to being saturated (about 2 mmol/L). At one fen site 2.5 meters below the water table, dissolved methane concentration was as high as 8.6 mmol/L. Methane profiles show increasing concentration with depth, consistent with an upward flux driven by the concentration gradient as described by Fick's First Law.

Methane may also be transported by groundwater flow. Hydraulic head measurements indicate that most bogs are located over groundwater discharge areas, where pore water moves upward. Hydraulic heads in the basal peat at several bogs were above the water table. We propose that the drought sufficiently has lowered the convex shaped, water-table mounds within bogs to allow upward regional groundwater flow systems to discharge to the bogs. The upward groundwater flow increases methane transport to the land surface by advection as well as diffusion. Similar enhancement of methane transport to the peat surface by ground water might be expected with long-term drought in the mid-continent such as suggested by global climate models incorporating increasing concentrations of greenhouse gases in the atmosphere.

PB-6-16 THE QUANTIFICATION OF METHANE EMISSIONS FROM MOUNTAIN LAKES AND WETLANDS LOCATED IN THE COLORADO FRONT RANGE. L.K. SMITH, AND W.M. LEWIS, JR. Center for Limnology, University of Colorado, Boulder, Colorado, USA.

Few measurements have been made to quantify methane emissions from freshwater lakes and their associated wetlands. In order to provide additional source rate information from such environments for global tropospheric methane models, the static chamber method was used to quantify methane emission rates from five sites located in the Colorado Rocky Mountains. Measurements were made either on a monthly (non-snow cover) or a seasonal basis (snow cover) over a fourteen month period. Emissions from both the lakes and their associated meadows exhibited pronounced temporal and spatial variability. Emissions were zero during the winter months and commenced rapidly once snow melt and/or ice-out occurred. Emissions from the meadows tended to be positively correlated with soil temperature in a given site, while emissions from the lakes tended to be positively related to surface water-column methane concentrations. Average ($\pm$ SE) emissions from the five meadow sites ranged from 0.01 ± 0.01 to $8.0 \pm 0.8 \text{ mmol m}^{-2} \text{ d}^{-1}$, which are comparable to those measured on the Alaska tundra. Mean methane emissions from the lake sites ranged from 0.07 ± 0.03 to $4.3 \pm 1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$. Emissions measured from a lake containing rooted aquatic macrophytes (*Nuphar luteum*) averaged $18.4 \pm 6.9 \text{ mmol m}^{-2} \text{ d}^{-1}$. These rates are similar to those measured from Amazon River floodplain lakes. The results from this study demonstrate that mountain lakes and their associated wetlands emit significant quantities of methane to the troposphere.

PB-11-7 THE GEOCHEMISTRY OF METHANE IN AN AMICTIC, PERMANENTLY ICE-COVERED LAKE IN ANTARCTICA. R.L. SMITH, L.G. MILLER, and B.L. HOWES. U.S. Geological Survey, Denver, CO. and Menlo Park, CA, USA, and Woods Hole Oceanographic Institute, Woods Hole, MA, USA.

The abundance, distribution and production of methane were determined from 1987-1990 in Lake Fryxell, an amictic stratified, permanently ice-covered lake located in the McMurdo Dry Valleys, Antarctica. Most lakes in this region are closed-basins, are nearly devoid of any plants and animals within their watersheds, and their biogeochemical cycles are predominantly controlled by processes internal to the lakes. In Lake Fryxell, solute movement is limited to diffusion through a uniform salinity gradient ($10\text{--}110 \text{ mM Cl}^-$) that extends through the entire water column. The lake is oxic ($0.5\text{--}1.0 \text{ mM O}_2$) from beneath the ice cover (5 m) down to 9.0 m, contains a steep oxycline from 9 - 9.25 m and is anoxic from 9.25 m down to the bottom (18.5 m). CH_4 concentrations were $< 1 \mu\text{M}$ above 9.5 m and increased exponentially below to $940 \mu\text{M}$ at 18 m. Sediment CH_4 was $1.1 \text{ mmol (L sed)}^{-1}$ in the upper 0 - 5 cm zone. Upward flux from the sediment was the source of the CH_4 , NH_4^+ , and DOC in the water column; CH_4 was 27% of the DOC + CH_4 carbon at 18 m. Incubations with sediment cores indicated that CO_2 reduction was approximately equal to acetate fermentation to CH_4 , rates for $\text{H}^{14}\text{CO}_3^- \rightarrow ^{14}\text{CH}_4$ were $0.4 \mu\text{mol (L sed)}^{-1} \text{ day}^{-1}$ in the 0 - 10 cm interval. There was no measurable CH_4 production in water column samples nor any evidence of CH_4 loss by bubble formation. However, normalized depth profiles of CH_4 , NH_4^+ and DIC demonstrated that a

significant CH_4 sink was evident in the anoxic, sulfate-containing zone of the water column (10-18 m), while the bulk DOC appeared to be refractory. The $\delta^{13}\text{CH}_4$ in this zone was constant with depth at -72 per mil, indicating that the consumption mechanism did not result in an isotopic fractionation. In contrast, $\delta^{13}\text{CH}_4$ increased to -55 per mil at 9 m due to aerobic oxidation, though this appeared to be a minor aspect of the CH_4 cycle. In short, on a total carbon basis, CH_4 consumption in the anoxic water column exerted a major effect on the flux of carbonaceous material from the underlying sediments and serves to exemplify the importance of CH_4 to carbon cycling in Lake Fryxell.

PA-4/5-17 BIOMASS BURNING: A HISTORICAL VIEW VIA ARCTIC ICE CORES. M.L. SPENCER, S. DRUMMEY, P. MAYEWSKI, Glacier Research Group, University of New Hampshire, Durham, NH, USA, G. HOLDSWORTH, Arctic Institute of North America, Calgary, Alberta, Canada, and K. TAYLOR, Desert Research Institute, University of Nevada System, Reno, Nevada, USA.

Historical atmospheric emissions from biomass burning have been investigated using chemical data from three Arctic ice cores. Two of these cores are from Greenland: the 20D core from Southern Greenland which covers the time period 1767-1984 and the GISP2 core from Central Greenland which covers the time period 750-1989. The third core was collected from Mt Logan in the Yukon Territory and spans the period 1685-1980.

The ice cores were sectioned and analyzed for a variety of chemical constituents including major anions and cations by ion chromatography, solid electroconductivity, acidity using a strong acid titration method, and hydrogen peroxide by an enzymatic fluorescence technique. Ammonia time series for all three sites show episodic high spikes attributable to biomass burning (Hegg et al., 1988). Elevated hydrogen peroxide levels are also associated with these sections resulting from the generation of hydrogen peroxide via photochemical oxidation of hydrocarbons released by the fires. Additionally, elevated nitrate levels are seen in sections having the highest ammonia concentrations. The considerably higher natural background level for nitrate renders small burning inputs difficult to detect. In general, the sections with elevated ammonia are also characterized by low acidities and low electroconductivity resulting from acid neutralization. This suggests that ammonia emissions from biomass burning are transported to these sites primarily in the gas phase since there still is appreciable neutralization capacity. In a few cases there is a 1:1 relationship between the non-background ammonia and nitrate signifying transport as ammonium nitrate.

The time series for ammonia varies from core to core, however, emissions from particularly large fires such as the 1871 Peshtigo fire in Wisconsin, which burned 1.2 million acres, are seen in all three cores. Additionally, we believe, the 1200 year Central Greenland ice core ammonia record provides a general historical record of biomass burning. Decreased fire incidence is seen from 1050 to 1300 and during the Little Ice Age period from 1600 to 1800. In Northwestern Minnesota, similar periods of decreased fire importance have been determined based upon lake sediment charcoal content data and have been attributed to a cold wet climate (Clark, 1988). The ice core data additionally suggests that the link between climate and forest fire incidence may be of general importance not just of regional significance.

O-9-4 SULFUR METABOLISM OF BENTHIC MARINE CYANOBACTERIA AND ITS POSSIBLE ROLE IN TRACE GAS EXCHANGE IN MICROBIAL MATS L.J. STAL.

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Cyanobacteria form dense communities on intertidal sediments. They build structures that are commonly known as microbial mats. The phototrophic cyanobacteria enrich the sediments with organic matter which forms the basis of a complex microbial ecosystem. Marine microbial mats are dominated by the sulfur cycle. Because marine microbial mats often are situated in the littoral they are frequently exposed to the atmosphere. Therefore microbial mats may possibly contribute to emission of sulfur gases. Since the bulk of the biomass in the microbial mats consists of cyanobacteria it seemed worthwhile to study their part in the sulfur cycle. The organic material produced by the photosynthetic activity of the cyanobacteria is liberated by (i) death and lysis of the cells (ii) excretion of glycolate due to photorespiration and (iii) excretion of fermentation products. The most constant sources of organic substrates in the mat are the excretion of glycolate in the light which is caused by photorespiration and the excretion of fermentation products during the anoxic conditions which prevail during the dark. Cyanobacteria ferment endogenous storage compounds to lactate, acetate, formate, ethanol, CO_2 and H_2 . All of these compounds are excellent substrates for sulfate reducing bacteria. High numbers of sulfate reducing bacteria were found in the cyanobacterial layer. Apart from the fact that cyanobacteria provide substrate for the sulfate reducing bacteria, they also contribute directly to the sulfur cycle. Mat-building cyanobacteria oxidize sulfide in the light to elemental sulfur or thiosulfate in a photosystem I-dependent reaction. In the dark elemental sulfur is reduced to sulfide. The sulfide which is produced is fixed in part as iron sulfide or pyrite. However, sulfide and other volatile sulfur compounds are also emitted.

PA-4/5-18 METHANE CONSUMPTION IN SOILS: AN INTERSITE COMPARISON. R.G. STRIEGL, L.N. WITHERBEE, C.M. TATE, AND T.A. MCCONNAUGHEY. U. S. Geological Survey, Box 25046, MS 413, Denver, Colorado 80225, USA.

Recent increases in the atmospheric concentration of methane have been attributed to culturally induced increases in global sources as well as to diminution of natural methane sinks. The most important terrestrial sink for atmospheric methane is consumption by soil bacteria, accounting for as much as 10 percent of the total global sink. However, worldwide heterogeneities in land-surface conditions far exceed the current ability to specify methane consumption rates (or cultural alteration of consumption rates) for all land cover types. We therefore attempt to generalize methane consumption by means of field measurement across environmental gradients. Field studies of soil methane consumption are in progress at hot, arid, nutrient-poor locations (the Mojave Desert - Great Basin transition zone, Nevada); at cool, moist, organically-rich locations (alpine and subalpine areas in the southern Rocky Mountains, Colorado) and in tallgrass prairie (the Konza Prairie Natural Resource Research Area, Kansas). The Konza Prairie study compares consumption in undisturbed prairie with consumption in prairie that has been converted to agriculture. An investigation of methane consumption in soil cover over buried waste is also in progress.

Methane consumption rates in undisturbed soils generally range from 0 to 3 $\text{mg/m}^2/\text{day}$. The rates are typically seasonally cyclic, with increased consumption corresponding with increased temperatures. However, both low and high soil moisture conditions inhibit consumption. Arid conditions apparently inhibit consumer metabolism, whereas increased soil saturation inhibits transport of methane to the consumers. Field experiments to evaluate the effects of nutrient enrichment and applications of agricultural chemicals are

in progress. In soils overlying buried waste, methane consumption rates increase to accommodate the additional waste-derived methane source.

PA-2-2 ROLE OF RIFTOGENIC HYDROGEN IN GLOBAL BUDGETS OF CRUST, OCEANS AND ATMOSPHERE (NEW MODEL OF OZONE HOLES FORMATION) V.SYVOROTKIN AND N.SADOVSKII, Geological faculty, Chemical faculty, Moscow University, 117234 Moscow USSR.

Most of industrial centers are located in the northern hemispheres while the largest ozone hole is located above the South Pole. This fact is in contradiction with the proposed industrial origin of this phenomena. Seismotomographic investigations demonstrated that near the rifts, especially around the Antarctic Continent, the mantle is unusually heated. Small ozone holes are situated also in the northern hemisphere, and most often they can be found above the northern part of Atlantic Ocean, Red Sea, Hawaiian Islands, the regions of active rifting and basaltic volcanogenic activity.

Hydrogen is the most wide-spread elements in the universe. Much hydrogen should be solved in the Earth nucleus, and it must be the most important fluid thrown out due to the rift magmatism. A lot of hydrogen must be injected into the atmosphere when the spreading occurs. In the ozone layer hydrogen reacts with ozone and forms water:

The reaction (1) has been studied in laboratories. It is a photochemical chain reaction. Ozone is destructed very effectively, almost as effective as in the presence of chlorine. The termination reactions give water, at low temperature ice. Clouds consisted of ice were found recently in stratosphere in polar regions. Water formed in the reaction of ozone with hydrogen falls down to the Earth. During 3-5 million years the level of the ocean due to this process could rise up to 100-200 m, in the agreement with the geological data. The period of regeneration of the ozone layer is near one year. Formation of ozone holes during some years is connected with the periods of solar activity, which stimulates tectonic and volcanic processes and thus, injection of hydrogen in the atmosphere. Decrease of solar activity will be followed by disappearance of ozone holes in some years. Destruction of the ozone layer during tectonic epochs caused decay and generation of different kinds of organisms.

O-9-1 BACTERIAL TRANSFORMATIONS OF ORGANIC SULFUR COMPOUNDS IN MARINE ENVIRONMENTS. B.F.TAYLOR, Rosentiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA.

Inputs of biogenic sulfur into the atmosphere from marine environments are largely organic, as dimethyl sulfide (DMS), in contrast to the mainly inorganic contributions from terrestrial regions. DMS comes principally from the osmolyte dimethylsulfoniopropionate (DMSP) of marine phytoplankton and macroalgae. Smaller amounts of DMS originate in thiol methyltransferase reactions with various methyl donors. Marine plants liberate DMS, but most is produced after release of DMSP into the environment by senescence, lysis and zooplankton feeding. Bacteria that cleave DMS from DMSP function in oxic and anoxic environments, but environmental concentrations of DMS are significantly lower than those of DMSP. Entry of DMS to the marine atmosphere is affected by bacteria which demethylate DMSP or oxidize DMS. DMSP is sequentially

demethylated to 3-methylpropionate and 3-mercaptopropionate in oxic and anoxic environments. Bacteria which aerobically demethylate DMSP have been isolated from marine sources and the anaerobic process has been outlined with anoxic slurries of marine sediments. DMS is aerobically oxidized by methylotrophic hyphomicrobia and autotrophic thiobacilli although isolates from marine environments have received little attention. Methanesulfonic acid (MSA) produced by the photochemical oxidation of DMS in the troposphere and a component of acid rain, is also metabolized aerobically by methylotrophic bacteria. Anaerobic metabolism of DMS has not been reported. In anoxic marine sediments DMS is oxidized to CO_2 by sulfate-reducers although, under certain conditions, DMS is available to methanogens.

Understanding of the net efflux of DMS to the marine atmosphere requires more knowledge on the ecology, physiology and interaction of microorganisms that metabolize DMSP, DMS and related sulfur species such as methanethiol and dimethyl sulfoxide (DMSO).

PA-2-3 THREE-DIMENSIONAL SIMULATIONS OF CFC-11 AND METHYL CHLOROFORM AND THE INFERRED DISTRIBUTION OF TROPOSPHERIC OH. X. TIE, J. KAO AND E.J.MROZ, Los Alamos National Laboratory, Los Alamos, New Mexico, USA.

A three-dimensional chemical tracer model of the global distributions and seasonal cycles of the surface concentrations of CFC-11 and CH_3CCl_3 are compared with surface observations from the Atmospheric Lifetime Experiment (ALE). Further comparisons are made with Project Airstream measurements of CFC-11 and CH_3CCl_3 made in the upper troposphere and lower stratosphere. The global distribution of OH inferred from the CH_3CCl_3 simulation indicates that the northern hemisphere contains about 1/3 of the OH of the southern hemisphere. This probably results from the higher concentrations of CO and non-methane hydrocarbons in the northern hemisphere which are important sinks for OH. Analysis of the seasonal cycles of CH_3CCl_3 indicates that atmospheric transport controls the CH_3CCl_3 seasonal cycle at locations north of 30°S . In the equatorial region between 30°N and 30°S , the observed seasonal cycles of CH_3CCl_3 are affected by both transport and OH. This results from the predominance of CH_3CCl_3 sources in the northern hemisphere and the larger amplitude of the OH seasonal cycle in the southern hemisphere. The globally averaged OH is about 7.0×10^5 and the global lifetime of CH_3CCl_3 is about 6.0 years. The inferred OH field will be used in planned simulations of the global distribution of atmospheric methane.

PB-6-17 CARBON AND ^{14}C BUDGET FOR ORGANIC-RICH CONTINENTAL SLOPE SEDIMENTS OF THE MIDDLE ATLANTIC BIGHT. S.E.TRUMBORE, Center for Accelerator Mass Spectrometry, L-397, Lawrence Livermore Laboratory, Livermore, CA 94550, R. F. ANDERSON and P. BISCAEY, Lamont-Doherty Geological Observatory, Palisades, NY 10964.

The degree to which organic carbon is preserved in sediments is determined by the availability of oxidants (dissolved O_2 , nitrate, sulfate), and the susceptibility of the deposited organic substrates to microbial degradation. Fluxes of organic carbon into and out of the sediments may be measured using sediment traps and modeling of pore water chemistry, while radiocarbon (^{14}C) measurements yield information about the origins and reactivity of sedimentary organic matter. We use measurements of organic carbon

and ^{14}C in sediments and sediment trap material to trace the origin, transport, remineralization and burial of sedimentary organic matter in the upper continental slope of the Middle Atlantic Bight. Organic rich (2% dry weight) sediments found on the upper slope have led to the hypothesis that this region is a depocenter for organic carbon, and possibly a significant sink for anthropogenic CO_2 .

The flux of organic carbon to the sediments over the upper slope (water depth 1000m) is nearly $70 \text{ mgC m}^{-2} \text{ d}^{-1}$. 45-90% of this flux is remineralized at the sediment-water interface. Less than 10% is remineralized in the bioturbated zone, with the remainder being buried. The majority of the carbon being deposited has been transported laterally into the region rather than derived directly from the overlying photic zone. ^{14}C measurements show that the sediment trap material is primarily older, resuspended or reworked material, with a smaller component containing carbon of recent origin. Essentially all of the organic matter with more modern ^{14}C is remineralized at the sediment-water interface; the carbon which bypasses remineralization at the sediment-water interface and in the bioturbated zone is old and refractory. Thus the high organic carbon contents observed in the upper slope sediments are due to the refractory nature of the deposited material, and burial of carbon in these sediments cannot be interpreted as a net sink for carbon produced by new or enhanced productivity in the continental shelf-slope region.

0-2-5 LONG-TERM TRENDS AND SEASONAL VARIATIONS OF ATMOSPHERIC METHANE IN JAPAN. H. TSURUTA, National Institute of Agro-Environmental Sciences, Tsukuba, Ibaraki-ken, Japan.

Atmospheric methane is a greenhouse gas, and plays important roles in atmospheric chemistry of both the troposphere and the stratosphere. Its concentration has been increasing at a rate of 1% per year. But its behavior in east Asia has not been clear due to the lack of data.

Atmospheric methane and non-methane hydrocarbons have been measured by an automated gas chromatograph equipped with a flame ionization detector in the air pollution monitoring network of Japan since 1981. The annual average methane concentration in Japan was 1.83 ppmv in 1989, and the data in the urban area of Tokyo, Kyoto, and Sapporo have clearly shown a gradual increase at an average rate of 0.7% per year. At these monitoring stations the methane concentration has shown a seasonal variation with a winter maximum and a summer minimum. This seasonal cycle is caused by maritime tropical air masses which are dominant in summer and relatively poor in methane, and by continental air masses which are dominant in the other seasons and relatively rich in methane. This is also affected by the local sources of methane and by a seasonal cycle of the magnitude of atmospheric stability in the planetary boundary layer. In contrast, the methane concentration at the stations surrounded by paddy fields clearly shows a summer maximum, and which is attributed to a summer maximum of methane flux from paddy fields. The higher concentration of methane in the Tokyo metropolitan area than in the surrounding area demonstrates that an urban-industrial area is a large a real source of methane. Landfill located along the coast of Tokyo Bay is estimated to be one of the anthropogenic sources of methane.

PB-6-18 A COMPARISON OF METHANE EMISSIONS FROM TROPICAL AND BOREAL WETLANDS: THE SEARCH FOR OLD METHANE. S.C. TYLER, G.W. BRAILSFORD, M. KELLER, National Center for Atmospheric Research, Boulder, Colorado, USA, and P. CRILL, University of New Hampshire, Durham, New Hampshire, USA.

We report results of an on-going study to determine the current potential of biogenically produced wetland methane to contribute significant amounts of ^{14}C -depleted methane to the atmosphere. We have made measurements of methane emissions from tropical wetlands in Panama and a northern boreal fen site in New Hampshire. Collections were made using both enclosures and bubble traps over water-covered surfaces. The data include analysis of $\delta^{13}\text{C}$ and ^{14}C of methane and CO_2 . In Panama wetlands, ^{14}C should be essentially modern because of relatively fast turnover times for decaying organic carbon. We found $\delta^{13}\text{C}_{\text{CH}_4} = -59.1 \pm 2.9$ and $^{14}\text{C} = 123.0 \pm 4.6 \text{ pmC}$ for bubble samples collected in April-May 1988. Additional measurements throughout a two-year period from mid-1986 to mid-1988 indicate little seasonal dependence in $\delta^{13}\text{C}_{\text{CH}_4}$ or flux rate of methane. In contrast, carbon stored in the peat of boreal wetlands can remain largely unreacted for several thousand years. We report preliminary measurements of $\delta^{13}\text{C}_{\text{CH}_4}$ and ^{14}C from seasonal studies being conducted in Sallie's fen, New Hampshire. We expect to use ^{14}C data to help determine how much older carbon is released from the peat. The isotopic signal in gases from peat sources could be distinct from other biogenic sources in that it could be ^{14}C -depleted while retaining its ^{13}C -depleted signal from its biogenic origin. Future detection of a change in the ^{14}C signal could be an early sign of global warming as it signifies rising temperatures with increasing biological activity in the older peat.

PA-7-11 ANTHROPOGENIC CHANGE OF ATMOSPHERE GEOCHEMISTRY OF EASTERN EUROPEAN PLAIN. Y.P. UCHVATOV, Institute of Soil Science and Photosynthesis, Academy of Science USSR, Puschino, Moscow Region, USSR.

Evaluation of present geochemical state and anthropogenic contamination of the atmosphere is one of the most acute problems of the environment. For each type of industry, there is a specific mechanism of atmosphere contamination. Atmospheric geochemical fluxes of polluting elements is reflected in the chemical composition of precipitation and solid atmospheric dust.

The aim of this study, carried out from 1975 to 1989, was to describe the natural atmospheric geochemical characteristics both in background areas and those under anthropogenic pressure in frontier of central and north-western parts of Eastern European Plain. Precipitation as collected in chemically neutral, polyethylene cups: rainwater samples were taken after each rain, fresh snow - three or four times in winter, snow cover - just before intensive melting. All samples were filtered on dense paper filter. Subsequent dry combustion of filters (450 to 500°C) allowed the determination of chemical composition of solid air aerosols. The content of chlorides, sulphates, various forms of nitrogen, total Fe, Ni, Cr, An, Pb, Cd were determined.

Analysis of the obtained data show that chemical composition of liquid fallout in background central and north-western parts of East European Plain differ considerably, resulting from different natural conditions of fallout formation. The central part of the plain is continental, while the north-western part experiences anthropogenic effects on the chemical composition of precipitation. The chemical composition of precipitation varies annually, seasonally and within shorter time periods. In precipitation, elements concentrations are considerably higher in industrialized areas. Coefficient of technogenic transformation of elements in precipitations reach n. 10 - n. 100 and sometimes n. 1000 for some plants. These differences are related to specific industrial technology of each industrial enterprise. The chemical composition and quantity of atmospheric dust in the

monitored regions of Eastern European Plain varies widely both in background areas and in those under modern technogenic effect. The content of elements in atmospheric dust from each of the studied regions differs from mean values 1.2, to 2 times, sometimes 3-5 times. In areas under industrial effect, as a rule, the content of an element in solid atmospheric aerosols coming in landscape is higher as compared with background territories in 1.5 to 10 (15) times. At the same time element fluxes in soil near the emission source are 0.5 to 2 orders higher than in background areas and determine by the income into landscape technogenic dust namely $(0.4 - 0.5 \text{ gm}^{-2} \text{ month}^{-1})$ in background areas from $150-250 \text{ g m}^{-2}$ in month in areas under modern technogenic effect.

These investigations allow us to establish the degree of anthropogenic pollution of the atmosphere by various industrial-pollutants. In addition, we can assess the degree of anthropogenic pollution of soil and vegetation.

PB-11-8 PH DEPENDENCE OF CH_4 AND CO_2 PRODUCTION IN TWO CONTRASTING HUDSON BAY LOWLAND WETLANDS. D.W. VALENTINE, E.A. HOLLAND, AND D.S. SCHIMMEL. NREL, Colorado State University, Fort Collins, CO, USA, and NCAR and UCAR, respectively, P.O. Box 3000, Boulder, CO, USA.

We incubated surface peat samples from the Hudson Bay Lowlands to evaluate the regulation of methane (CH_4) and carbon dioxide (CO_2) production rates by substrate availability, temperature, and pH. CO_2 production rates were $3-7 \mu\text{mol g}^{-1} \text{ h}^{-1}$, which was 3-4 orders of magnitude faster than CH_4 production rates ($<20 \text{ nmol g}^{-1} \text{ h}^{-1}$). CH_4 and CO_2 production rates were much higher in slurries from the early-successional, minerotrophic Coastal Fen than in the older ombrotrophic bog at Kinosheo Lake. Higher temperatures (20°C vs. 10°C) in the Coastal Fen slurries resulted in 3-4 fold and 1.2 - 1.4 fold increases in CH_4 and CO_2 production rates, respectively, while EtOH (an acetate precursor) additions increased both rates by about 5-fold. Lowering the pH from 6.2 to 3.6 with H_3PO_4 cut production rates dramatically, by 66-fold and 3-fold for CH_4 and CO_2 , respectively. Production rates of CH_4 and CO_2 from Kinosheo Lake peats were extremely low even with EtOH additions at 20°C , but tripled within 1 week to $2.5 \text{ nmol g}^{-1} \text{ h}^{-1}$ and $6.8 \mu\text{mol g}^{-1} \text{ h}^{-1}$, respectively, when NaOH additions increased pH from 3.9 to 6.2. These data suggest an increasingly important role of pH in limiting respiration and CH_4 production as these wetlands age.

O-9-3 SULFUR CYCLING IN MARINE MICROBIAL MATS: DISTRIBUTION OF COMPOUNDS AND FUNCTIONAL GROUPS OF SULFUR BACTERIA. P.T. VISSCHER AND H. VAN GEMERDEN. Dept. of Microbiology, University of Groningen, NL-9151 NN Haren, The Netherlands.

The sulfur cycle of a benthic marine microbial mat was studied by measuring depth profiles of several organic and inorganic sulfur compounds in the top 50 mm of the sediment. Additionally, profiles of oxygen, nitrogen compounds, photopigments, pH and salinity were measured. Simultaneously, the vertical distribution of functional groups of sulfur bacteria, i.e. sulfide producers, aerobic thiosulfate oxidizers, aerobic dimethylsulfide (DMS) utilizers and phototrophic sulfide oxidizers, was assessed by most-probable number (MPN) incubations, and total cell count by epifluorescence microscopy. Microbial dynamics were evaluated by rate measurement of sulfate

reduction, and dimethylsulfonio-propionate (DMSP) and thiosulfate consumption.

The MPN counts revealed an increase of microbial population during the growth season (May through November). Highest numbers of all functional groups of bacteria, including the sulfate reducers, were found in the upper 10 mm. Sulfate reduction, DMSP consumption and thiosulfate consumption were also the highest in this layer. Polysulfides were present in the highest concentration ($<170 \mu\text{mol cm}^{-3}$ sediment) of all inorganic sulfur compounds measured and DMS ($<200 \text{ nmol cm}^{-3}$ sediment) was the major organic sulfur species. Laboratory experiments with pure cultures of *Thiobacillus* spec. and *Thiocapsa roseopersicina* revealed kinetic parameters for growth on both DMS and several inorganic sulfur compounds. The cyanobacterial community within the mat was found to contain DMSP, a precursor of DMS. The close proximity of organisms in combination with high bacterial numbers of both autotrophs and heterotrophs give rise to a very dynamic, relative closed community in which sulfur compounds, including the volatile ones, are expected to be recycled rapidly.

O-4-1 TRACE GAS EXCHANGES IN AGRICULTURAL ECOSYSTEMS. P.M. VITOUSEK, Department of Biological Sciences, Stanford University, Stanford, CA 94305, USA.

Agricultural systems represent significant global sources of methane and nitrous oxide, and agricultural intensification can have both positive and negative effects on flux. There is substantial information on emissions of methane from rice paddies during the cropping period, and on nitrogen trace gas fluxes during the period immediately following cultivation. However, integrated fluxes in cropping systems are poorly known -- and subject to substantial change.

O-7-8 BURIAL OF ORGANIC CARBON IN ESTUARINE ZONES: A CASE STUDY IN GUANABARA BAY, RIO DE JANEIRO. A. DE LUCA REBELLO WAGENER. Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, 22453 Rio de Janeiro, Brazil.

Estuarine and coastal areas under the influence of anthropic activities that release nitrogen and phosphorus to the environment may play a significant role in CO_2 uptake. This is especially true in tropical areas where temperature and intensive sun light over the whole year guarantee high primary production as long as nutrients are available.

In those areas weathering processes are naturally fast and have been enhanced due to land occupation, deforestation and agriculture activities. This provides fast sedimentation rates which will contribute to the preservation of a more significant fraction of the organic carbon fixed via photosynthesis. Guanabara Bay receives about $20 \text{ m}^3/\text{s}$ of untreated domestic sewage derived from the city of Rio de Janeiro. This, load together with fast nutrient cycling within the system, is responsible for nitrogen and phosphorus concentration of the order of $30-40 \mu\text{mol N/l}$ and $2 \mu\text{mol P/l}$, respectively. The net primary production (NPP) determined in the bay was $1260 \text{ g C/m}^2/\text{year}$, which places Guanabara Bay among the most productive marine systems of the world.

Sedimentation rates estimated from Pb^{210} profiles are between 1.3 to 2 cm/year , a range which is applicable to a large area in the bay for the last 30 years. In order to evaluate the fraction of the NPP buried in the sediments several cores were analysed for the organic carbon and nitrogen content, total solids and water content. The average solid content found was 25%, of which 3% was of organic origin.

The average respiration rate in the water column resulting from measurements performed at various stations in the bay is around 70 mmol O₂/m²/day. This means that about 40% of the carbon fixed is recycled before reaching the sediments. Taking this into account and using the data given above it follows that about 100 g C/m²/year are buried in the sediments.

Assuming a constant NPP over the last 40 years, a value of 10% for the amount buried is obtained. This means that only in the area of Guanabara Bay about 10⁵ tons of carbon are removed from the short term cycle. As Guanabara Bay presents unusually high respiration rates in the water column this is to be taken as a lower limit for the preserved fraction in the sediments. Considerations concerning the respiration in the sediments and the C/N ratio will also be added.

O-1-6 CO₂ CONCENTRATION IN BUBBLE AIR FROM 1550 TO 1940 AD FROM THE GISP2 ICE CORE FROM CENTRAL GREENLAND. M. WAHLEN, D. ALLEN and B. DECK, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA.

Initial measurements of the CO₂ concentration were made for air samples trapped in bubbles of the GISP2 ice core from Central Greenland. An extraction system to crush small ice samples under dry and cold conditions is used to liberate the air. The whole air is then collected at 30°K, and subsequently released into an infrared cell where the CO₂ concentration is determined by tunable diode laser absorption spectroscopy on a single rotation-vibration transition at low pressure. A series of standard gases provides the calibration. The experimental uncertainty is ±1% or ±3 ppmv for 0.07 cm³ of air.

The age of the trapped air was determined by locating the depth of the ¹⁴CO₂ bomb peak in the trapped air [Wilson and Donahue 1990, and additional data, A. Wilson, pers. comm.] corresponding to the year 1963, and then applying the depth/age relationship for the GISP2 ice core. The age difference between air and ice thus determined is 220 years.

The concentration of CO₂ in the air is found to be constant at 280 ± 5 ppmv between 1550 and 1800 AD. After 1800 AD the concentration rather abruptly rises to about 310 ppmv in 1940. There is no apparent offset between the youngest ice CO₂ concentrations in 1940 and the earliest atmospheric observations at Mauna Loa in 1951 (Keeling et al. (1989)). The two records seem to join smoothly.

O-2-8 THE METHANE CYCLE: GLOBAL BUDGET AND PROCESS STUDIES USING STABLE ISOTOPES AND ¹⁴C AS TRACERS. M. WAHLEN and B. DECK, Scripps Institution of Oceanography, University of California, San Diego La Jolla, CA 92093, USA.

The atmospheric concentration of CH₄, a greenhouse gas, is increasing today at a rate of 1 percent/year (Blake and Rowland (1988)). Compared to preindustrial times today's atmospheric concentration is 2.5 times higher (Stauffer et al. (1985)). Measurements of the isotopic composition of worldwide samples of atmospheric CH₄ (δ¹³CH₄, δD and ¹⁴C in CH₄) have been made for several years. These results are compared to the isotopic composition of CH₄ emitted from the major methane sources, namely natural wetlands and tundra, rice paddies, ruminants and possibly termites, landfills, fossil CH₄ (natural gas), and CH₄ from biomass burning (incomplete combustion producing CH₄). This comparison reveals constraints on source strengths, and enables the construction of a

global CH₄ budget. ¹⁴C in CH₄ is especially useful to assess the contribution by fossil CH₄.

The stable isotopes can provide a variety of information on the processes of methane generation and destruction. We will present process oriented studies on methane from landfills, methane oxidation on dry soils, and on methane in the stratosphere.

O-1-1 GEOLOGIC HISTORY OF THE BIOGEOCHEMICAL CYCLES OF CARBON AND OXYGEN. J.C.G. WALKER, Department of Atmospheric, Oceanic, and Space Sciences and Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 49109.

The processes that might control the amounts of oxygen and carbon dioxide in the atmosphere are analyzed in terms of reservoir amounts and the rates of transfer of material between reservoirs. Exchange of material between the atmosphere and the biotic reservoir by photosynthesis and by respiration is rapid, but the biotic reservoir is too small compared with the amount of oxygen in the atmosphere and the amount of carbon in oceans and sedimentary rocks for these rapid processes to have a lasting impact on the atmospheric concentrations of oxygen and carbon dioxide. The residence time of oxygen in the atmosphere is about 5 million years. The concentration appears to be controlled by a balance between the rate of consumption of oxygen in the oxidative weathering of reduced constituents of sedimentary rocks and the rate at which net photosynthetic oxygen is left behind in the atmosphere as photosynthetically produced organic matter is sequestered in sedimentary rocks. In the very long term, the amount of reduced material in sedimentary rocks is controlled by exchange with the interior of the Earth.

On a time scale longer than decades, the carbon dioxide content of the atmosphere is determined by equilibrium with the ocean, and this equilibrium depends on the rates of supply of carbon and neutralizing cations by volcanism and weathering and the rates of removal in the precipitation of carbonate minerals. On time scales of millions of years or longer, the carbon dioxide concentration of the atmosphere is determined by the balance between weathering rates and precipitation rates. On time scales of billions of years there is an important exchange of carbon between the surface of the Earth and the interior. Exchange with the biota affects atmospheric carbon dioxide only on a time scale of decades to centuries.

O-6-6 METHANE OXIDATION AT DEEP METHANE MAXIMA IN COASTAL CALIFORNIA WATERS. B. B. WARD, Marine Sciences Program, University of California, Santa Cruz, CA, USA.

Methane concentration in the water column of the Southern California Bight exhibits two or more maxima. In near surface waters, a subsurface concentration maximum is often observed, usually near the bottom of the euphotic zone, but not correlated with euphotic zone or nutrient parameters. Deeper maxima are often detected, well below the euphotic zone and separated from the sediments, which suggests an advective source from continental shelf sediments. We measured methane concentrations and oxidation rates in an attempt to quantify the flux and variability of methane concentrations throughout the water column in the Santa Monica Basin, one of the semi-enclosed basins in the Southern California Bight. The study site was an offshore transect with stations between 55 and 900 m depth, which was sampled during several seasons over 4 years.

The subsurface methane concentration maximum was a variable feature; during fall it appeared as a discrete maximum. In summer and winter, the maximum was less well defined, but appeared as a broad supersaturation feature whose shape and depth appeared to be controlled by density distribution. Methane oxidation rates measured

using $^{14}\text{CH}_4$ were negligible throughout the surface layer, with turnover times of several to many years. Inshore stations had low surface oxidation rates but rates increased with depth towards the shallow sediments. Methane flux to the atmosphere was variable and not adequately represented by a simple diffusion model.

Layers of methane rich water were detected in the mid water column (500-800 m) at the deeper stations, with concentrations exceeding those found in the subsurface maximum. Oxidation rates in these layers represented turnover times on the order of a few months. The source of the midwater methane is probably advection from petroliferous sediments in the margin of the borderland, rather than diffusion from underlying anoxic sediments in the basin. Relatively higher oxidation rates at depth imply the presence of a community adapted for the utilization of methane as a carbon source, a community which is not found in surface waters.

PA-7-12 APPLICATION OF SUBMICROSCOPIC METHODS FOR INVESTIGATION OF HEAVY METAL POLLUTED SOILS. J. WEBER. Agricultural University of Wrocław, Institute of Soil Science and Agricultural Environment Protection, Wrocław, Poland.

Studies by numerous investigators have shown that atmospheric fallout from ore smelters can contribute significantly to soil contamination with heavy metals and may pose a significant health hazard. Most of the previous works on the soils polluted by smelting has attempted to assess the degree of contamination and to explain the trace elements distribution in the soil in terms of distance from the smelter and depth in the soil profile. Chemical forms of heavy metals, their solubility, mobility and availability to plants have been studied as well. However, there are still not enough information about micromorphological forms of pollutants existed in soil material, because conventional microscopic methods did not allow to analyze chemical composition of particles constituting soil microstructure. That can be done when submicroscopic methods (scanning electron microscopy with x-ray fluorescence spectroscopy, ion microscopy, etc.) have been used. The object of this work is to indicate suitability of submicroscopic methods for investigations of heavy metal polluted soils, especially as regarding to analyses of trace elements distribution.

This study examines soils in an area which has been greatly affected by two copper smelters at Lower Silesia, Poland. Samples of loose soil material as well as 25 mm thin sections of undisturbed resin impregnated soil material were examined. Light polarizing and then scanning electron microscope Stereoscan 180 Cambridge (SEM-EDXRA) and electron microprobe analyzer Jeol JXA-5A (EMA) were used. The investigations revealed the presence of pitchy substance nodules containing very fine oval grains of lead and zinc. These small grains as well as larger grains with increased content of copper were also found as existed directly among mineral grains. Apart of that compound nodules of silicate-like material with heavy metal rich particles embedded in it and single particles consisted of lead or copper or zinc sulfides and/or oxides were recognized. Further research seems to be necessary to determine all different kinds of industry originated particles emitted into heavy metal polluted soils.

O-10-2 HOBr FORMATION BY SEAWEEDS: IMPACT ON THE BIOSPHERE. R. WEYER and M.G.M. TROMP, E. C. Slater Institute for Biochemical Research, Plantage Muidergracht 12, 1018 TV Amsterdam, The Netherlands.

Macroalgae are a significant source of bromoform and other volatile halogenated methanes and they release large amounts of these compounds in the marine ecosystem. There is substantial evidence that part of the bromoform detected in the Arctic Ocean in the

Spitsbergen area is produced by seaweed belts. It is conceivable that the production of bromoform is related to the peak in bromine present during the spring period in aerosols which were collected on Spitsbergen. This peak and seasonal dependence is not only observed at this location but also at Point Barrow, Alaska and Alert (Canadian Arctic) and is therefore not a local phenomenon. There are strong indications that the source of bromine containing particles is biogenic. There is considerable interest in this phenomenon since it was also demonstrated that, at polar sunrise, ozone destruction occurs in the lower Arctic atmosphere and that there was a strong correlation with the presence of filterable bromine in aerosols.

We have recently identified and characterized a number of vanadium bromoperoxidases in brown (Laminariales and Fucales) and in red seaweeds (Corallinaceae). The purified enzymes produce HOBr and Br_2 when hydrogen peroxide and bromide are added and they are involved in the biosynthesis of brominated compounds by these seaweeds via some unidentified pathway. Some of these enzymes appear to be located on the surface of these plants and may be extracellular and this prompted us to study the release of these brominated agents by seaweeds. Indeed, most of the seaweeds studied by us were able to brominate exogenous organic substrates when hydrogen peroxide was added to the intact plants in seawater. One of the species studied (*Ascophyllum nodosum*) was also able to carry out this bromination reaction in the absence of hydrogen peroxide when the seaweed in seawater was exposed to sunlight. In the dark no reaction occurred. The amounts of HOBr generated under illumination were substantial. The rate of bromination of an organic compound (phenol red) added to the seawater by the seaweed corresponded to 68 nmol HOBr generated per gram of wet alga per hour. This seaweed grows in large quantities in the North Atlantic and a biomass of 2×10^8 g is estimated along one of the main dikes (length 30 km) in Holland. This site could therefore produce 2×10^6 g HOBr per year. Although the fate of HOBr generated is not known, it may react with dissolved organic matter in seawater to give rise to formation of bromoform. Indeed, it has been reported that this plant generates bromoform and dibromomethane. However the rates reported are about 4 % of the value found for the HOBr generation. Therefore, it is conceivable that some fraction of the HOBr formed escapes from the seawater and is directly released to the air. The distribution of seaweed species in the North Atlantic and Arctic Ocean is well known and in some of the species from the North Atlantic (*Laminaria saccharina*, *L. digitata*, *Aegaria esculenta*, *Fucus discichus* and *A. nodosum*) bromoperoxidases have been detected. These species can also be found along the coasts of Greenland and Spitsbergen. We propose therefore that the annual peak in bromine content in aerosols in the Arctic atmosphere is due to the release of HOBr and brominated compounds by these seaweeds and this process may be triggered by light in spring.

O-11-2 THE ROLE OF TUNDRA AND TAIGA IN THE GLOBAL METHANE BUDGET. S. C. WHALEN AND W.S. REEBURGH. Institute of Marine Science, University of Alaska Fairbanks, Fairbanks, Alaska, 99775-1080, U.S.A.

Tundra and taiga have the highest stored soil carbon contents observed in natural terrestrial ecosystems, and are expected to play a important roles in the global CH_4 and CO_2 budgets. We report results of time-series measurements of methane flux at fixed sites representing important tundra and taiga components. Our tundra sites are located in the University of Alaska Arboretum and have been studied at weekly intervals for five years. Our taiga sites are located in the Bonanza Creek Long Term Ecological Research area and have been studied for two years.

We estimate that tundra contributes about 50 Tg yr^{-1} to the global atmospheric CH_4 budget. Vascular transport by sedges dominates tundra sources. Interannual variability is high (25 to $100 \text{ Tg CH}_4 \text{ yr}^{-1}$), and appears to be sensitive to water table level. Lowered water table increases soil oxidation, so current wet tundra areas could become an atmospheric CH_4 sink under warmer, drier conditions.

Taiga contributes a much smaller amount of CH_4 (5 to 15 Tg yr^{-1}) to the atmosphere. Our inability to evaluate the importance of point-source forested bogs within large areas of taiga that are actively consuming atmospheric CH_4 makes this estimate uncertain.

O-12-3 OXIDATION OF METHANE BY BOREAL FOREST SOILS: A COMPARISON OF FIVE INDEPENDENT METHODS OF OXIDATION RATE MEASUREMENT. S.C. WHALEN, W. S. REEBURGH, AND V. BARBER, Institute of Marine Science, University of Alaska Fairbanks, Fairbanks, Alaska 99775-1080, U.S.A.

Static chamber measurements of methane flux in moist upland soils of the Bonanza Creek Long Term Ecological Research area showed consistent decreases in chamber CH_4 concentration during the 1990 and 1991 field seasons, indicating net consumption of atmospheric methane. The methane sink strength of these soils is $-0.2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$.

These observations of methane oxidation were confirmed with five independent methods: jar incubations on soil samples collected over a depth range of 60 cm in contact with headspaces containing (a) ambient and (b) above ambient (200 ppm) CH_4 concentrations, (c) tracer experiments using $^{14}\text{CH}_4$ and consumption rates calculated from soil CH_4 distributions with (d) and without ^{222}Rn transport correction. (e). All methods establish that microbially mediated CH_4 oxidation occurs in these soils. Methane oxidation by soils is a process capable of not only modulating CH_4 fluxes to the atmosphere, but also capable of providing a negative feedback on possible future atmospheric CH_4 increases.

PB-9/10-5 BIOLOGICAL PRODUCTION AND CONSUMPTION OF DIMETHYL SULFIDE (DMS) IN THE MARINE PHOTIC ZONE: RESULTS OF RADIOLABELLED TRACER EXPERIMENTS. G.V. WOLFE and T.S. BATES, University of Washington, Seattle, WA, and NOAA/PMEL, Seattle, WA.

The flux of DMS to the marine atmosphere, hypothesized to have an important climatic link via the formation of marine tropospheric aerosol and cloud-condensation nuclei, depends critically on the rapidity of biological cycling of DMS in the water column. Recent studies (Kiene & Bates 1990, Kiene, in press) have suggested that the biological destruction of DMS in the water column is much more rapid than its turnover by air-sea exchange. We investigated the processes and rates of biological production and destruction of DMS and of its precursor, dimethyl sulfoniopropionate (DMSP) using a combination of ^{14}C -labelled tracer techniques and gas chromatography during the PSI-III experiment off the Washington coast in April 1991. Kinetic and tracer incubations were conducted with ^{14}C -DMS to measure *in situ* rates of destruction and to examine the relative importance of the compound as an energy and carbon source for marine bacteria. We also examined the production of algal DMSP using $\text{H}^{14}\text{CO}_3^-$ incubations to construct an initial model for the

seawater cycling of DMS and DMSP. These data will be compared with the air-sea exchange of DMS measured during the experiment.

O-2-1 THE DIRECT AND INDIRECT EFFECTS OF GREENHOUSE GASES ON CLIMATE. D.J. WUEBBLES, Group Leader, Atmospheric and Geophysical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue/L-262, Livermore, California, USA.

There are many factors, both natural and human related, that are influencing the Earth's climate. Of these factors, there is particular concern about the potential changes to climate that may be occurring due to growing atmospheric concentrations of gases that absorb terrestrial infrared radiation, termed greenhouse gases. Much of this concern has centered around carbon dioxide (CO_2) because of its importance as a greenhouse gas and also because of the rapid rate at which its atmospheric concentration has been increasing. However, in the last decade, it has been shown that other greenhouse gases are contributing to about half of the overall increase in the greenhouse effect on climate. Some of the important greenhouse gases include: methane (CH_4), nitrous oxide (N_2O), and several chlorofluorocarbons (CFCs). In addition to the direct radiative effects from atmospheric concentrations of these gases, research studies have shown that chemical interactions in the atmosphere can lead to additional "indirect" effects on climate, such as those relating to changes in the distribution in ozone in the troposphere and stratosphere. This paper will examine what is known about the greenhouse gases, and the direct and indirect influences they can have on climate.

O-12-6 SOURCES OF METHANE IN CHINA: RICE FIELDS, BIOGAS PITS, CATTLE AND INDUSTRIAL. WANG MING-XING¹, WOLFGANG SEILER², AND REI A. RASMUSSEN³, 1) Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China; 2) Fraunhofer Institute for Atmosphere Environment Research, FRG; 3) Oregon Graduate Center, USA.

Continuous measurements of the methane flux from rice fields in Hangzhou, Eastern China were carried out by using a chamber technique. An automatic sampling and analysing system was used. The results show that the methane flux from rice fields has a strong diurnal variation which may be explained by the soil temperature effects and rice plant growing activities, and that the day-mean flux has a large seasonal variation which may be related to soil temperature and the availability of organic substrates in the soil. Based on the experiments conducted over the past 5 years in Eastern China and Sichuan, we obtained the average methane fluxes from Chinese rice fields: $7.8 \text{ mg/m}^2/\text{hr}^{-1}$ for early rice, $28.6 \text{ mg/m}^2/\text{hr}^{-1}$ for late rice, and $60 \text{ mg/m}^2/\text{hr}^{-1}$ for single rice. Thus we estimate that the total emissions of methane from rice fields in China are $(23 \pm 6) \text{ Tg/yr}$. Methane leakage from biogas pits is very little on the whole, with a range of $60 - 320 \text{ mg/hr/pit}$. The total emission from biogas pits in China may be of the order of 0.01 Tg/yr . Total emissions of methane from cattle in China are estimated to be 3.9 Tg/yr . Coal and oil mining may emit 0.6 Tg/yr . There is an important source of methane in China that has not been measured. Sewage in China is often treated in cesspools, which are similar to the biogas pits. However, no methane is recovered from such cesspools. We estimate that the total flux of methane from such sources may be of the order of 10 Tg/yr . The total emissions of methane from sources in China are estimated to be about $40 \pm 10 \text{ Tg/yr}$.

O-4-2 SPATIAL AND TEMPORAL VARIATIONS OF METHANE FLUX FROM RICE PADDY FIELDS. K.

YAGI AND K. MINAMI. National Institute of Agro-Environmental Sciences, Tsukuba, JAPAN.

Methane (CH_4) fluxes from paddy fields to the atmosphere were studied in Japanese paddy fields for three cultivation periods by using a closed chamber method. Large spatial variations of the CH_4 fluxes, having CV to range from 19 to 47%, were observed within the individual plots when a chamber having a cross-sectional area of 0.09 m^2 was used. In the case of using a chamber with 0.36 m^2 CV did not exceed 28% except in the case of the bubbling transport being observed. The CH_4 fluxes showed a diurnal variation with early morning minimum and late afternoon maximum, which closely correlated with soil temperature in the surface layer. The CH_4 fluxes were doubled with the increase in the soil temperature from 25 to 35°C at the depth of 2 cm.

Strong seasonal variations of CH_4 fluxes were observed during a cultivation period. The fluxes began to increase 3-4 weeks after flooding with the decrease of the redox potential (Eh) of paddy soil. The highest fluxes were observed during August. The variations of the CH_4 fluxes during a cultivation period were related to the soil Eh at a depth of 2 cm. Annual emission rates of CH_4 from the mineral and the rice straw plot ranged 8.2 - 40.6 and 27.0 - 43.1 g/m^2 , respectively, in three cultivation periods. The soil Eh level had a significant influence on the annual variation of the CH_4 fluxes.

O-7-4 THE RESPIRATORY CHAIN COUPLED TO OXIDATION OF Fe^{2+} IN *THIOBACILLUS FERROOXIDANS*. T. YAMANAKA, T. YANO, M. KAI, H. TAMEGAI AND Y. FUKUMORI. Department of Life Science, Tokyo Institute of Technology, Nagatsuta, Yokohama 227, Japan.

The respiratory chain coupled to oxidation of Fe^{2+} in *Thiobacillus ferrooxidans* has been studied in terms of the purified components of the chain. We have purified Fe(II)-cytochrome g-552 oxidoreductase, soluble and membrane-bound cytochromes g-552 and cytochrome g oxidase from the bacterium, and also rusticyanin by our procedure. We have characterized these components and especially examined the interaction between the two each of the components.

Rusticyanin, a copper protein, has been sequenced. The protein is composed of 154 amino acid residues and its Mr is ca. 16,400. Soluble cytochrome g-552 has Mr of 14,000 and its reduced form is not autoxidizable even at pH 2.5. Its E_m' is 0.360 V. Membrane-bound cytochrome g-552 has Mr of 22,300 and its E_m' is 0.336 V.

Fe(II)-cytochrome g-552 oxidoreductase is an Fe/S protein. Its Mr is 63,000 and its molecule is composed of 8-10 molecules of subunits with Mr of 6,400. The amino acid sequence of the subunit (unpublished results) is very similar to that of HiPIP of *Rhodocyclus tenuis*. The enzyme reduces ferricytochrome g-552 with Fe^{2+} at pH 3.0-3.5, but not rusticyanin. Rusticyanin is reduced by the enzyme with Fe^{2+} in the presence of cytochrome g-552 . Although the enzyme is unstable when it is in contact with cytochrome g-552 , the presence of rusticyanin seems to protect the enzyme from the inactivation by cytochrome g-552 .

Cytochrome g oxidase has one molecule of haem g and one atom of copper per the minimal structural unit (Mr , 90,000) consisting of three subunits with molecular masses of 54, 21 and 15 kDa, respectively. The enzyme oxidizes soluble ferrocyclochrome g-552 and the optimal pH of the reaction is 3.5. The reduced forms of membrane-bound cytochrome g-552 and rusticyanin are also oxidized by the oxidase.

The finding that *T. ferrooxidans* cytochrome g oxidase functions optimally at pH 3.5 suggests that the reduction of O_2 by the enzyme may occur at the periplasmic side of the cytoplasmic membrane. If so, ΔG° for the oxidation of Fe^{2+} will be $-16.2 \text{ kcal/2Fe}^{2+}$, although it will be $-1.3 \text{ kcal/2Fe}^{2+}$ if the reduction by the oxidase of O_2 occurs at the cytoplasmic side of the cytoplasmic membrane as has been assumed previously.

O-5-6 PRODUCTION OF METHANE AND NITROUS OXIDE BY ORGANIC SOILS WITHIN NORTHERN HARDWOOD FORESTS. J.B. YAVITT, AND T.J. FAHEY. Department of Natural Resources, Cornell University, Ithaca, New York, USA.

Forests in north temperate and boreal regions occur mostly on well-drained soils that produce only small amounts of nitrous oxide and consume atmospheric methane. Saturated soils often occur within these systems, and they may be larger sources of biogenic gases. In this study we sampled forest air (beneath the canopy) in northern hardwood forests at the Hubbard Brook Experimental Forest in New Hampshire and in the Adirondack Park Region of New York State and found that methane concentrations were consistently greater than 2.00 ppmv, despite measuring methane consumption by upland soils and methane concentrations of about 1.80 ppmv in well-mixed air -above the canopy. The source within the forest seemed to be organic soils (peat soils, histosols) adjacent to first- and second-order streams. Gas production by peat samples was estimated monthly using incubations of intact peat cores. Methane production ranged from 15-250 $\text{pmol cm}^{-3} \text{ min}^{-1}$, and nitrous oxide production ranged from 30-300 $\text{pmol cm}^{-3} \text{ min}^{-1}$ produced presumably through denitrification. Gas fluxes across soil- or peat-air interfaces were estimated monthly using static chambers. Methane fluxes from organic soils averaged 108 $\text{pmol cm}^{-2} \text{ min}^{-1}$ compared to consumption rates of 13 $\text{pmol cm}^{-2} \text{ min}^{-1}$ by upland soils. Emission rates for nitrous oxide were more than an order of magnitude higher for organic soils than upland soils. Although organic soils occupy less than 10% of watershed area within northern hardwood forests, methane and nitrous oxide production by these soils apparently influence concentrations of biogenic gases in air throughout the forest. If rainfall increases with future climate change, the increased extent of saturated soils may lead to increased fluxes of methane and nitrous oxide from temperate and boreal forests.

PB-9/10-6 WINTER ACTIVITY OF SOILS IN NORTH AND CO_2 PLANETARY MAXIMUM IN THE ATMOSPHERE. S.A. ZIMOV, S. P. DAVIODOV, Y. V. VOROPAIEV, S. F. PROSIANNIKOV. North-East Scientific Station, Pacific Institute Geography, Far-East Branch, USSR Academy of Sciences, Chersky, Yakutiya, USSR. I. P. SEMILETOV. Pacific Oceanological Institute, Far-East Branch, USSR Academy of Sciences, Vladivostok, USSR.

To estimate the contribution of the ecosystems in Northern Siberia to forming high-latitude maximum of the atmospheric CO_2 concentration and variation, studies of CO_2 balance have been carried out in the lower reaches of the Kolyma river from May 1989 until January 1991. The measurements of CO_2 fluxes were taken in ten points in various kinds of landscapes. At the same time, the breathing of soil monoliths with vegetation of wide species diversity was studied. CO_2 fluxes were measured by means of the chamber-dynamic and profile methods using a IR analysis and a gas chromatograph. Investigations indicated that photosynthesis of shrubs, grass, moss and lichen does not compensate the summer CO_2

flux released from soil. The mean CO_2 flux released from the surface to the atmosphere was above 400 g/m^2 . CO_2 absorption, when photosynthesis of trees and shrubs occurs, was not taken into account, but its production value is explicitly less than this one in our region (northern boundary of the forest). Therefore, these ecosystems were CO_2 sources. Large autumn fluxes have been registered: $50 - 300 \text{ g C/m}^2$ of CO_2 have been released from soil from September until the end of December. Moreover, in October and November fluxes exceeded those registered in September. This is explained, in our view, by the fact that soils in the North are excessively humidified in summer. However in October their freezing occurs. At this time moisture is drawn up to the surface and at depth a highly-porous, well-aerated horizon is formed that activates aerobic organisms. We refer the following interesting phenomenon to their activity. According to postulates of permafrostology, in autumn in our region the soil should freeze from below. However, it may be seldom seen. Moreover, we identified that ground melting occurred until January and occasionally the temperature rose up to 3°C . The calculations performed indicate that the energy released while functioning soil aerobes (when $50 - 300 \text{ g C/m}^2$ is oxidized) is sufficient to provide this heating up. At present to northern Siberia, the depth of the ground melting has increased due to the comprehensive disturbance of the surface conditions. Aerobes oxidize the carbon, previously conserved in the permafrost regime. Additional energy released associated with this results in the increase of the melting depth as far as 2 meters and soil remains melted. The landscapes of the lower reaches of the Kolyma river are representative of a large territory. Therefore we can relate formation of winter planetary CO_2 maximum in the atmosphere with the phenomenon of undersnow activity of soil.

PB-9/10-7 EARTH'S VEGETATION COVER RESPONSE TO CHANGING ATMOSPHERIC CO_2 CONCENTRATION. S.A. ZIMOY, V. I. CHURPRIONIN, A. P. ORESHKO, S. M. KRASNOPEEV. Pacific Institute of Geography, Far-East Branch, USSR Academy of Sciences, 7, Radio-Street, Vladivostok, USSR.

The atmospheric CO_2 concentration increase is supposed to bring about significant climatic changes which will effect the Earth's vegetation cover. But CO_2 is known to be the most important resource for photosynthesis; on assimilation of 1 g CO_2 , plants spend hundreds of grams of water. Therefore changes of the atmospheric CO_2 should affect vegetation even if climatic changes are not essential. A large number of experiments on plants growing confirmed their productivity. However, it is difficult to predict phytocenosis response to the slow rise of the CO_2 concentration as with reduction of the water demand the root biomass and profile of their distribution in depth will change. This will affect the foliage biomass and its vertical distribution, soil humidity, in turn, will influence the nitrogen fixation activity. This will inevitably result in changes of phytocenosis species competition. Such complicated phenomena may be predicted only by use of deductive models. We succeeded in developing a model of this kind. It describes plant growth, propagation and interspecies competition for main resources, makes it possible to calculate dynamics of the vegetation cover in different areas of the Earth, considers vertical distribution of biomasses in the different vital plant forms and estimates changes in location of the principal boundaries of the Earth's vegetation zones. By means of this model, the retrospective analysis of the vegetation dynamics of the Pleistocene-Holocene boundary when the atmospheric CO_2 concentration had increased 1 - 5 times and

predicted analysis of the CO_2 concentration increase under study have been carried out. By their scales, these variations yield to the reconstruction predicted in the vegetation cover in connection with the climatic changes expected.

PB-9/10-8 ON BIMODAL WINTERTIME OSCILLATIONS IN ATMOSPHERIC CO_2 CONCENTRATION. S.A. ZIMOY, I.P. SEMILETOV. North-Eastern Science Station, Chersky, Pacific Oceanological Institute, Vladivostok, RUSSIA.

In general, the northern $50 - 70^\circ$ latitude belt is the area of maximal season amplitudes and absolute value of air CO_2 (Tucker et al., 1986, Fung et al., 1987). Also the high latitude wintertime bimodal oscillations in atmospheric CO_2 content were registered (Wong et al., 1984). The cause of foregoing effect is not known (Higushi, 1990).

The previous study of CO_2 flux from the "thawing" layer of Alaska permafrost shows the positive CO_2 concentration gradient towards the atmosphere from subnivean layer with a maximal value during a frozen-unfrozen time (Kelley et al., 1968; Coyne, Kelley, 1974). Our investigation of CO_2 release from Siberian tundra active layer continue this study. We have determined also the value of CO_2 diffusion coefficient in a snow with different conditions. These values were used for the calculation of CO_2 flux in Siberian and Alaska area. Our study was carried out in different types of landscape, alpine and tussok tundra. The initial calculation of the minimal total CO_2 flux from tundra during the coldest months, December - February, shows that the value of CO_2 release might approach about $0.1 \times 10^{15} \text{ g C}$. The joint analysis of Siberian and Alaska data had been showing the total CO_2 soil release from September - June was about $0.23 \times 10^{15} \text{ g C}$. The maximal CO_2 signal in the atmosphere was registered over late Autumn and Spring. It is conformed with changes in CO_2 flux from northern soil. In consequence we guess that bimodal oscillations are mainly connected with CO_2 tundra signal. It's supported by the dilution of CO_2 signal towards the South (Wong et al., 1990).

Note that CO_2 tundra signal might be amplified by means of CO_2 soil release and slow winter respiration of trees in the boreal zone. This hypothesis is supported by large content of a litter in the "thawing" soil layer and similar regime of radiation, evaporation, precipitation and temperature (Bolin, 1980; Schlesinger, 1984). In consequence the CO_2 flux from thawing depth of permafrost in boreal area might be not less than in Arctic. Therefore we estimate the total wintertime CO_2 release from soil of the $60 - 70^\circ\text{N}$ belt with the value about $0.5 \times 10^{15} \text{ g C}$. The mechanism of "cold" CO_2 generation is discussed in this issue. We also realize that this effect is giving a better insight into the mechanism of bimodal distribution of atmospheric CO_2 concentration which are presented for North American background stations.

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1991 ISEB Deadlines

Advanced Registration	July 15
Mono Lake Fieldtrip Payment	July 1
Housing Forms and Deposit	July 1
Wolf Vishniac Award Manuscripts	July 15
Receipt of Manuscript	August 19

Appendix C

**ISEB 10 DEMOGRAPHIC
STATISTICS**

COUNTRY	ATTENDEE NAME	STUDENT	GUESTS	COUNTRY TOTAL
<u>Australia</u>	Denmead, O. T. Summons, Roger E.			
			AUSTRALIA	2
<u>Brazil</u>	Wagener, Angela de Luca Rebella			
			BRAZIL	1
<u>Canada</u>	Brown, Ann Higuchi, Kaz Knowles, Roger Moore, Tim R. Roulet, Nigel T. Thompson, Joel B.		1	
			CANADA	7
<u>Denmark</u>	Ambus, Per Christensen, Torben Finster, Kai	X		
			DENMARK	3
<u>Finland</u>	Alm, Jukka Martikainen, Pertti Nykanen, Hannu Silvola, Jouko			
			FINLAND	4
<u>France</u>	Nguyen, Ba C. Pelet, Regis Raynaud, Dominique		1	
			FRANCE	4
<u>Germany</u>	Andreae, M. O. Bak, Friedhelm Conrad, Ralf Havel, Jurgen Huber, Harold Naguib, Monir Papen, Hans Schdlowski, M. Wuppertal, Heinrich		1 1	
		X		
			GERMANY	11
<u>India</u>	Mohanraju, R.	X		

**ISEB 10 DEMOGRAPHIC
STATISTICS**

COUNTRY	ATTENDEE NAME	STUDENT	GUESTS	COUNTRY TOTAL
	Muthuchelian, K.		INDIA	2
<u>Israel</u>	Nissenbaum, Arie		1 ISRAEL	2
<u>Italy</u>	Ciardi, Carlo Cotrufo, Maria F. Nannipieri, Paolo		2 3 ITALY	8
<u>Japan</u>	Minami, Katsuyuki Nouchi, Isamu Yagi, Kazu Yamanaka, Tateo		JAPAN	4
<u>P.R. China</u>	Lin, Ma Bao Pu, Fan Pu, Wang Sheng		P.R. CHINA	3
<u>Poland</u>	Weber, Jerzy		POLAND	1
<u>Spain</u>	Gallardo, Juan F.		SPAIN	1
<u>Sweden</u>	Borjesson, Gunnar Hallberg, Keif Mikkela, Catarina Nilsson, Mat Sundh, Ingvar		SWEDEN	5
<u>The Netherlands</u>	Oenema, Oene Prins, Maarten A. Prins, Rudolf A. Stal, Lucas Visscher, Pieter Wever, Ron	X	THE NETHERLANDS	6

**ISEB 10 DEMOGRAPHIC
STATISTICS**

COUNTRY	ATTENDEE NAME	STUDENT	GUESTS	COUNTRY TOTAL
<hr/>				
<u>United Kingdom</u>				
	Nedwell, David B.			
			UNITED KINGDOM	1
<hr/>				
<u>USA</u>				
	Abu-Saba, Khalil E.	Volun.		
	Alperin, Marc			
	Anderson, Iris C.			
	Anderson, Suzanne P.	X		
	Barber, Timothy R.	X		
	Baublitz, Michael T.	X		
	Benjamin, Susan			
	Bereal, Ed			
	Betancourt, Julio L.			
	Blair, Neal			
	Blake, Nicola J.			
	Blum, Jodi Switzer			
	Boone, David			
	Bronson, Kevin F.			
	Brooks, Paul			
	Buffington, Rosemary			
	Burke, Jr., Roger			
	Butler, James H.			
	Caffrey, Jan			
	Chambers, Randy			
	Chanton, Jeff P.			
	Chappellaz, Jerome			
	Chatfield, Robert B.			
	Cicerone, Ralph J.			
	Corredor, Jorge			
	Coutlakis, M. Denise			
	Cox, Lea	Volun.		
	Crill, Patrick			
	Culbertson, Charles W.			
	Cynar, Skip	X		
	Davidson, Eric			
	Des Marais, David			
	Dignon, Jane			
	Dungan, Jennifer			
	Edwards, Blake			
	Ehrlich, Henry L.			
	Elkins, James W.			
	Engle, Diana			
	Evans, William C.			
	Fall, Ray			
	Fazio, Joe	Volun.		
	Fisher, Charles			
	Flegal A. R.			
	Fung, Inez Y.			
	Germain, Claire			

**ISEB 10 DEMOGRAPHIC
STATISTICS**

COUNTRY	ATTENDEE NAME	STUDENT	GUESTS	COUNTRY TOTAL
	Glaser, Paul			
	Goodwin, Kelly D.	X		
	Groffman, Peter			
	Hamilton, Steven K.	X		
	Harriss, Robert C.			
	Hines, Mark E.			
	Hitzman, Donald O.			
	Hoehler, Tori M.	X		
	Holden, Patricia A.	Volun.		
	Horgan, Erin J.	Volun.		
	Hren, Jan			
	Janetos, Anthony			
	Jahnke, L. L.			
	Joye, Samantha B.	X		
	Kaplan, Ian R.		1	
	Kasting, James F.			
	Kaufman, Mollie	Volun.		
	Keller, Michael			
	Khalil, Aslam K.			
	Kiene, Ronald P.			
	King, Gary M.			
	Klinger, Lee F.			
	Ko, Malcolm			
	Kuivila, Kathryn			
	Kvenvolden, Keith A.			
	Lansdown, John M.	X		
	Lashof, Daniel A.			
	Lidstrom, Mary E.			
	Lipkind, Lawrence S.			
	Loewenstein, Max			
	Lorenson, Thomas D.			
	Lovley, Derek			
	Martens, Chris			
	Matson, Pamela A.			
	Matthews, Elaine			
	Mauzerall, Denise	X		
	McCarty, Perry L.			
	McConnaughey, Ted			
	Meyers, Philip A.		1	
	Miller, Laurence G.			
	Miller, Norman			
	Moore, George T.			
	Mosier, Arvin R.			
	Mroz, Gene J.			
	Neil, John M.			
	Ni, Shuisong	X		
	Nishiguchi, Michele	Volun.		
	Oremland, Ronald S.			
	Payne, Greg			
	Perlman, David			
	Poth, Mark			

**ISEB 10 DEMOGRAPHIC
STATISTICS**

COUNTRY	ATTENDEE NAME	STUDENT	GUESTS	COUNTRY TOTAL
	Reeburgh, William			
	Romanowicz, Ed			
	Sansone, Francis J.			
	Sass, Ron			
	Schimmel, Joshua			
	Schlesinger, William H.			
	Shaw, Becky	Volun.		
	Singh, Hanwant B.			
	Sippel, Suzanne	X		
	Skujins, John			
	Smalheer, Deborah	Volun.		
	Smith, Lesley K.			
	Spencer, Mary Jo			
	Staley, James T.			
	Stotzky, Guenther			
	Strohmaier, Frances			
	Tamareisis, John	X		
	Taylor, Barrie F.			
	Torn, Margaret	X		
	Trumbore, Susan			
	Tyler, Stan C.			
	Valentine, David W.		1	
	Vitousek, Peter M.			
	Wahlen, Martin			
	Walker, J.C.G.			
	Ward, Bess M.			
	Whalen, S. C.			
	Wolfe, Gordon V.	X		
	Wuebbles, Donald J.			
	Yavitt, Joseph B.			
			USA	129
<hr/>				
USSR	Andronova, Natasha G.			
	Ivanov, Michail V.			
	Lein, Alla Yu			
	Panikov, Nikolay			
	Rivkina, Elizaveta M.			
	Samarkin, Vladimir A.			
	Zimov, Sergey A.			
			USSR	7
<hr/>				
Venezuela	Donoso, Loreto			
	Sanhueza, Eugenio			
			VENEZUELA	2
<hr/>				
TOTAL				
ALL COUNTRIES				203

END

**DATE
FILMED**

9 / 15 / 92